New Developments in the Coordination Chemistry of Inorganic Selenide and Telluride Ligands

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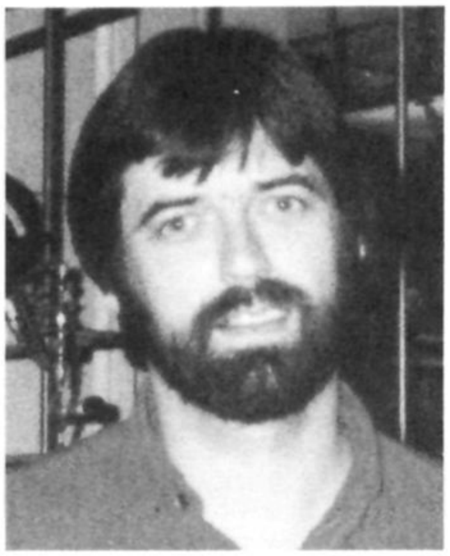

Joe Kolis was born in Rhode Island in 1957 and received his B.S. from Worcester Polytechnic Institute in 1979 with distinction. He migrated to the midwest and received his Ph.D. in 1984 from Northwestern University under the joint direction of Du Shriver and Fred Basolo. After 2 years of postdoctoral experience with Ron Gillespie at McMaster University, he joined the faculty of Clemson University in 1985, where he is currently Associate Professor. He is a recipient of an Alfred P. Sloan Fellowship (1990–1992). His interests include synthesis of unusual molecules, main-group cages and clusters, chemistry in supercritical solvents, and softball.

Lisa Roof was born in Charlotte, NC, in 1965. She received her B.S. degree from Presbyterian College in 1988 and entered graduate school at Clemson University the following fall. Under the direction of Professor Joseph W. Kolis, she anticipates receiving her Ph.D. in May 1993. Her research interests in Prof. Kolis's group have involved the synthesis and reactivity of transition-metal chalcogenide compounds.

1. Introduction and Perspective

In striking contrast to the metal sulfides,[1] which have a long and venerable chemical history,[2] most of the studies of metal selenide and telluride chemistry have occurred in the last 10–15 years. There are several reasons for this truncated history. One is a decreased driving force due to a somewhat lesser amount of obvious and immediate practical application of the heavier metal chalcogenides relative to the metal sulfides. Metal sulfide clusters occur at the active site of a large number of proteins[3] and are also involved in some very important catalytic industrial processes such as hydrodesulfurization.[4] Recently, however, selenium and tellurium have begun to assume increasing significance in a variety of important applications. For example, selenium has recently been found to occur in a surprising number of proteins.[5] Also metal selenides and tellurides have considerable industrial usage, especially in low-bandgap semiconductors, photovoltaics, and IR detection applications.[6] Aside from these more worldly matters, metal selenides and tellurides have not attracted attention until recently because convenient synthetic routes necessary to gain access to their chemistry simply have not been available. Many of the traditional reagents in metal sulfide chemistry, such as H_2S, are not simply transferable to their heavier congeners. However, with the recent development of suitable synthetic methodologies, the chemistry of metal selenides and tellurides is growing at a rapid rate. Finally

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there is the perception that selenium and tellurium chemistry is solely the realm of the extraintrepid due to the toxicity and stench associated with these compounds. However, the extreme toxicity and odor traditionally attributed to these molecules is almost always due to low weight, neutral organic species such as $(CH_3)_2E$ (E = Se, Te). We have found that metal complexes of selenium and tellurium usually have no odor to speak of, and when handled properly, using routine modern controlled-atmosphere techniques, create no greater or lesser peril than any other class of compound.

It is our intention to demonstrate that the relatively new chemistry of metal selenides and tellurides is fascinating, alive, accessible and laden with potential. As synthetic reagents become available and crystallography and various forms of spectroscopy (especially multinuclear NMR) become easier to do, the field will expand rapidly. This growth will continue to be marked by the preparation of a striking variety of compounds which often bear no resemblance to metal sulfides, and also challenge existing theories of bonding and structure. Though an immediate practical application for many of these compounds is not obvious, there rarely is for any truly new class of compounds. In general, the work is still quite exploratory and many obvious voids are often more attributable to the simple fact that no one has *done* the reactions, rather than any inherent chemical reason. Opening up the basic descriptive chemistry is the first task in any new area and it is this process which is currently underway in most labs in this field.

Most of the references date from the last decade, since most of the progress has occurred in this period. An excellent review covering the general aspects of this area appeared several years ago,[7] and several other reviews dealing with more specific topics have also appeared,[8] but the area is developing so rapidly that a further comprehensive review seems appropriate. The descriptive part of the review will be demarcated by the groups of the periodic table. While this approach is somewhat dogmatic, it provides a useful framework for critical discussion. Most of this discussion will focus on synthetic and structural aspects, since this is where most of the current progress is occurring. The possible coordination modes of chalcogenide ligands are well diagrammed in the previous review by Ansari and Ibers.[7] Little extensive reaction chemistry or fundamental mechanistic work has been reported, although these will be discussed when available. Similarly, detailed spectroscopic investigations of new compounds have often not been reported. One interesting exception is multinuclear NMR. Both ^{77}Se and ^{125}Te are accessible spin $^1/_2$ nuclei. Their natural abundance is not high (7.58 and 6.99%, respectively), but modern instruments have made their observation routine in many cases. The wide range of shifts, and the coupling information available from the observation of satellite peaks, has made this technique quite useful. The review by Ibers contains extensive tabulated data of known shifts and coupling constants for metal selenides and tellurides.[7] (See also ref 8b for metal telluride data.) Finally, in keeping with the theme of this issue, novel coordination aspects will be discussed, and wherever appropriate, significant nonexistent compounds will be mentioned.

The scope of the article will be limited to ligands containing only selenium and tellurium, as organoselenide and -telluride complexes often bear close resemblance to their sulfur analogs and have been the subject of several excellent reviews.[9] The emphasis is on compounds of a mostly molecular nature, but in keeping with the current trend throughout all of chemistry, solid-state compounds will be introduced and discussed when appropriate. Densely packed, thermodynamically stable, predominantly salt-like phases lie beyond the scope of this article. However there have been a number of interesting solids prepared recently that have ligand characteristics related to molecular compounds and these will be presented in the context of coordination chemistry. Many of the reactions given are not completely understood and the routes to the products are not obvious. Most reactions form a mixture of products, some in very low yields. Thus in some cases equations cannot be balanced with confidence. Some indication of yields and byproducts are given where appropriate and the major product is always delineated.

In many cases we will contrast the chemistry of selenides and tellurides to that of sulfides, since metal sulfides are the benchmark in this area. It is clear that, however, in many cases the known chemistry of sulfur is an entirely inadequate precedent. Also, despite the large amount of elegant work done with metal sulfides, the fundamental understanding of their chemistry is often still quite primitive. Interestingly, the tellurides sometimes appear to demand more of the spotlight than selenides, despite the fact that their chemistry seems "harder" to do. The selenides are somewhat better developed and, while often unique, are generally more closely related to their classical sulfur counterparts. However, the tellurides, with their larger size, diffuse orbitals, and increased metallic character, possess a much more nonclassical chemistry, and it is this potential for truly unusual structures and bonding which many chemists find so attractive.[10]

2. Synthetic Approaches

2.1. Use of H_2Se and H_2Te

It is the authors' opinion that one of the main reasons that the chemistry of metal selenides and tellurides has languished until recently has been the lack of suitable synthetic entries to this field. The historical approaches to metal sulfides have almost invariably involved the use of H_2S at some point. It is either used to displace metal oxides, in a condensation reaction (eq 1[11a]), or bubbled into aqueous base to be deprotonated, generating sulfide or polysulfides (eq 2) which can then be reacted with an appropriate metal complex (as in eq 3[11b] for example).[1b] This approach is not suitable for

$$MoO_4^{2-} + H_2S \rightarrow MoS_4^{2-} + H_2O \qquad (1)$$

$$H_2S + OH^- + S \rightarrow S_n^{2-} \qquad (2)$$

$$S_n^{2-} + Cu(OAc)_2 \cdot H_2O \rightarrow [Cu_3(S_4)_3]^{3-} \qquad (3)$$

extension to the heavier congeners because H_2Se is extremely toxic, malodorous, expensive, and often leads to impure mixtures of products. Hydrogen telluride suffers all of the same disadvantages in addition to being unstable at room temperature with respect to disproportionation to H_2 and Te. Although their general use as a routine reagent is generally not convenient, the binary hydrides have been employed successfully on some occasions (eq 4).[12] Hydrogen telluride in particular has produced some interesting results when generated in situ by the reaction of a proton source with a reduced telluride (eq 5).[13]

$$MoO_4^{2-} + H_2Se \rightarrow MoSe_4^{2-} + H_2O \tag{4}$$

$$Al_2Te_3 + H^+ + Cp^*Re(CO)_2THF \rightarrow [Cp^*Re(CO)_2]_2Te_2 + [(Cp^*Re(CO)_2]_2Te \tag{5}$$

2.2. Soluble Anions

A much more useful alternative to the binary hydrides has been the development of soluble Zintl ions in anhydrous solvents. The discovery that soluble, stable polyselenides and -tellurides could be conveniently prepared and handled in polar organic solvents provided the breakthrough for full-scale development of the area.[14] It was well-known that selenium and tellurium could be reduced in ammonia and ethylenediamine to form linear polynuclear anions,[15] but these solvents are not generally convenient for routine coordination chemistry. However, once it was realized that Zintl salts are quite soluble and stable in solvents like DMF and acetonitrile, the field was poised for rapid expansion.[14] Thus amorphous Zintl phases of the nominal composition A_2E_n, where A is an alkali metal, E is any chalcogenide, and n is generally 2–6, can be prepared either by melting the elements or by reacting the elements in liquid ammonia, followed by removal of the ammonia. The resultant solids are stable powders which are convenient reagents for exploratory reactions. Another method of preparing lithium salts of sulfides and selenides is to use soluble borohydrides as the reducing agents (eq 6). This methodology, originally developed by Gladysz and co-workers,[16] provides a source of Li_2E which is quite reactive but usually generates clean products in good yield. The procedure is somewhat expensive due to the cost of the soluble borohydride, but it is quite convenient and is one of the original methods of entry to synthesis in this area.

$$Se + LiEt_3BH \xrightarrow{THF} Li_2Se + H_2 + Et_3B \tag{6}$$

The ionic species which result from the solubilization of polychalcogenide Zintl phases are a complex equilibrium mixture of mostly linear chains of various lengths, commonly ranging from two to five atoms in lengths though longer chains have been isolated.[17] Several elegant attempts have been made to characterize these solutions by techniques like NMR[18] and UV–vis spectroscopy,[19] but the dissolved species have, for the most part, defied complete characterization. It is well-known that radical anions such as S_3^- are present in polysulfide solution.[20] There is some evidence that similar species are also present in polyselenide solutions, but the polytellurides have not been investigated. Chains of various lengths can be readily isolated and characterized using large organic countercations such as R_4N^+, R_4P^+, PPN^+ or various cryptating agents. However, the chain lengths in the resulting salts seem to be determined by the solvents and counterions employed, rather than the identity of the starting material. To complicate matters further, a new type of anion has recently been isolated, namely a nonlinear species containing one or more central chalcogenide elements ligated by other polychalcogenides (Figure 1).[21] All that can be stated with certainty is that polychalcogenide anions are involved in complicated, facile equilibria in solution.[17a] It seems that, in some cases, the resultant coordination chemistry is affected by the nature of the starting materials, but in other cases it is not. In most reactions it appears that the metal center "chooses" a polychalcogenide chain of desired length from the reaction mixture. This can result in some amazing and unpredictable coordination chemistry which can often only be rationalized after the fact.

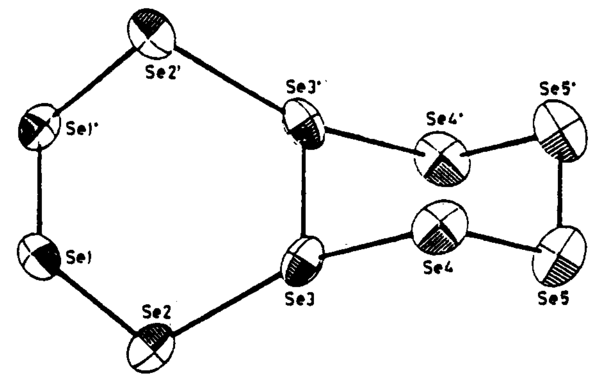


Figure 1. $[Se_{10}]^{2-}$, a bicyclic polyselenide (reprinted from ref 20d; copyright 1990 VCH Verlagsgesellschaft mbH).

Solution complexity notwithstanding, solutions of polychalcogenide anions are convenient reagents for the preparation of new coordination compounds. They are most often reacted directly with metal salts to form new products in metathesis reactions (eq 7,[22] 8,[23] and 9[24]). The polychalcogenides anions can also be reacted with metal carbonyls to form either carbonyl-containing clusters or completely decarbonylated binary anions (eqs 10[25] and 11[26]). This direct route of using soluble polychalcogenide anions with metal complexes has been the primary method of choice in the last few years and its potential is by no means exhausted.

$$CrCl_3 + 2Te_4^{2-} \rightarrow [Cr_3(Te_4)_6]^{3-} \tag{7}$$

$$AgNO_3 + Se_4^{2-} \rightarrow [Ag_4(Se_4)_3]^{2-} \tag{8}$$

$$MnCl_2 + Se_n^{2-} \rightarrow [Mn(Se_4)_2]^{2-} \tag{9}$$

$$Mn_2(CO)_{10} + Se_4^{2-} \text{ (excess)} \rightarrow [Mn(Se_4)_2]^{2-} \tag{10}$$

$$Ru_3(CO)_{12} + Se_4^{2-} \rightarrow [Ru(CO)_2(Se_4)_2]^{2-} \tag{11}$$

2.3. Neutral Atom Transfer Reactions

The methodology of transferring a formally neutral atom from one reagent to another has been a workhorse for many years in derivatizing metal sulfide complexes (eq 12).[27] Recently this has been extended to the

$$MoS_4^{2-} + S_8 \rightarrow [S{=}Mo(S_4)_2]^{2-} \tag{12}$$

preparation of metal selenides with considerable success. Sometimes the use of the thermodynamically stable infinite polymeric chain of selenium (gray selenium) is sufficient. However, there is a second, more reactive allotrope, Se_8 (red selenium) known, which is the direct counterpart to S_8 and is generally more reactive under mild conditions (eq 13).[28]

$$WSe_4^{2-} + Se_8 \rightarrow [W_2Se_{10}]^{2-} \qquad (13)$$

There is no stable tellurium analog to Se_8, which is somewhat of a hinderance, as bulk metallic tellurium is considerably less reactive than its lighter congeners. However, a series of reagents which serve the same purpose is the organophosphine tellurides such as $Et_3P{=}Te$. These compounds were first prepared 25 years ago,[29] but just recently have proven to be excellent synthons for the transfer of a single tellurium atom to a metal complex. They can be made quite simply by reaction of a triorganophosphine with bulk tellurium and are quite stable. However, the P=Te orbital overlap is so poor that a tellurium atom is readily transferred to a metal center with formation of a trivalent phosphine (eq 14),[30] rather than the reverse

$$Et_3P{=}Te + Et_2Hg \rightarrow HgTe + Et_3P + C_4H_{10} \qquad (14)$$

reaction which is used to abstract sulfur or selenium from metal complexes (for example, see eq 15).[31] These

$$[Mo_2S_9]^{2-} + 2Ph_3P \rightarrow [Mo_2S_7]^{2-} + 2S{=}PPh_3 \qquad (15)$$

reagents work with a variety of metals and should see extensive development in the years to come.

A similar type of reaction is the combination of bulk chalcogenide with a metal complex containing a vacant coordination site (eq 16).[32] This works especially well

$$Cp^*_2M_2(\mu\text{-}CO)_2 + E \rightarrow Cp^*_2M_2(CO)_2E_2 \qquad E = S, Se, Te \quad (16)$$

with low valent organometallic complexes. Thus a photolyzed metal carbonyl, an unsaturated metal dimer, or a complex with a labile group reacts readily with red selenium to form metal selenide clusters (eq 17).[33] For

$$[CpCr(CO)_3]_2 + Se_8 \rightarrow Cp_2Cr_2(CO)_4Se_2 \qquad (17)$$

the reasons described above, this reaction usually works better with selenium than tellurium.

2.4. Trialkylsilyl and Related Reagents

The instability of H_2E has promoted the search for suitable analogs, and the trialkylsilyl compounds, $(R_3Si)_2E$ (E = Se, Te), have proven to be excellent replacements. The replacement of H with Me_3Si to impart stability to main-group complexes is well-known. For example, $Me_3SiN{=}S{=}NSiMe_3$ is an important building block in S–N ring chemistry, but the hydrogen analog has not been isolated due to its instability.[34] In the same vein, the silylated chalcogenides are easily prepared,[35] reasonably stable, and can be used as replacements for the simple hydrides (eq 18). These

$$Li_2E + 2Me_3SiCl \rightarrow R_3SiESiR_3 + 2LiCl \qquad E = S, Se, Te \quad (18)$$

reagents exploit the strength of the Si–O and Si–Cl bond to abstract a halide, alkoxide, or oxide and generate a stable leaving group under very mild and controlled conditions. This is a relatively new technique which has seen some use as a sulfur transfer reagent, but most recently has been used to prepare an enormous variety of outstanding metal chalcogenide clusters[36] (eqs 19,[37] 20,[38] and 21[39]). Again, this reaction type is in its

$$Nb(OEt)_5 + (TMS)_2S + (TMS)S^- \rightarrow [Nb_6S_{17}]^{4-} \qquad (19)$$

$$NiCl_2(PPh_3)_2 + 2(TMS)_2Se \rightarrow [Ni_{34}Se_{22}(PPh_3)_{10}] \qquad (20)$$

$$R_3SiSeSiR_3 + NH_4VO_3 \rightarrow V_2Se_{13}^{2-} \qquad (21)$$

infancy and should continue to lead to exciting new breakthroughs. At this point there have been few examples of metal tellurides prepared in this fashion, although suitable starting materials such as (*t*-Bu-$Me_2Si)_2Te$ are known.[35]

2.5. Reduction of Chalcogen Oxides with Metal Carbonyl Anions

The reduction of main-group oxides by transition-metal carbonyl anions is one of the oldest methods known to introduce chalcogenides into metal clusters. It was first developed in the 1950s by Hieber, who obtained an enormous variety of transition-metal main-group clusters.[40] Since single-crystal X-ray diffraction was not readily available, he was unable to determine the structures of many of his compounds, but subsequent work has shown that this is indeed a fruitful entry to new metal clusters (eqs 22 and 23).[41] The

$$HFe(CO)_4^- + Na_2SeO_3 \rightarrow Fe_2(CO)_6Se_2 \qquad (22)$$

$$HFe(CO)_4^- + K_2TeO_3 \rightarrow Fe_3(CO)_9Te_2 \qquad (23)$$

driving force for such reactions is most likely the reduction of the main group center by the metal anion, with oxygen atom transfer oxidizing a coordinated CO to labile CO_2. This generates a vacant coordination site for metal–main-group-element bond formation. Both selenides and tellurides have been synthesized by this method, often in very high yield. Indeed this is still the method of choice for making simple building blocks like $Fe_2(CO)_6E_2$ (E = Se, Te).[42] Presumably metal carbonyl anions could react with main-group halides as well, via simple substitution reactions (eq 24). This has been well-developed for earlier main group

$$CpCr(CO)_3^- + Se_2Cl_2 \rightarrow Cp_2Cr_2(CO)_4(Se_2) \qquad (24)$$

halides but the selenium and tellurium halides have received only scant attention.[43]

2.6. Reaction of Cationic Clusters with Metal Carbonyls

Although the chemistry of naked cationic clusters of main-group elements is actually quite old, it was not until the 1970s and -80s that many of their structures were determined.[44] A large variety of cations such as S_{19}^{2+}, Te_4^{2+}, Se_8^{2+} and Bi_9^{5+} can be prepared by oxidation of the elements (eq 25) or reduction of a high valent

$$8Se + 3AsF_5 \rightarrow [Se_8][AsF_6]_2 + AsF_3 \qquad (25)$$

metal halide with the parent metal in the presence of a Lewis acid to complex the halide ions (eq 26). Recently

$$TeCl_4 + 7Te + 4AlCl_3 \rightarrow 2[Te_4][AlCl_4]_2 \qquad (26)$$

workers in Karlsruhe have been able to oxidize elemental tellurium with high-valent transition-metal halides to obtain new polytellurium cations (eq 27).

$$4Te + WCl_6 \xrightarrow{150\ °C} [Te_8][WCl_6]_2 \qquad (27)$$

These solid-state compounds have thus far shown no tendency to interact with the transition metal in the solid state, but the technique is still a very unique and promising one.[45]

The sensitivity of these cations to even mild nucleophiles necessitates the use of extremely weak bases such as $AlCl_4^-$ and SbF_6^- as counterions. The cationic clusters were originally prepared and characterized in the solid state, but Gillespie and co-workers discovered that their salts are soluble and quite stable in SO_2.[44b] This has enabled their reaction chemistry to be investigated and recently it was discovered that they will form complexes with metal carbonyls (eqs 28[46] and 29[47]). Thus far only

$$Te_4^{2+} + W(CO)_6 \rightarrow [W(CO)_4(cyclo\text{-}Te_3)]^{2+} \qquad (28)$$

$$Fe(CO)_5 + W(CO)_6 + Se_4^{2+} \rightarrow [WFe(CO)_8(Se_2)]^{2+} \qquad (29)$$

a few complexes have been reported, but a great deal of exploration is still to be done.

2.7. Reactions of Metals with Molten Polychalcogenides

Alkali-metal polychalcogenide salts, like K_2Se_5, melt at moderate temperatures (250–500 °C). These melts readily react with metal powders to form ternary compounds containing metal complexes of polychalcogenides.[48] The molten polychalcogenide acts as both a solvent and a reagent, in that the polychalcogenide chain oxidatively adds to the zero-valent metal in the melt, forming a complex. The melt also acts as a flux, expediting the growth of single crystals (eqs 30[48] and 31[49]). The technique is especially advantageous for highly oxophilic metals. Since most soluble metal selenides and tellurides are formed in highly polar oxygenated solvents such as DMF, formation of complexes with highly oxophilic metal centers such as f elements is quite difficult. However, use of the molten salt as the solvent circumvents this problem (eqs 30 and 32[50]). This method begins to blur the boundaries between molecular coordination chemistry and solid-state chemistry. The temperature of these reactions is relatively low and this allows for the isolation of kinetically stabilized compounds, rather than dense, closely packed phases obtained from traditional high-temperature reactions. Thus compounds are prepared which contain either discrete molecular clusters or, more often, extended arrays which possess clearly recognizable coordination environments where covalent bonding directs structure.[51] Inclusion of these compounds in this article may help the reader to more easily bridge the rapidly disappearing gap between molecular and solid-state chemistry. The reactive molten salt methodology is only in its infancy and emerging very rapidly. In fact all of the results have come in the last 5 years. It is clear that, as the technique evolves, it will be a major source of novel compounds.

$$Ti + 2Na_2Se_4 \xrightarrow{375\ °C} Na_2Ti_2Se_8 \qquad (30)$$

$$1.5K_2Te + Cu + 6Te \xrightarrow{350\ °C} K_4Cu_8Te_{11} \qquad (31)$$

$$U + K_2Se_4 \xrightarrow{300\ °C} K_4U(Se_2)_4 \qquad (32)$$

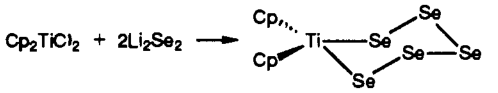
These constitute the bulk of the synthetic methods used to generate metal–selenide and –telluride complexes. There are other miscellaneous methods for forming metal–chalcogen bonds, but the vast majority of compounds are formed by some derivative of the methods described here.

3. Transition-Metal Selenides and Tellurides

3.1. Group 4

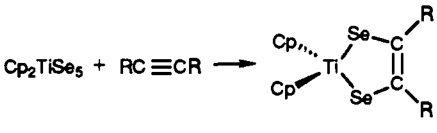
The chemistry of group 4 selenides is not very well-developed. This may be due to several factors, including the fact that group 4 elements are generally quite hard Lewis acids and are less inclined to form strong bonds with soft centers such as selenides and tellurides. Another reason is that the very polar oxygenated solvents used to handle the chalcogenide anions are reactive and difficult to get very dry. Thus they serve to block reaction sites of tetravalent group 4 centers. This could account for the fact that there are no binary molecular clusters of the group 4 chalcogenides. In addition, the simplest building blocks such as $TiSe_4^{4-}$ would have very high anionic charges which would destabilize the molecules, especially in solution.

There are several organometallic complexes known, however. Cp_2TiCl_2 will react with polyselenides to form Cp_2TiSe_5, which is directly analogous to the well-known sulfur compounds (eq 33).[52] Like the sulfur analog, it



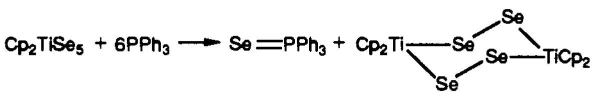
(33)

readily reacts with activated acetylenes to extrude selenium and form coordinated diselenolenes (eq 34).



R = CO(O)C (34)

It can also react with selenium-abstracting reagents such as PPh_3 to generate a bridged dimer (eq 35).[52,53]



(35)

These complexes have found use as group-transfer reagents to introduce pentaselenide or diselenolene fragments into rings leading to new selenides (eqs 36–38). The parent Cp_2TiSe_5 can also be used to transfer

$$\mathrm{S_2Cl_2 + Cp_2TiSe_5 \rightarrow cyclo\text{-}S_2Se_5 + Cp_2TiCl_2} \qquad (36)$$

$$\mathrm{Cp_2Ti(Se_2C_2R_2) + \mathit{cis}\text{-}PtCl_2(PPh_3)_2 \rightarrow (PPh_3)_2Pt(Se_2C_2R_2) + Cp_2TiCl_2} \qquad (37)$$

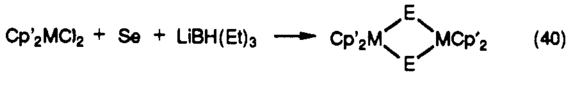
$$\mathrm{Cp_2Ti(\eta^2\text{-}Se_2)_2TiCp_2 + 2S_2Cl_2 \rightarrow S_4Se_4 + 2Cp_2TiCl_2} \qquad (38)$$

a diselenide fragment to various titanium porphyrins to form μ^2-Se_2 complexes (eq 39).[54]

$$\mathrm{(por)TiF + Cp_2TiSe_5 \rightarrow (por)Ti(\mu^2\text{-}Se_2)} \quad \text{por = TPP, OEP, etc.} \qquad (39)$$

One of the first successful reactions using molten polychalcogenides was conducted with titanium and sodium polyselenide to form $Na_2Ti_2Se_8$.[48] The structure consists of infinite one-dimensional chains with a repeat unit consisting of two seven-coordinate Ti(IV) centers bridged by three μ_2,η^2-Se_2^{2-} and two μ_2-Se^{2-} fragments (Figure 2).

The dimers $Cp'_2M(\mu_2\text{-}E)_2MCp'$ ($Cp' = C_5H_5$, C_5Me_5, C_5H_4(t-Bu); E = Se, Te; M = Zr, Hf) can be prepared either from the reaction of E^{2-}, prepared in situ, with the metal halide (eq 40).[55] The reactivity of these compounds is virtually unexplored.



$$\mathrm{Cp'_2MCl_2 + Se + LiBH(Et)_3 \longrightarrow Cp'_2M\overset{E}{\underset{E}{\diamond}}MCp'_2} \qquad (40)$$

$$\mathrm{Cp'_2M(C_2H_4)(C_2H_2) + E \longrightarrow Cp'_2M(\mu_2\text{-}E)_2MCp'} \qquad (41)$$

Fenske and co-workers have exploited the use trimethylsilyl (TMS) reagents to prepare an extensive series of Cp titanium clusters containing sulfur, selenium, and tellurium (eqs 42–45).[57] All the chalcogenides are in bridging positions and serve to tie the clusters together (Figure 3).

$$\mathrm{Cp_2TiCl_2 + (TMS)_2Se \rightarrow Cp_3Ti_2(\mu\text{-}Se)Cl} \qquad (42)$$

$$\mathrm{CpTiCl_3 + (TMS)_2Se \rightarrow Cp_4Ti_4Se_7O} \qquad (43)$$

$$\mathrm{Cp'_2TiCl_2 + (TMS)_2E \rightarrow Cp'_4Ti_2(\mu\text{-}E_2)} \quad \text{E = Se, Te} \qquad (44)$$

$$\mathrm{CpTiCl_3 + (TMS)_2E \rightarrow Cp'_5Ti_5(\mu_3\text{-}E)_7} \quad \text{E = Se, Te} \qquad (45)$$

Recently Keane and Ibers have been able to prepare the novel solid-state telluride $K_4M_3Te_{17}$ (M = Zr, Hf) using molten polytelluride in a fashion similar to that for the metal selenides and sulfides (eq 46 and Figure 4).[58] This reaction is of considerable significance, not only because the structure contains ditelluride fragments in almost every conceivable bridging coordination environment, but it also contains a tritelluride fragment. Since the reaction was performed at 900 °C, it is clear that these polychalcogenide fragments are quite thermally stable and low temperatures are not always necessary for their formation.

$$\mathrm{M + K_2Te + Te \xrightarrow{900\,°C} K_4M_3Te_{17}} \quad \text{M = Zr, Hf} \qquad (46)$$

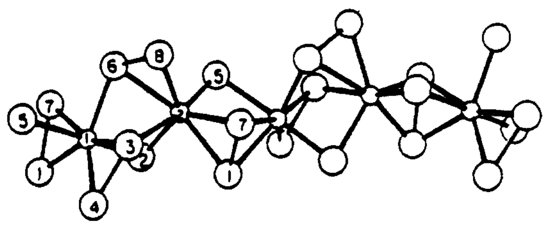


Figure 2. $[Ti_2(Se_2)_3(Se)_2]^{2-}$ (reprinted from ref 47; copyright 1988 American Chemical Society).

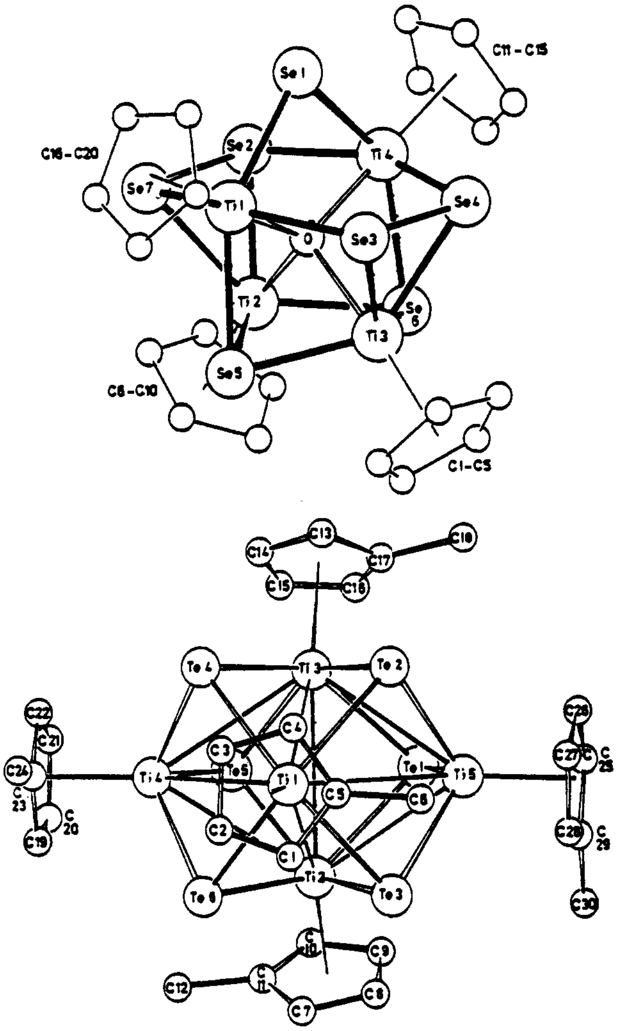


Figure 3. $Cp_4Ti_4Se_7O$ and $Cp'_5Ti_5(\mu_3\text{-}E)_7$ (reprinted from refs 56 and 57; copyright 1988 and 1990 Zeitschrift fur Naturforschung).

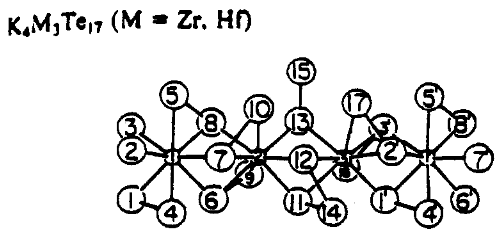


Figure 4. The $[Hf_3(Te_3)(Te_2)_7]^{4-}$ chain. Small circles represent Hf atoms; large circles are Te atoms. The atoms with primed numbers are related by translation (reprinted from ref 57; copyright 1991 American Chemical Society).

An interesting result was recently obtained by Christou and Arnold, who were able to induce elimination of R_2Te from $(RTe)_4M(dmpe)$ to form a compound containing the first group 4 metal telluride terminal double bonds (eq 47).[59]

$$(RTe)_4Zr(dmpe) + dmpe \rightarrow Te{=}M(RTe)(dmpe)_2 \quad M = Zr, Hf \quad R = sitel, Si(SiMe_3)_3 \quad (47)$$

3.2. Group 5

The coordination chemistry of group 5 elements is considerably richer than that of group 4 for both selenides and tellurides. In fact the chemistry of the heavier chalcogenides is, in many ways, somewhat better developed than that of sulfides. There is a number of exciting compounds in this triad which have no sulfur analogs.

The molecule $(CH_3C_5H_4)_2VSe_5$ can be prepared by reaction of $Cp'VCl_2$ and Li_2Se_5, and has a structure like that of corresponding titanium sulfide. Like Cp'_2VS_5, it undergoes thermolysis to form a novel dimer (eq 48 and Figure 5).[60] However, to our knowledge no further

$$(CH_3C_5H_4)_2VSe_5 \xrightarrow{\text{refluxing THF}} [(CH_3C_5H_4)_2V]_2Se_5 \quad (48)$$

reaction chemistry has been reported analogous to the vanadium pentasulfide and the well-explored titanium pentachalcogenides, nor is any corresponding telluride derivative known.

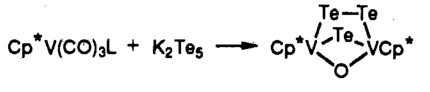
The selenide and telluride bridging dimers (μ-E)$[V(CO)_3(dppe)]_2$ have been prepared by reaction of the organometallic anion $[V(CO)_3(dppe)]^-$ with Na_2SeO_3 and Na_2TeO_3 (eqs 49 and 50). The linear configuration

$$[V(CO)_3(dppe)]^- + Na_2SeO_3 \xrightarrow{H_3PO_4} (dppe)(CO)_3V{=}Se{=}V(CO)_3(dppe) \quad (49)$$

$$[V(CO)_3(dppe)]^- + Na_2TeO_3 \xrightarrow{NaOH} (dppe)(CO)_3V{=}Te{=}V(CO)_3(dppe) \quad (50)$$

around the chalcogen center (180° for Se and 165° for Te) and the extremely short bond lengths (2.298(2) Å for V-Se and 2.518 Å for V-Te) suggest that there is substantial multiple bonding between the chalcogenide and the metal.[61] The reactivity of such multiply bonded species has been investigated to a certain degree for the vanadium complexes, but has been more fully explored for corresponding group 6 complexes (vide infra).

An extensive series of vanadium dimers containing mixed, bridging chalcogenide fragments has been prepared by reacting $Cp^*V(CO)_3L$ (where L = SMe_2, MeCN) with polytellurides to form $Cp^*V(\mu,\eta^2\text{-}Te_2)(\mu\text{-}Te)(\mu\text{-}O)VCp^*$, which is then reacted with a number of sulfur and selenium sources to form a variety of mixed chalcogen complexes (eqs 51–53).[62] Most of these



$$Cp^*V(CO)_3L + K_2Te_5 \longrightarrow Cp^*V(\mu\text{-}Te_2)(\mu\text{-}Te)(\mu\text{-}O)VCp^* \quad (51)$$

$$Cp^*_2V_2Te_3O + H_2S \longrightarrow Cp^*_2V_2Te_2S_2 \quad (52)$$

$$Cp^*_2V_2Te_3O + Na_2E_2 \longrightarrow Cp^*_2V_2Te_2EO \quad E = S, Se \quad (53)$$

compounds have not been structurally characterized aside from ^{51}V NMR spectroscopy.

The only soluble binary vanadium selenides are VSe_4^{3-} [63] and $[V_2Se_{13}]^{2-}$ [39] (eqs 54[63] and 55[39] and Figure 6). The cluster from eq 55 consists of two seven-coordinate V(IV) centers in a face capped trigonal prismatic coordination environment. The d^1–d^1 configuration and V–V distance of 2.779 Å indicate the presence of a metal–metal bond. The bridging pentaselenide is quite unusual although there is some precedent in the sulfide $[Mo_2(NO)_2(S_2)_3(S_5)(OH)]^{3-}$.[64] The coordination characteristics of the bridging diselenides bear a resemblance to those of the solid-state compound V_2Se_9, which also contains an infinite chain of vanadium atoms bridged by various diselenide fragments.[65] There are no reported reactions of VSe_4^{3-}, nor are there any vanadium telluride clusters known.

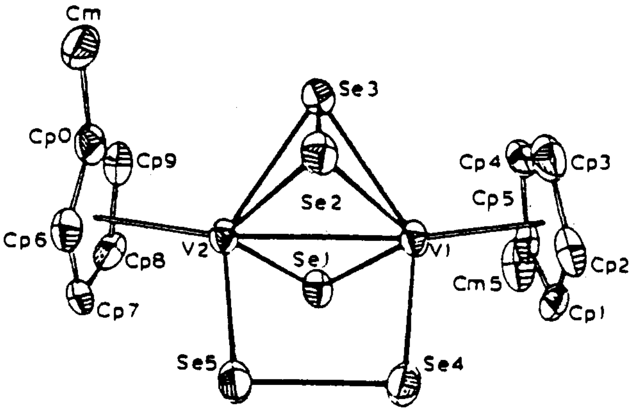


Figure 5. (η^5-$C_5H_4Me)_2V_2Se_5$ (reprinted from ref 59; copyright 1990 Elsevier Science Publishers B.V.).

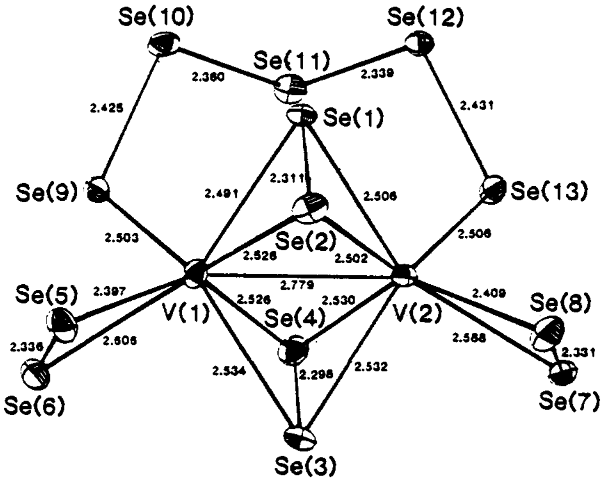


Figure 6. $[V_2Se_{13}]^{2-}$ (reprinted from ref 38; copyright 1987 American Chemical Society).

$$VO_4^{3-} + H_2Se \rightarrow VSe_4^{3-} + H_2O \quad (54)$$

$$VO_4^{3-} + (Me_2octylSi)_2Se \text{ (excess)} \rightarrow [V_2(\eta^2\text{-}Se_2)_2(\mu\text{-}\eta^2Se_2)_2(Se_5)]^{2-} \quad (55)$$

The heavier group 5 elements have a very rich structural chemistry with Se and Te, but much of it involves extended insoluble solids with some recognizable molecular coordination properties. The tetraselenometalates have been prepared only recently by solid-state reactions (eq 56).[66] These appear to be

$$K + M + Se \xrightarrow{850\,°C} K_3MSe_4 \quad M = Nb, Ta \quad (56)$$

unstable in solution, and all attempts to utilize them as soluble reactants result in decomposition. However,

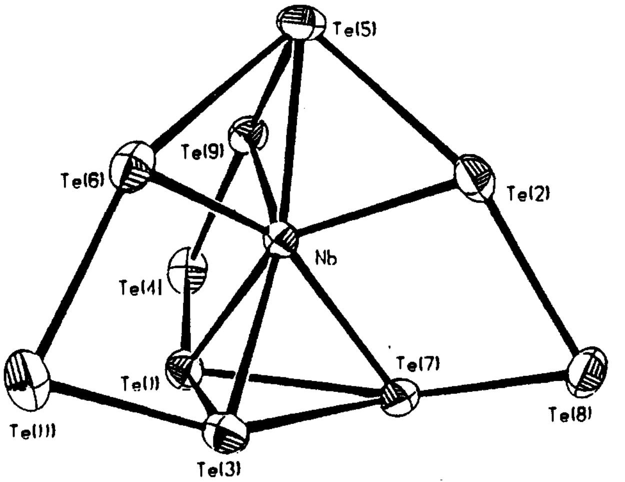


Figure 7. $[NbTe_{10}]^{3-}$ (reprinted from ref 66; copyright 1988 American Chemical Society).

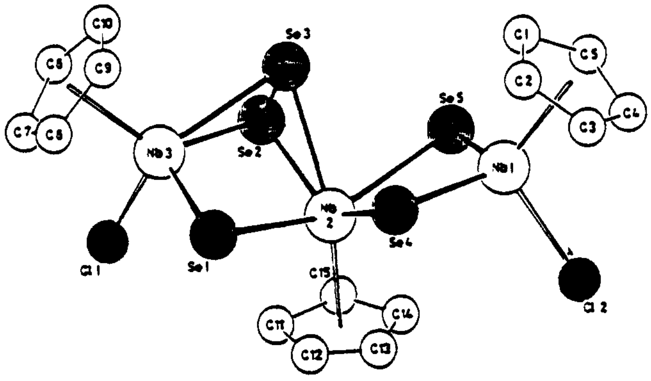


Figure 8. $Cp_3Nb_3Se_5Cl_2$ (reprinted from ref 69; copyright 1989 Zeitschrift fur Naturforschung).

recent successes with NbS_4^{3-} is encouraging.[67] There is no report of the corresponding tellurides.

A very unusual molecule can be isolated in good yield from the reaction of metal pentachlorides with polytellurides (eq 57 and Figure 7).[68] This compound

$$NbCl_5 + Te_4^{2-} \rightarrow NbTe_{10}^{3-} \quad (57)$$

contains a 10-membered tellurium cage with an interstitial Nb atom. (The tantalum analog has been subsequently isolated as well.[68b]) The oxidation state of the metal center is not obvious. It is situated in an irregular seven-coordination environment within the tellurium cage. Simple electron counting rules predict an excess of four electrons delocalized over the tellurium framework. We postulate that the large size and diffuse orbitals of the tellurium atoms account for the stability of this unusual molecule. A detailed calculation on this nonclassical molecule shows it to be electron rich with a pair electrons residing in a high-lying nonbonding orbital, with favorable orbital overlap between Nb and Te responsible for its stability.[69] (All attempts to prepare the analogous metal selenides and sulfides have thus far resulted only in insoluble powders.)

Fenske has used the (trimethylsilyl)selenide route to prepare an organometallic niobium selenide which again contains a series of bridging selenides and diselenides (eq 58 and Figure 8).[70] Note that in the reaction a redox

$$CpNbCl_4 + (TMS)_2Se \rightarrow Cp_3Nb_3(\mu_2,\eta^2\text{-}Se_2)(\mu\text{-}Se)_3Cl_2 \quad (58)$$

reaction has also taken place in that two of the niobium atoms have been formally reduced to Nb^{4+}.

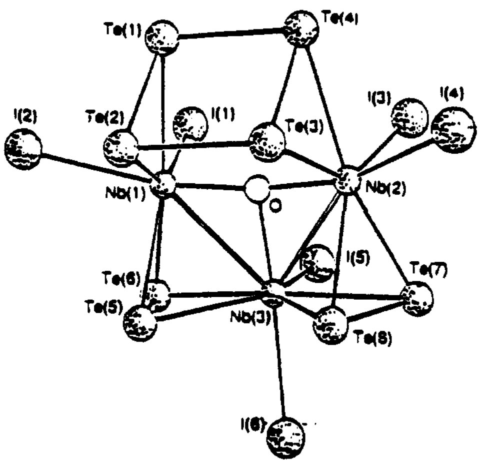


Figure 9. $[Te_4Nb_3O(Te_2)_2I_6]^+$ (reprinted from ref 70; copyright 1992 Royal Society of Chemistry).

A number of metal selenide and telluride clusters have been prepared directly from the elements or from simple complexes by selenium-transfer reactions (eqs 59,[71] 60,[72] and 61[73a]). These compounds are molecular

$$2Nb + NbOI_3 + 8Te + 4I_2 \xrightarrow{680\ °C} [Nb_3Te_4O(Te_2)_2I_6]I \quad (59)$$

$$Nb + E + X_2 \xrightarrow{1075\ °C} Nb_2(\mu\text{-}\eta^2E_2)X_6 \quad X = Br, I \quad E = Se, Te \quad (60)$$

$$NbBr_4(NCMe)_2 + Sb_2Se_3 \rightarrow Nb_4Br_{10}(\mu\text{-}\eta^2Se_2)(\mu\text{-}Se)(NCMe)_4 \quad (61)$$

in appearance but little evidence has been given regarding their solubility or stability in solution.[73] They all contain the ubiquitous bridging dichalcogenide with the metal center in a high oxidation state, usually M(IV) with a metal–metal bond. The metal centers are commonly in a seven- or eight-coordinate environment. The product from eq 59 is especially unique, with a capping Te_4^{2+} ring helping to hold the cluster together (Figure 9).[71]

The heavy group 5 metals have also proven amenable to reaction with molten polychalcogenides, generating solids containing infinite chains of metals bridged by dichalcogenide fragments (eq 62).[74] The structure of

$$3K_2Se + 10Se + Nb \xrightarrow{375\ °C} K_3Nb_2Se_{11} \quad (62)$$

the compound from eq 62 contains recognizable $Nb_2(Se_2)_4(Se)_2$ fragments bridged by another Se_2 fragment (Figure 10), giving each fragment a structure similar to the molecular species $[Mo_4S_{18}O_4]^{2-}$.[75] Like many of the other compounds of this type, each metal is in the 5+ oxidation state and has an irregular seven-coordinate environment.

By far the largest amount of work on heavier group 5 chalcogenides has involved the one-dimensional chains having formulas like $NbSe_3$, $NbTe_4$, and $(TaSe_4)_nI$.[76] These compounds are made by traditional high-temperature methods, and continue to attract a great deal of attention because of their very unusual physical

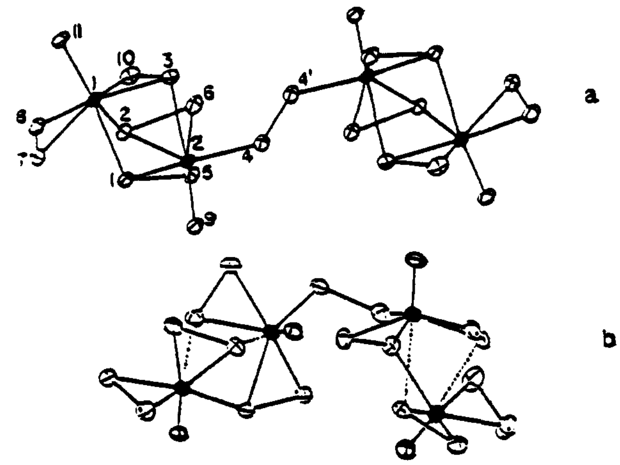


Figure 10. $[Nb_4Se_{22}]^{6-}$ in comparison to $[Mo_4S_{18}O_4]^{2-}$ (reprinted from ref 74; copyright 1989 American Chemical Society).

properties, specifically non-Ohmic conductivity.[77] They generally consist of a one-dimensional array of metal centers coordinated by rectangular units of chalcogenides, which are actually better thought of as interacting E_2^{2-} units. These solids can be doped with various amounts of iodine to generate a new class of one-dimensional conductors, which have been the subject of some very detailed investigations.

3.3. Group 6

Like their sulfide analogs, the group 6 selenides and tellurides have proven to be fertile ground for study. Though not quite as extensively investigated as the sulfides, the metal selenides, and to a lesser extent the tellurides, have proven themselves to be quite stable and amenable to chemical manipulation. It is generally accepted that the stability of the molybdenum sulfides is due to the favorable overlap between the metal d and sulfur p orbitals. Based on chemistry which has evolved in the last 5 years, the same argument seems to hold true for the selenium p orbitals as well. It would appear that the selenide orbital overlap is especially favorable for tungsten. In fact the tungsten selenides seem to be the closest heavier analogs to the molybdenum sulfides, which is supported by the extensive chemistry recently developed for the W–Se system.

Chromium selenides and tellurides, like their corresponding sulfides, are not very common relative to the Mo and W complexes. In fact, to our knowledge, there is no binary chromium sulfide molecular complex. There is however, one example of a molecular binary chromium selenide known, as well as its corresponding tellurium analog (eq 63 and Figure 11).[22] The structure

$$CrCl_3 + 2E_4^{2-} \rightarrow [Cr_3(E_4)_6]^{3-} \quad E = Se, Te \quad (63)$$

consists of three Cr(III) ions in a linear array, with the terminal Cr atoms chelated by three E_4^{2-} ligands, generating an octahedral coordination environment. A metal-bound atom on each of the chelating E_4^{2-} groups bridges to the central Cr atom, creating an octahedral-coordination environment around it as well. The Cr atoms are too far apart to have any direct interaction, but magnetic studies indicate that there is weak antiferromagnetic coupling through the bridging ligands.[78]

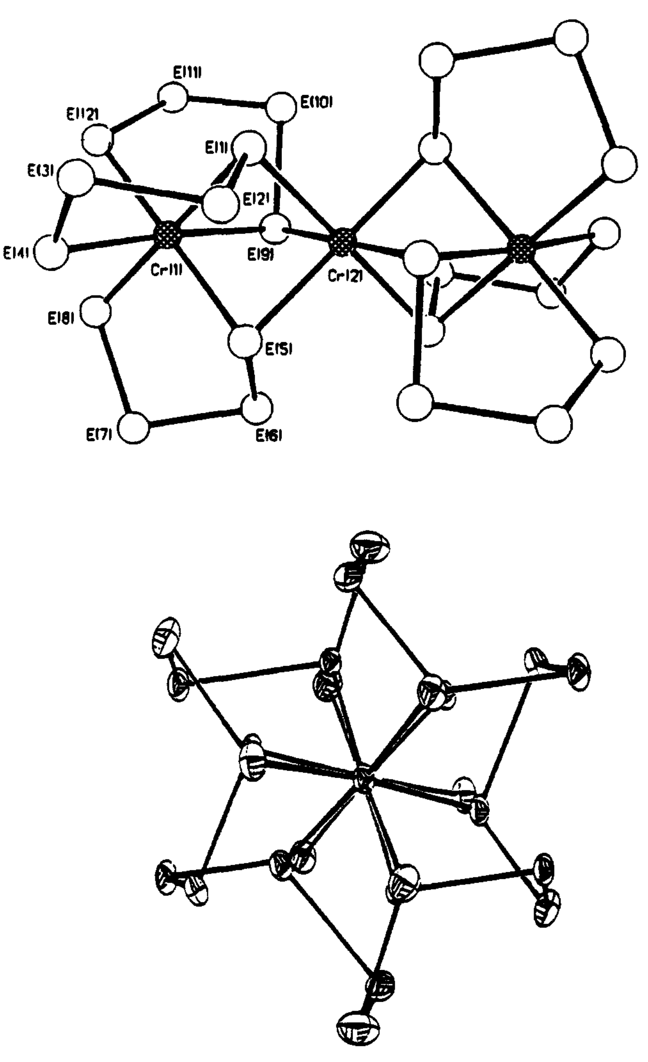


Figure 11. Side and end view of the $[Cr_3E_{24}]^{3-}$ anion (reprinted from ref 21; copyright 1988 VCH Verlagsgesellschaft mbH).

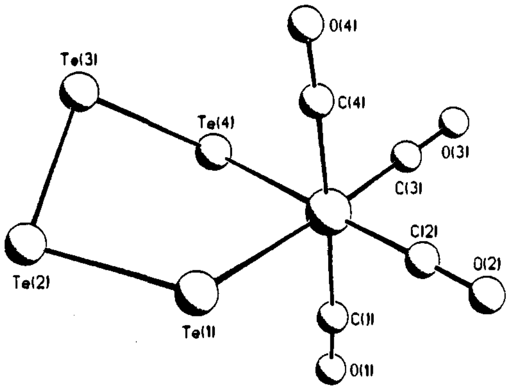


Figure 12. $[(CO)_4Cr(Te_4)]^{2-}$ (reprinted from ref 79; copyright 1988 American Chemical Society).

The remainder of the chromium selenide and telluride complexes reported are all organometallic complexes. The Te_4^{2-} fragments reacts cleanly with equimolar amounts $Cr(CO)_6$ to yield a complex containing a chelated tetratelluride fragment (eq 64 and Figure 12).[79]

$$Cr(CO)_6 + Te_4^{2-} \rightarrow [(CO)_4Cr(Te_4)]^{2-} \quad (64)$$

Identical products are obtained if $Mo(CO)_6$ or $W(CO)_6$ are used. The coordination environment around the metal center is not substantially distorted from octahedral, indicating no special steric demands on the part of the large tellurium ligands. The five-membered ring crystallizes in an envelope conformation similar to that observed in many coordinated tetrasulfides and -selenides. At the time this was the first metal complex of a polytelluride of this type isolated. Surprisingly, the molecule is stable and the tetratelluride fragment is quite unreactive, showing no tendency to extrude elemental tellurium to form a shorter fragment, either during thermolysis or photolysis.

If an excess of metal carbonyl is used in the presence of various polytellurides, several multinuclear products can be isolated (eqs 65–67 and Figure 13).[80] The

$$3Cr(CO)_6 + Te^{2-} \rightarrow [Cr_4(CO)_{20}Te_2]^{2-} \quad (65)$$

$$3Cr(CO)_6 + Te_2^{2-} \rightarrow [Cr_4(CO)_{18}Te_2]^{2-} \quad (66)$$

$$3Cr(CO)_6 + Te_n^{2-} \rightarrow [Cr_4(CO)_{20}Te_3]^{2-} \quad n = 3\text{–}5 \quad (67)$$

products of eqs 65 and 67 are adducts of polytelluride fragments, with the metal carbonyl fragments merely acting as Lewis acids toward the lone pairs on the tellurium atoms. The product from eq 66 is a result of oxidative addition across two Cr atoms, forming metal–metal bonded Cr(I) centers. In all cases the metals are octahedrally coordinated. The corresponding reactions of polyselenides and chromium carbonyl are not straightforward and are currently under investigation. If a reaction is carried out using Na_2Se or Na_2Te in a protic solvent such as methanol, no clusterification is observed, but rather a protonated chalcogenide can be isolated (eq 68).[81]

$$M(CO)_5THF + Na_2E \xrightarrow{CH_3OH} [M(CO)_5(EH)]^- \quad E = Se, Te \quad M = Cr, W \quad (68)$$

A fairly extensive series of dimers containing bridging selenides has been investigated. The reactive $Cp_2Cr_2(CO)_x$ ($x = 4, 6$) dimers can combine with selenium transfer reagents,[33] or the parent anions can reduce selenates[82] to form a series of selenide bridging dimers. The most interesting of these contain linear multiply bonded selenide (eqs 69 and 70). These complexes are

$$Cp_2Cr_2(CO)_6 + Se_8 \rightarrow (CO)_2CpCr{=}Se{=}CrCp(CO)_2 \quad (69)$$

$$[CpCr(CO)_3]^- + SeO_3^{2-} \rightarrow (CO)_2CpCr{=}Se{=}CrCp(CO)_2 \quad (70)$$

proposed to contain multiply bonded selenides on the basis of their extremely short Cr–Se bond lengths, the linearity of the bonds, and the electron count around the metal center. Indeed, these compounds behave like unsaturated centers, inserting methylene fragments or more selenium (eqs 71 and 72). The corresponding reaction with tellurium shows a decreased tendency to form multiply bonded metal tellurides. The parent anion $CpM(CO)_3^-$ reacts to form the saturated bridging species, but carbon monoxide does not dissociate upon heating or photolysis to produce unsaturated species (eq 73).[83] This is not unexpected given the decreased π overlap ability of tellurium relative the its lighter congeners. Interestingly, however, $Cp_2M_2(CO)_6(\mu\text{-}Te)$ can be protonated at the telluride to form one of the

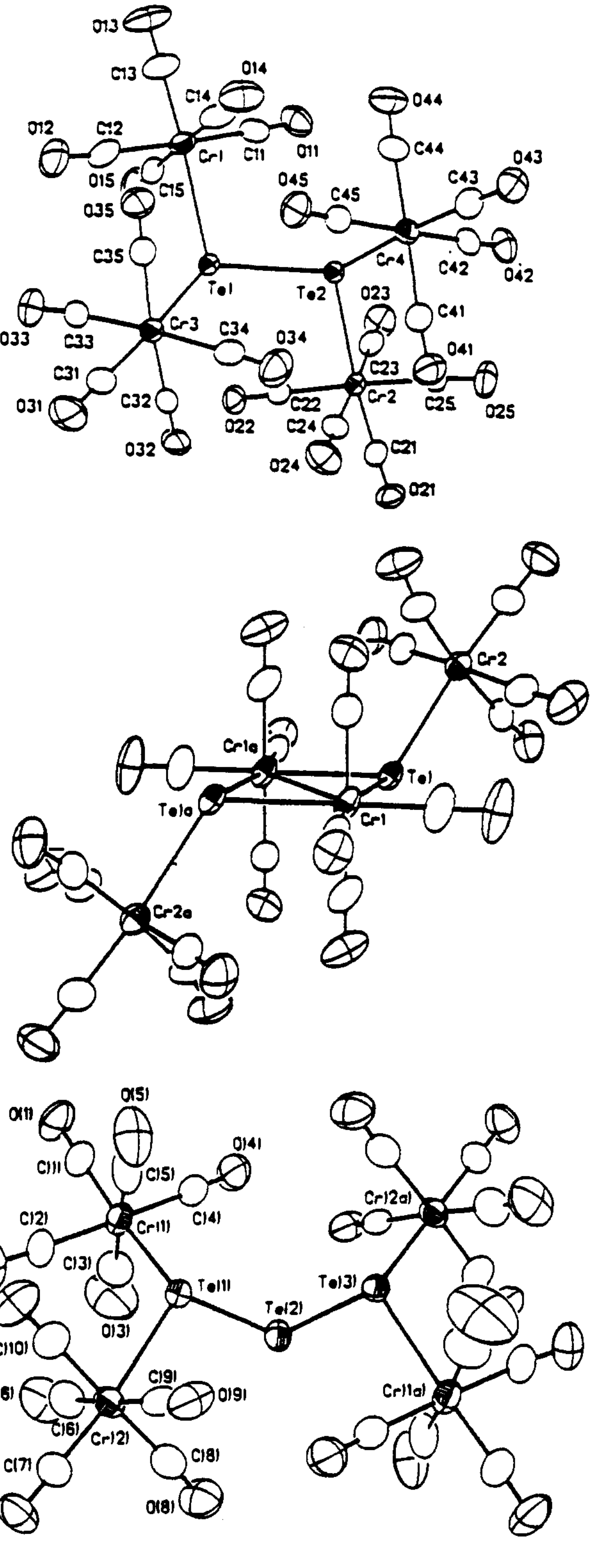


Figure 13. $[Cr_4(CO)_{20}Te_2]^{2-}$, $[Cr_4(CO)_{18}(Te)_2]^{2-}$, and $[Cr_4(CO)_{20}Te_3]^{2-}$ (reprinted from ref 80; copyright 1992 American Chemical Society).

$$(CO)_2CpCr{=}Se{=}CrCp(CO)_2 + Se_8 \rightarrow [CpCr(CO)_4](\mu_2\text{-}\eta^2\text{-}Se_2) \quad (71)$$

$$(CO)_2CpCr{=}Se{=}CrCp(CO)_2 + CH_2N_2 \rightarrow Cp_2Cr_2(CO)_4(\mu\text{-}CH_2Se) \quad (72)$$

$$CpM(CO)_3^- + K_2TeO_3 \rightarrow Cp_2M_2(CO)_6(\mu\text{-}Te) \quad (73)$$

rare examples of a coordinated TeH^- groups (eq 74).

$$Cp_2M_2(CO)_6(\mu\text{-}Te) + HBF_4 \rightarrow [Cp_2M_2(CO)_6(\mu\text{-}TeH)]^+BF_4^- \quad (74)$$

Unsaturated cyclopentadienyl metal carbonyl dimers will also react with elemental chalcogens to form a series of dimers and cubanes with various type of bridging chalcogenides (eqs 75 and 76).[33,84] Finally, the cubane $(MeC_5H_4)_4Cr_4E_4$ (E = Se, Te) can be prepared by heating chromocene or $Cp_2Cr_2(OCMe_3)_2$ and the elemental chalcogen in toluene for several hours.[85]

$$Cp_2Cr_2CO_6 + Se_8 \xrightarrow{\Delta} Cp_2Cr_2(CO)_6(\mu\text{-}Se) \quad (75)$$

$$Cp_2Cr_2(CO)_6(\mu\text{-}Se) \xrightarrow{Se_8} Cp_2Cr_2(CO)_5(\mu_1,\eta^2\text{-}Se_2) \rightarrow Cp_2Cr_2(CO)_4(\mu_2,\eta^2\text{-}Se_2) \quad (76)$$

The selenides of molybdenum and tungsten are not as well-explored as the sulfides, but extensive progress has been made in the last several years. The original synthesis of the principal building blocks, MSe_4^{2-}, is quite old and is similar to the corresponding tetrathiometalates.[12] However, recently several improved methods have become available[86-88] which considerably simplify the preparation and isolation of the tetraselenometalates (eqs 77–79).

$$W(t\text{-}NBu)_2(t\text{-}NHBu)_2 + H_2Se \rightarrow WSe_4^{2-} \quad (77)$$

$$M(CO)_6 + Se_4^{2-} \rightarrow MSe_4^{2-} \quad (78)$$

$$MO_4^{2-} + (Me_2octylSi)_2Se \rightarrow MSe_4^{2-} \quad (79)$$

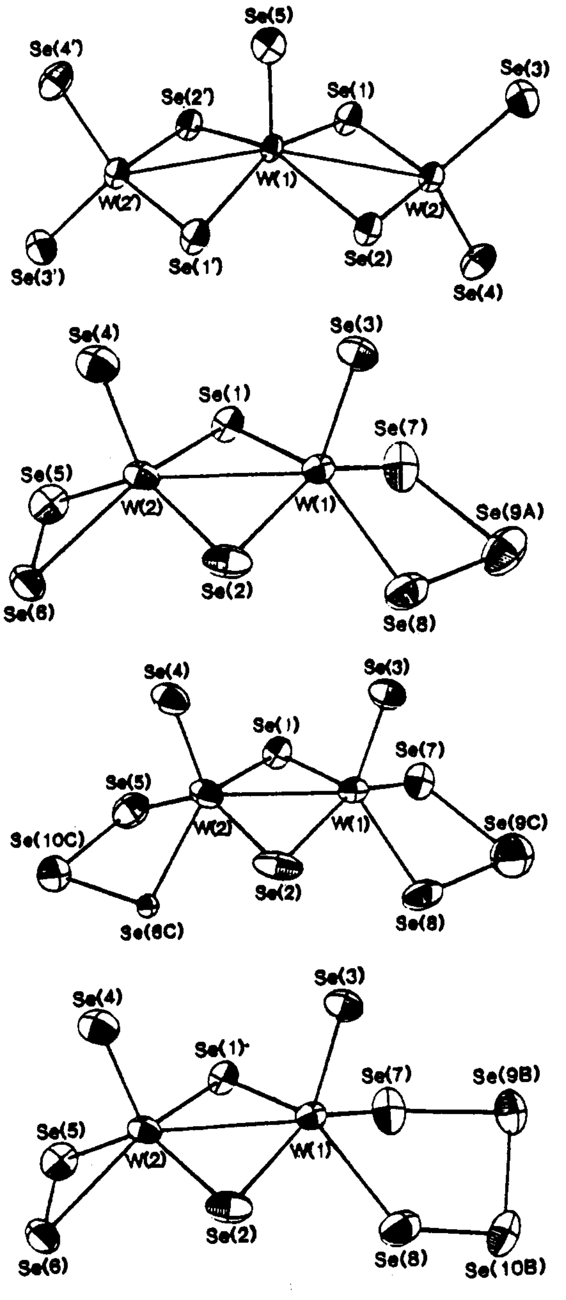


Figure 14. $[W_3Se_9]^{2-}$, $[W_2Se_9]^{2-}$, and the two isomers of $[W_2Se_{10}]^{2-}$ (reprinted from ref 27; copyright 1987 American Chemical Society).

With these important tools in hand, the chemistry has been opened up rather dramatically in the last 5 years. Perhaps the most impressive work has been the development of a large number of binary metal selenides. Many of these have been made using the same approaches used with metal sulfides. However, the reactions are often considerably different, and in some cases there are no sulfur analogs to the new metal selenides (eqs 80,[87] 81,[88] 82,[88] and 83–85[28,89] and Figure 14). The synthetic chemistry leading to these compounds is quite complex. Ibers and co-workers have elegantly worked out much of the solution chemistry using ^{77}Se NMR.[89] These species all contain W(V) ($W_3Se_9^{2-}$ also contains one W(VI)) metal centers which are in square pyramidal coordination environments. They all contain terminal selenides as well as chelating di-, tri-, and tetraselenide fragments. In that regard they are similar to the molybdenum sulfides. It should be noted that there are very few examples of polychalcogenide chains longer than four coordinated to metals to the right of group 5 in the periodic table. The availability of the new anions has allowed preliminary exploration of their chemistry. Some of the new clusters can undergo further chemistry leading to new binary anions by reduction of selenium–selenium bonds (Figure 15).[90] The reduction of coordinated polyselenides should be a general reaction type, although not many examples have yet been reported (eq 86).

$$MoSe_4^{2-} + Se_8 \rightarrow [Se{=}Mo(Se_4)_2]^{2-} \quad (80)$$

$$MSe_4^{2-} + SSe_2 \rightarrow [S{=}M(Se_4)_2]^{2-} \quad (81)$$

$$MSe_4^{2-} + pip_2Se_4 \rightarrow [O{=}M(Se_4)_2]^{2-} \quad (82)$$

$$WSe_4^{2-} + CH_3COOH \rightarrow [W_3Se_9]^{2-} \quad (83)$$

$$WSe_4^{2-} + PPh_4Cl \xrightarrow{85\ ^\circ C} [W_2Se_9]^{2-} \quad (84)$$

$$WSe_4^{2-} + \text{gray Se} \rightarrow [W_2Se_{10}]^{2-} \quad \text{two isomers} \quad (85)$$

$$[W_2Se_{10}]^{2-} + BH_4^- \rightarrow [W_2Se_6]^{2-} \quad (86)$$

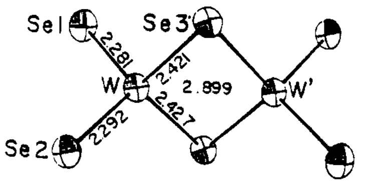


Figure 15. $[W_2Se_6]^{2-}$ (reprinted from ref 90; copyright 1989 American Chemical Society).

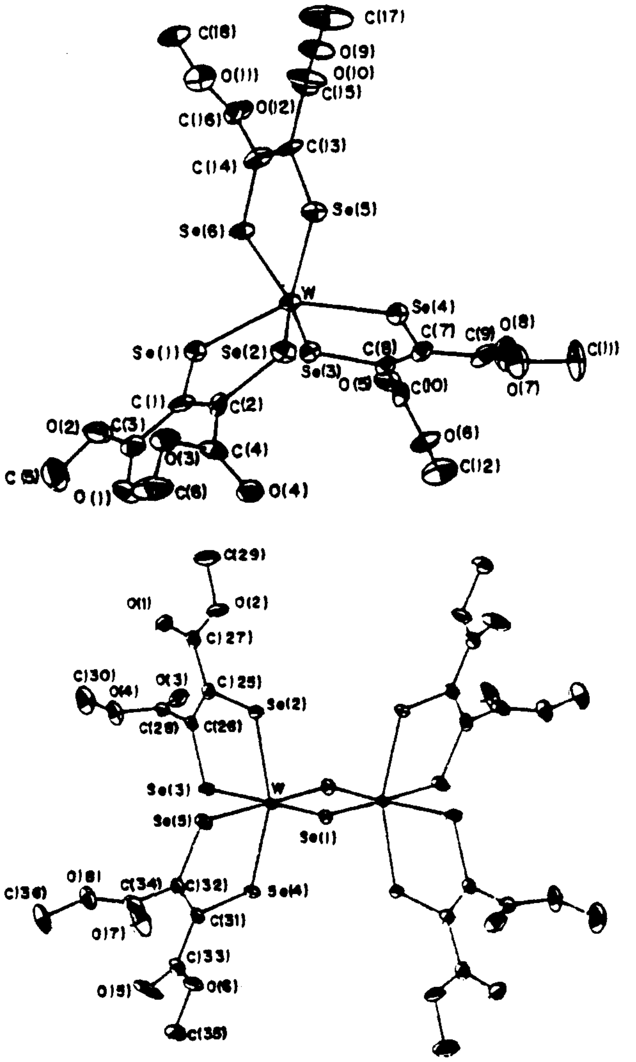


Figure 16. $[W(Se_2C_2(COOCH_3)_2)_3]^{2-}$ and $[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]^{2-}$ (reprinted from ref 91; copyright 1989 American Chemical Society).

The new complexes containing coordinated tetraselenides can undergo reactions with activated acetylenes leading to formation of complexes of coordinated diselenolenes with structures similar to Mo/S compounds (eqs 87 and 88 and Figure 16)[91] The tetraselenometalates themselves can also act as ligands toward metal complexes. Although this aspect of their chemistry is not as well-developed as with the tetrathiometalates, preliminary results indicate that it has enormous potential. However some classical complexes like those below have been isolated.[92,93] The isolation of $[Ni(Se_2)(WSe_4)]^{2-}$ (Figure 17) from the reaction of $Ni(acac)_2$ and WSe_4^{2-} indicates that the chemistry is more complex than originally thought.[93] In this case, the tetraselenometalate is acting both as a ligand and a sacrificial source of diselenide. There is no obvious reason for this redox chemistry to take place, as the Ni(II) does not change oxidation states, but the tungsten atom gets reduced through induced internal redox reaction. There is no precedent for this reaction in tetrathiometalate chemistry, suggesting that further exploration of MSe_4^{2-} reactivity will lead to further novel results.

$$W_2Se_9^{2-} + DMAD \rightarrow [W(Se_2C_2(COOCH_3)_2)_3]^{2-} \quad (87)$$

$$W_2Se_{10}^{2-} + DMAD \rightarrow [W_2Se_2(Se_2C_2(COOCH_3)_2)_4]^{2-} \quad (88)$$

DMAD = dimethyl acetylenedicarboxylate, $CH_3O(O)C{\equiv}C(O)OCH_3$

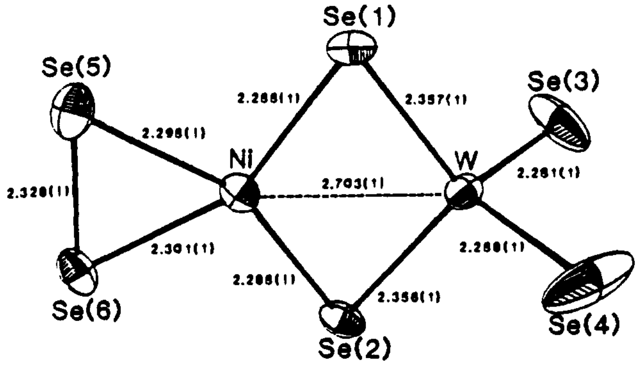
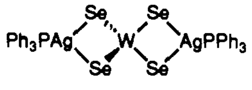
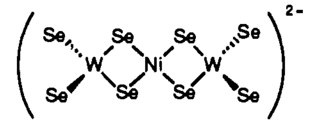


Figure 17. $[Ni(Se_2)(WSe_4)]^{2-}$ (reprinted from ref 93; copyright 1989 American Chemical Society).





The tetraselenometalates undergo complex internal redox chemistry by reaction with thiuram ($R_2NC(S)SSC(S)NR_2$, where R = CH_3) to form a M(V) complex with a side-bonded diselenide (eq 89).[94] This involves both oxidation of the coordinated selenides and reduction of the metal center, along with a reduction of the thiuram. Analogous induced internal redox chemistry is well-known with metal sulfides.[1e] The tetraselenometalates also act as nucleophiles toward other electrophilic main-group clusters, leading to formation of some highly unusual complexes (eqs 90–92).[95,96] The product of eq 90 contains W(IV) in an irregular 6-fold coordination environment with two new ligands, a side-bonded PSe_2^- and a chelating PSe_4^{3-} (Figure 18). The side-bonded PSe_2^- has no sulfur analog and is isoelectronic with nitrite or allyl. The complexes from eqs 91 and 92 contain W(V) and Mo(IV), also in irregular 6-fold

$$WSe_4^{2-} + R_2NC(S)SSC(S)NR_2 \rightarrow WSe_2(S_2CNR_2)_3 \quad (89)$$

$$WSe_4^{2-} + P_4Se_4 \rightarrow [Se{=}W(PSe_2)(PSe_4)]^{2-} \quad (90)$$

$$WSe_4^{2-} + As_4Se_4 \rightarrow [W_2(\mu\text{-}Se)_3(AsSe_5)_2]^{2-} \quad (91)$$

$$MoSe_4^{2-} + As_4Se_4 \rightarrow [Mo(AsSe_5)_2]^{2-} \quad (92)$$

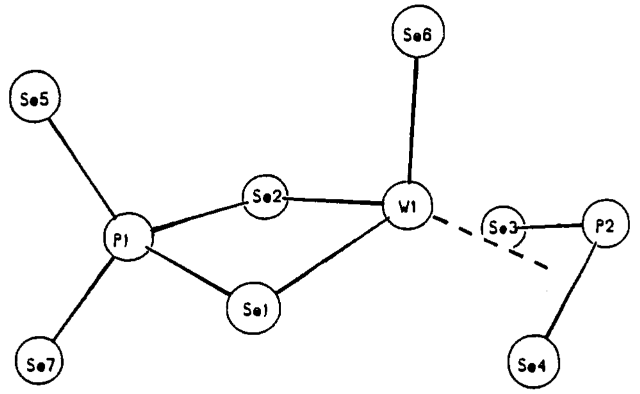


Figure 18. [Se=W(PSe$_2$)(PSe$_4$)]$^{2-}$ (reprinted from ref 95; copyright 1990 VCH Verlagsgesellschaft mbH).

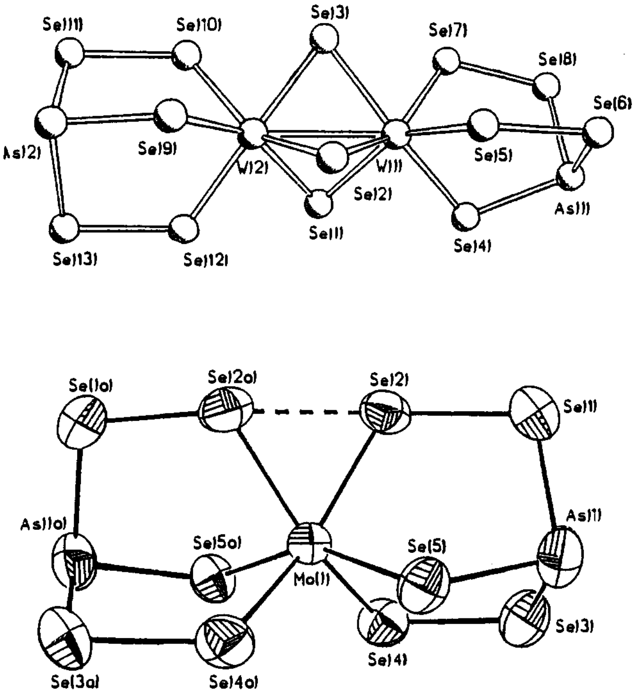


Figure 19. [W$_2$(μ-Se)$_3$(AsSe$_5$)$_2$]$^{2-}$ and [Mo(AsSe$_5$)$_2$]$^{2-}$ (reprinted from ref 96; copyright 1991 American Chemical Society).

coordination environments (Figure 19). They are each ligated by the novel tridentate AsSe$_5$$^{3-}$ ligand, forming a hybrid cage structure. These complexes do not have any sulfur analogs. The original reaction of this type was done using an arsenic sulfide and MoS$_4$$^{2-}$, but its product bears no structural resemblance to these selenides.[97] All of our attempts to further develop the corresponding phosphorus and arsenic sulfide chemistry have thus far met with failure, and it is our subjective feeling that the selenide complexes are considerably more stable with respect to decomposition in solution, and their chemistry correspondingly richer.

A large number of tungsten and molybdenum selenides contain halide or phosphine ligands and form clusters with face-bridging selenides. Some examples are given below (eqs 93–95 and Figure 20).[98–100] Many of these have sulfur analogs with cubane or octahedral shapes.

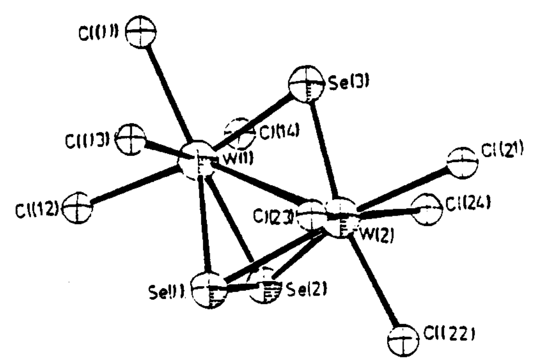


Figure 20. [W$_2$(μ-Se)(μ_2-η^2Se$_2$)Cl$_8$]$^{2-}$ (reprinted from ref 98; copyright 1979 American Chemical Society).

$$WCl_3Se + AsPh_4Cl \rightarrow [AsPh_4]_2[W_2(\mu\text{-}Se)(\mu_2\text{-}\eta^2Se_2)Cl_8] \quad (93)$$

$$Mo_3Se_4Cl_4(PEt_3)_5 + Ni(cod)_2 \rightarrow Mo_3Ni_2(\mu_3\text{-}Se)_4Cl_4(PEt_3)_5 \quad (94)$$

$$[Mo_2O_2(\mu\text{-}Se)_2(cysteine)_2]^{2-} + BH_4^- \xrightarrow{H_2O/H^+} [Mo_4(\mu_3\text{-}Se)_4(H_2O)_{12}]^{5+} \quad (95)$$

There has been, of course, an enormous amount of work done on the class of solid-state molybdenum selenides known as the Chevrel phases. These densely packed solids consist of molybdenum octahedra face capped with selenides and have been the subject of intense scrutiny because of their superconductivity.[101] Though it would not be appropriate to discuss these compounds in depth here, several interesting aspects deserve mention. If the reaction stoichiometries, times, and temperatures are altered slightly, a new series of compounds, A$_2$Mo$_6$E$_6$ (A = a univalent metal; E = S, Se, Te), can be isolated.[102] These phases have a channel structure with infinite chains of face-sharing molybdenum octahedra surrounded by capping selenide atoms, with the monocations occupying the channels. The chains can be cleaved by reaction of the solids with various ratios of Mo$_6$E$_8$. Depending on the relative amounts of the two reactants, a fascinating series of compounds can be obtained having the formula A$_{2n-2}$Mo$_{6n}$E$_{6n+2}$ (n = 1–5). These structures are actually a series of shortened chains of face-sharing octahedra capped by chalcogenides (Figure 21). The properties of these exciting molecules have not been investigated in depth.[103] Interestingly, however, they can be solubilized. In an important piece of work, Tarascon and co-workers have discovered that these solids will dissolve in highly polar solvents such as N-methylformamide to generate solutions presumably containing molybdenum selenide chains.[104]

Another unusual series of solid-state molybdenum selenide clusters have been prepared hydrothermally via reaction of K$_2$Se$_n$ (n = 2,4) with molybdenum metal or MoO$_3$ in water at 135 °C (eqs 96–98).[105,106] These

$$Mo + K_2Se_4 \rightarrow [K_2Mo_3Se_{18}]_n \quad (96)$$

$$MoO_3 + K_2Se_2 \rightarrow K_8Mo_9Se_{40}\cdot 4H_2O \quad (97)$$

$$Mo + 2K_2Se_4 \rightarrow K_{12}Mo_{12}Se_{56} \quad (98)$$

compounds all contain Mo(IV) trimers held together by Mo–Mo bonds and various polyselenide fragments (Se$_n$$^{2-}$, n = 1–4) (Figure 22). The coordination environment of the metal core is similar to that in classical

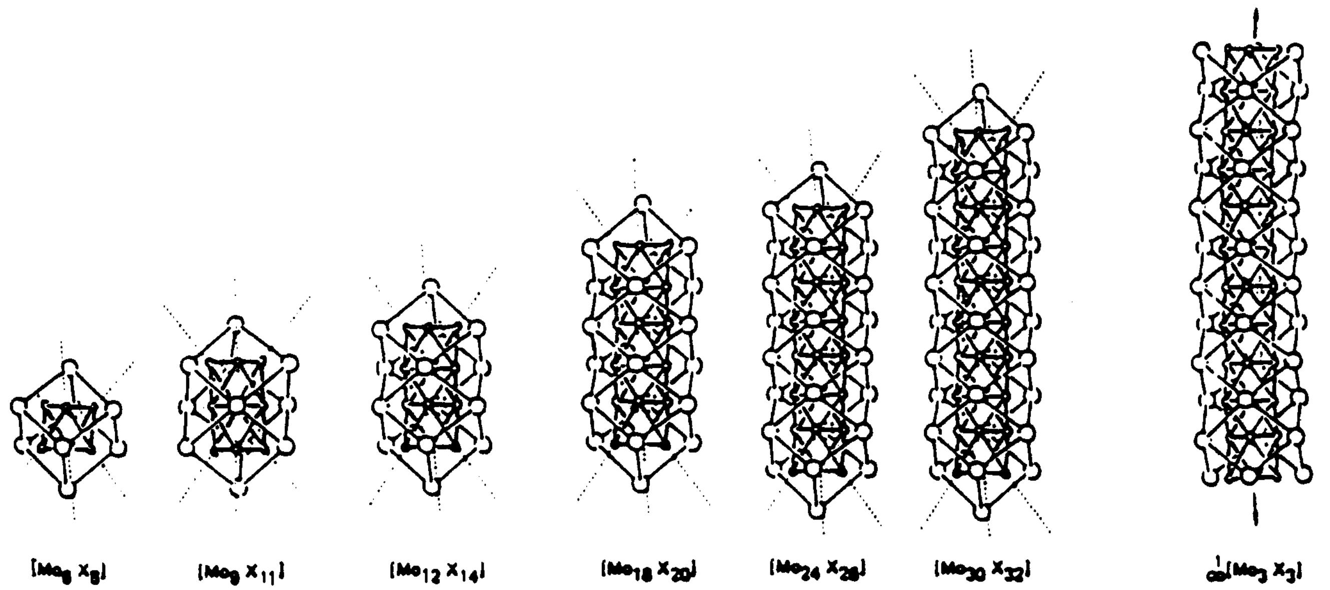


Figure 21. Cluster condensation of $Mo_{3n}X_{3n+2}$ (reprinted from ref 98; copyright 1985 Academic Press, Inc).

molybdenum sulfur halide complexes such as $Mo_3S_7Cl_4$.[107] However, the arrangement of the polyselenides, and their role in linking the clusters together to form polymeric chains of clusters, is quite unique, making them another series of solid-state stabilized species which have recognizable molecular coordination characteristics.

Surprisingly, the corresponding tellurides are quite undeveloped. The most noticeable absence are the tetratellurides $MoTe_4^{2-}$ and WTe_4^{2-}. A number of attempts to prepare these important building blocks have met with little success.[108] In fact, it has only been recently that the first terminal metal telluride bond of any type has been reported (eq 99).[109] This compound

$$W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H + Te \rightarrow W(PMe_3)_4(Te)_2 \quad (99)$$

clearly contains two W=Te double bonds, as the W–Te bond length (2.596(1) Å) is considerably shorter than other W–Te single bond distances (2.68–2.88 Å). The ease of preparation and stability of this compound augurs well for the future of metal tellurides.

Polytellurides react readily with W and Mo salts to form several new telluride complexes. For example quadrupally bonded $Mo_2(OAc)_4$ reacts with polytellurides to form an unusual cluster which contains two Mo–Mo triply bonded fragments with terminal μ_2,η^1 $Te_2{}^2$ fragments, along with bridging $Te_3{}^{2-}$ and $\mu_2\text{-}\eta^1,\mu_2\text{-}\eta^1$ $Te_2{}^{2-}$ fragments (eq 100 and Figure 23).[110] Reaction

$$Mo_2(OAc)_4 + Te_4{}^{2-} \xrightarrow{\text{en}} [Mo_4(Te)_{16}(en)_4]^{2-} \quad (100)$$

of polytellurides with high-valent metal halides results in good yields of oxytellurides (eq 101). The origin of

$$MCl_n + Te_4{}^{2-} \xrightarrow{\text{DMF}} [O{=}M(Te_4)_2]^{2-} \quad M = Mo, W \quad n = 4\text{–}6 \quad (101)$$

the terminal oxo ligand is not known but may come from either DMF solvent or trace water contamination.[111] Both complexes contain M(IV) in a square pyramidal coordination environment (Figure 24) very similar to those in such classical species as $[S{=}Mo(S_4)_2]^{2-}$. The accessibility of these complexes has made it possible to investigate some of their reaction chemistry. The polytelluride ligands react with activated acetylenes to form the first examples of coordinated ditellurolenes (eq 102). The molybdenum complex will

$$[O{=}Mo(Te_4)_2]^{2-} + DMAD \rightarrow [O{=}Mo(Te_2C_2(COOCH_3)_2)_2]^{2-} \quad (102)$$

also react with BH_4^- to form another oxytelluride, $[Mo_2(O)_2(\mu_2\text{-}Te)_2(\eta^2\text{-}Te_2)_2]^{2-}$ (Figure 25), which contains two Mo(V) centers with square pyramidal coordination environments and a M–M bond.[112] The molecule has both sulfur and selenium analogs, but in both of the lighter congeners, the oxo ligands are cis, while in the telluride complex they are trans.[113] The oxidation of the metal centers from Mo(IV) to Mo(V) with a reducing reagent is another example of the complex internal redox chemistry which often accompanies reactions of these coordinated polychalcogenides.

There is also a very rich and growing coordination chemistry of selenides and tellurides with organometallic metal centers, particularly metal carbonyls. For example group 6 carbonyls react with cationic polychalcogen clusters to form novel cationic metal carbonyl complexes (eqs 103[114,115] and 104[46,47] Figure 26). The

$$M(CO)_6 + Se_4{}^{2+} \rightarrow [M_2(CO)_{10}(Se_4)]^{2+} \quad (103)$$

$$M(CO)_6 + Te_4{}^{2+} \rightarrow [M(CO)_4(\eta^3\text{-}Te_3)]^{2+} \quad (104)$$

tritelluride complexes are the only examples to date of a closed three-membered ring containing only group 16 elements (Figure 27). All other examples of E_3 fragments are open. A mixed metal cluster with a side-bonded diselenium cation has been made using the same methods (eq 105).[116] These complexes are some of the

$$W(CO)_6 + Fe(CO)_5 + Se_4{}^{2+} \rightarrow [WFe(CO)_8(\mu_2,\eta^2\text{-}Se_2)]^{2+} \quad (105)$$

very few molecules containing cationic polychalcogens.

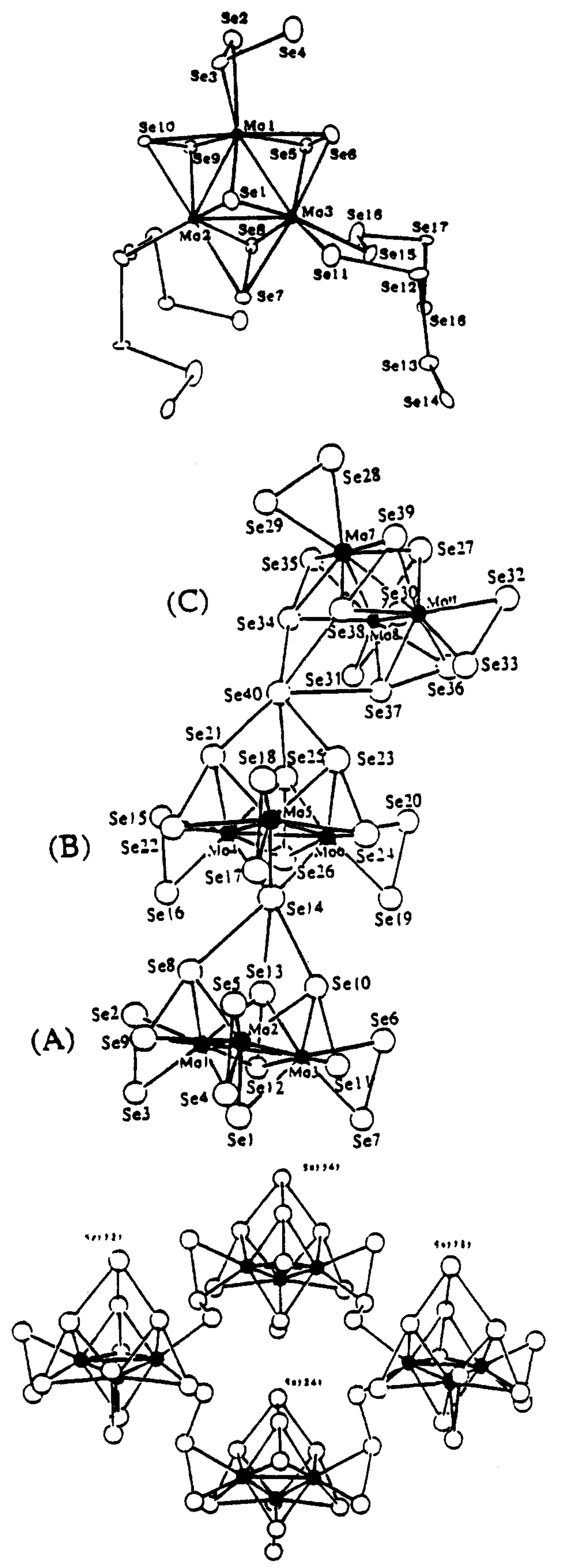


Figure 22. $[K_2Mo_3Se_{18}]_n$, $K_8Mo_9Se_{40}{\cdot}4H_2O$, and $K_{12}Mo_{12}Se_{56}$ (reprinted from refs 105 and 106; copyright 1990, and 1992 American Chemical Society).

However, their stability and unusual structures suggest that there is still a large amount of unexplored chemistry here.

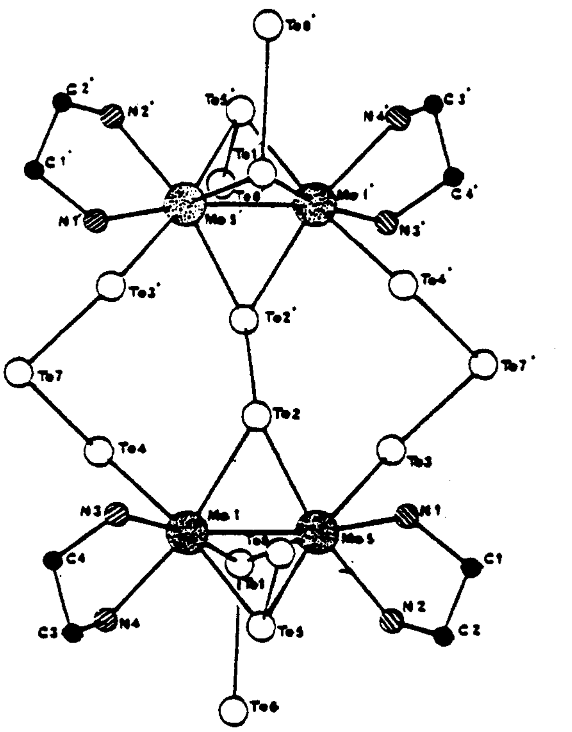


Figure 23. $[Mo_4Te_{16}(en)_4]^{2-}$ (reprinted from ref 110; copyright 1988 American Chemical Society).

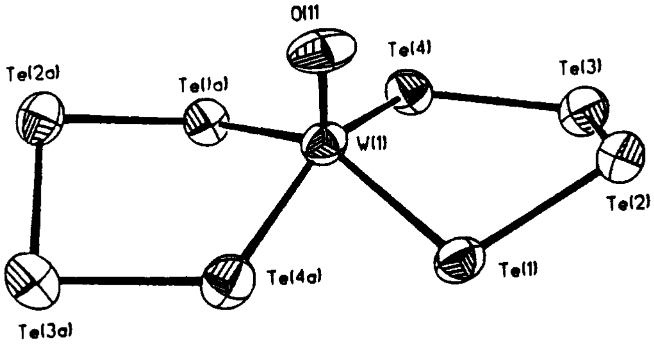


Figure 24. $[O{=}M(Te_4)_2]^{2-}$ (reprinted from ref 111; copyright 1989 American Chemical Society).

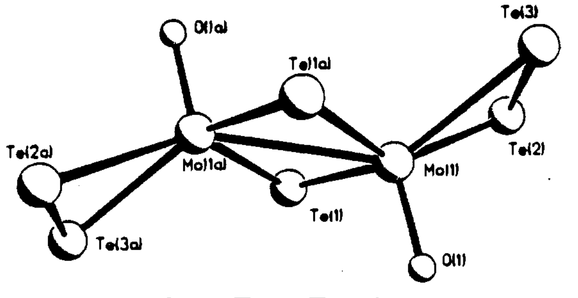


Figure 25. $[Mo_2(O)_2(\mu_2\text{-}Te)_2(\eta\text{-}Te_2)_2]^{2-}$.

The heavy group 6 carbonyls also react with anionic polychalcogenides (eqs 106,[79] 107,[80] and 108[117]). The

$$M(CO)_6 + Te_4^{2-} \rightarrow [M(CO)_4(Te_4)]^{2-} \quad M = Mo, W \tag{106}$$

$$3W(CO)_6 + Te_2^{2-} \rightarrow [W_4(\mu_3\text{-}Te)_2(CO)_{18}]^{2-} \tag{107}$$

$$3W(CO)_6\ Te_4^{2-} \rightarrow [W_6(Te_2)_4(CO)_{18}]^{2-} \tag{108}$$

product of eq 106 is a simple ligand substitution reaction, but those of eqs 107 and 108 are the result of

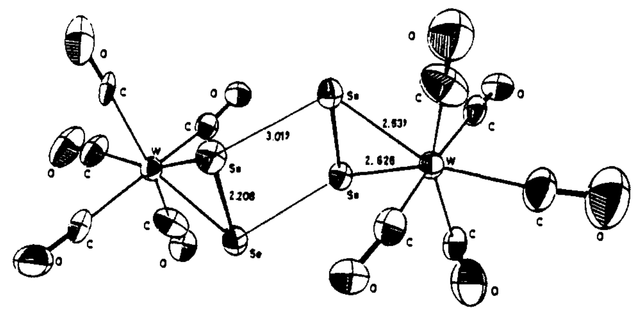


Figure 26. $[M_2(CO)_{10}(Se_4)]^{2+}$ (reprinted from ref 114; copyright 1985 Royal Society of Chemistry).

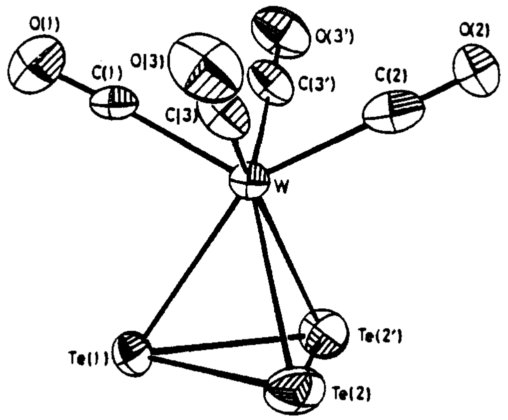
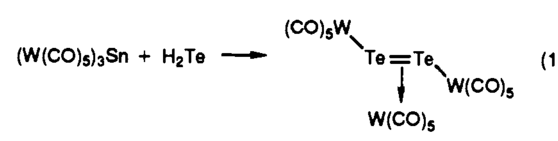


Figure 27. $[M(CO)_4(cyclo\text{-}Te_3)]^{2+}$ (reprinted from ref 44; copyright 1987 Royal Society of Chemistry).

oxidation of the excess zero-valent metal center to W(I) by the Te–Te bonds. This results in tungsten–tungsten bond formation and a shortened polytelluride fragment (Figure 28). It appears that use of excess metal carbonyl is necessary to induce the internal electron transfer. The product of eq 108 is one of the few 14-vertex clusters known and is electron precise if all four pairs of electrons of the central ditellurides (counted as Te_2) are involved in bonding. However, the central tellurium atoms are in a planar coordination environment with respect to the three tungsten atoms. This means that each central tellurium is sp^3 hybridized, but is in a trigonal pyramidal environment. It is this kind of orbital and structural flexibility which makes telluride chemistry so fascinating. The corresponding reactions involving polyselenides and excess metal carbonyls are somewhat complex and are currently under investigation.[118] Another unusual tungsten ditelluride can be prepared via a transmetalation of a tin complex using H_2Te generated in situ (eq 109). The complex contains a

 (109)

$$(W(CO)_5)_3Sn + H_2Te \longrightarrow (CO)_5W{-}Te{=}Te{-}W(CO)_5,\ Te \rightarrow W(CO)_5 \qquad (109)$$

ditelluride fragment with a bond length of 2.686(4) Å, which is intermediate between a single and double bond, in keeping with its side-bonding coordination to an unsaturated $W(CO)_5$ fragment.

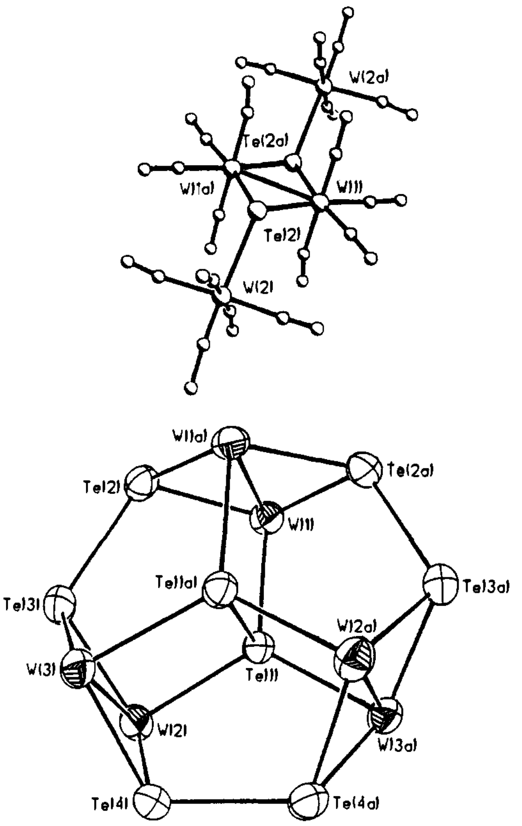


Figure 28. $[W_4(\mu_3\text{-}Te)_2(CO)_{18}]^{2-}$ and $[W_6(Te_2)_4(CO)_{18}]^{2-}$ (reprinted from refs 80 and 117; copyrights 1992 and 1990 American Chemical Society).

$$Cp_2M_2(CO)_6 + Se_n^{\ 2-} \rightarrow [CpM(CO)_2(\eta^2\text{-}Se_2)]^- \qquad (110)$$

$$Cp_2M_2(CO)_6 + Se_n^{\ 2-}\ (\text{excess}) \rightarrow [CpM(Se_4)_2]^- \qquad (111)$$

$$M = Mo, W$$

$$Cp^*M(NO)_2I + E_n^{\ 2-} \rightarrow Cp^*M(NO)(E_5) \quad M = Cr, Mo, W \quad E = S, Se \qquad (112)$$

The cyclopentadienyl complexes of molybdenum and tungsten also undergo oxidative decarbonylation in the presence of polyselenides (eqs 110 and 111).[120,121] Both molecules have sulfur analogs made in much the same fashion.[122] The product of eq 112 contains a M(IV) in a piano stool or pseudo square pyramidal environment (Figure 29) and, as such, is an organometallic analog of the well-known $[E{=}Mo(Se_4)_2]^{2-}$ (E = O, S, Se). Preliminary studies indicate that the chemistry of pentamethylcyclopentadienyl derivatives is somewhat more complex than that of the parent.[123] Interestingly a reaction of $Cp^*M(NO)_2I$ with polyselenides or -sulfides leads to isolation of a product containing a six membered ring with a somewhat rare chelating pentachalcogenide.[124]

There are a number of organometallic complexes with bridging selenides usually prepared by variations of methods already discussed. Some examples are given below (eqs 113,[125a] 114,[125b] and 115[84]). The product of eq 114 contains a linear bridging selenide with a short bond distance (2.323(1) Å), suggesting some metal ligand multiple bonding character. Finally, an extensive series of group 6 selenide cubanes, $Cp'_4M_4Se_4$, have been prepared in high yield via reaction of $Cp'MCl_4$ and HSe^-.[126] These have been investigated by a variety of physical methods.

3.4. Group 7

The coordination chemistry of group 7 selenides and tellurides is very poorly developed except for the

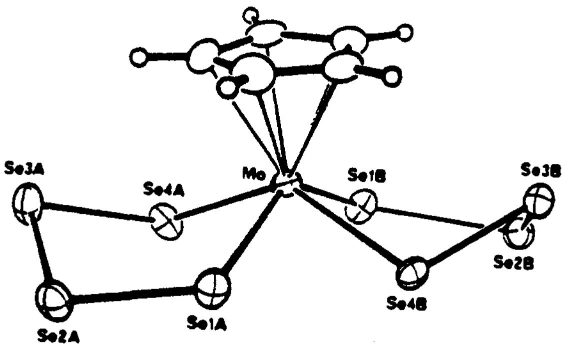


Figure 29. $[CpM(Se_4)_2]^-$ (reprinted from ref 121; copyright 1989 Pergamon Press plc).

$$CpW(CO)_3^- + SeOCl_2 \rightarrow trans\text{-}Cp_2W_2(O)_2(\mu\text{-}Se)_2 \tag{113}$$

$$(HB(pz)_3)Mo(CO)_3H + Se \rightarrow [HB(pz)_3)Mo(CO)_2](\mu\text{-}Se) \tag{114}$$

$$Cp_2M_2(CO)_4 + E \rightarrow Cp_2M_2(CO)_4(\mu\text{-}E) + Cp_2M_2(CO)_4(\mu\text{-}E)_2 + Cp_2M_2(CO)_4(\mu\text{-}E)_3 \quad M = Mo, W \quad E = S, Se, Te \tag{115}$$

organometallic complexes. To a large extent, this situation parallels that of the metal sulfides. For example to date there has been only one binary manganese sulfide reported, $[Mn(S_5)(S_6)]^{2-}$, whose chemistry is unexplored.[127] Similarly there has only been one binary manganese selenide made, $[Mn(Se_4)_2]^{2-}$, which was reported almost simultaneously by three different groups (eqs 116[24,128] and 117[25]). This complex

$$MnCl_2{\cdot}4H_2O + Se_n^{2-} \rightarrow [Mn(Se_4)_2]^{2-} \tag{116}$$

$$Mn_2(CO)_{10} + Se_4^{2-}\ (\text{excess}) \rightarrow [Mn(Se_4)_2]^{2-} \tag{117}$$

is a member of the large class of molecules containing a divalent metal center coordinated by two tetrachalcogenides in tetrahedral fashion (Figure 30). In fact this structural class is so stable that there are more examples of selenides than sulfides known. There are no reported binary molecular tellurides of group 7 to date, nor have there been any binary molecular rhenium compounds reported.

The reaction of $Mn_2(CO)_{10}$ and Se_4^{2-} leads to several manganese selenide carbonyl clusters which can be shown to be precursors to $[Mn(Se_4)_2]^{2-}$ (eqs 118–120).[25]

$$Mn_2(CO)_{10} + Se_4^{2-} \rightarrow [Mn_2(Se_2)_2(CO)_6]^{2-} \tag{118}$$

$$[Mn_2(Se_2)_2(CO)_6]^{2-} + Se_4^{2-} \text{ or } Se_8 \rightarrow [Mn_2(Se_4)_2(CO)_6]^{2-} \tag{119}$$

$$[Mn_2(Se_4)_2(CO)_6]^{2-} \xrightarrow{\Delta} [Mn(Se_4)_2]^{2-} \tag{120}$$

Both carbonyl intermediates contain manganese which has been oxidized by tetraselenide to form Mn(I). Each metal center is pseudo-octahedrally coordinated, and as with most chalcogenido carbonyl complexes, the carbonyl coordination environment is virtually undistorted (Figure 31). The reaction of $Re_2(CO)_{10}$ with tetraselenide leads to formation of $[Re_2(Se_4)_2(CO)_6]^{2-}$, which is isostructural with the corresponding manganese analog.[129] However, no further chemistry has been done with this molecule.

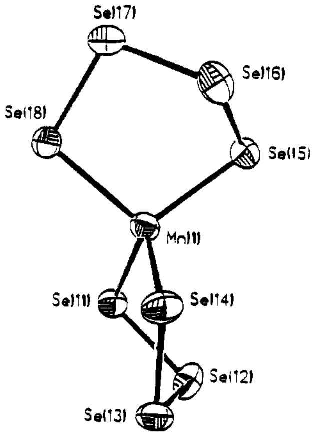


Figure 30. $[Mn(Se_4)_2]^{2-}$ (reprinted from ref 24; copyright 1990 American Chemical Society).

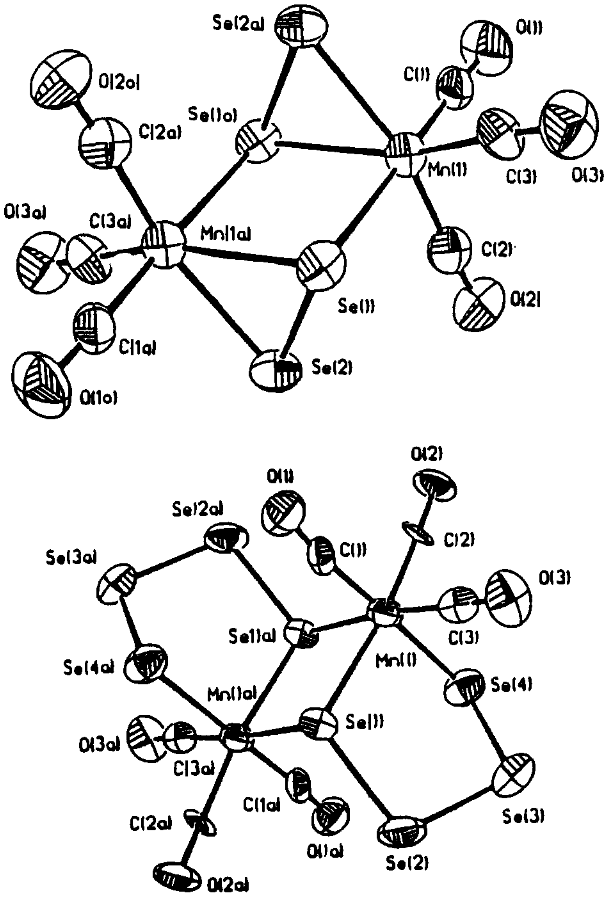


Figure 31. $[Mn_2(Se_2)_2(CO)_6]^{2-}$ and $[Mn_2(Se_4)_2(CO)_6]^{2-}$ (reprinted from ref 24; copyright 1990 American Chemical Society).

Most of the other known group 7 complexes consist of mono- or dichalcogenide fragments bridging dimeric metal carbonyl or Cp units. In relatively early work Vahrenkamp used organostannyl reagents to introduce selenides and tellurides into metal dimers (eqs 121 and 122). The stannyl groups can be displaced by protons, forming bridging HE^- groups.[130]

Manganese carbonyl dimer will react with $Et_3P{=}Te$ to generate $[Mn_2(Et_3P)_4(CO)_6(\mu_2\text{-}Te_2)]$, with each Mn center octahedrally coordinated by four COs, one end

$$M(CO)_5X + 2(Me_3Sn)_2E \rightarrow Mn_2(CO)_8(\mu\text{-}ESnMe_3)_2 \quad (121)$$

$$Mn_2(CO)_8(\mu\text{-}ESnMe_3)_2 + 2HCl \rightarrow Mn_2(CO)_8(\mu\text{-}EH)_2 \quad (122)$$

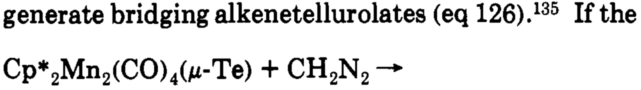
$$M = Mn, Re \qquad E = Se, Te$$

of a ditelluride fragment, and two phosphine ligands resulting from the transfer of tellurium to the metal center. This complex has been shown to produce MnTe upon thermolysis.[131] Reaction of the coordinatively unsaturated rhenium center in $CpRe(CO)_2(Et_2O)$ with Se_8 leads to three new products, $CpRe(CO)_2(\eta^2\text{-}Se_2)$, $Cp_2Re_2(CO)_4(\mu\text{-}Se)$, and $Cp_2Re_2(CO)_2(\mu_2\text{-}Se_2)(\mu_2\text{-}Se_3)$, all of which have been structurally characterized.[132] The rhenium carbonyl cation $Re(CO)_5^+$ reacts with all three chalcogenide dianions to form a trimeric Lewis acid base adduct (eq 123). All three adducts have been

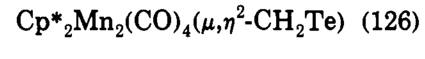
$$3Re(CO)_5^+ + E^{2-} \rightarrow [(Re(CO)_5)_3E]^+ \qquad E = S, Se, Te \quad (123)$$

structurally characterized, showing the S and Se complexes to be planar around the central atom, probably indicating some degree of delocalization of the remaining lone pair of chalcogen electrons. The telluride analog is somewhat more pyramidal (cone angle is 337.8°) indicating less delocalization, most likely due to the large size and decreased orbital overlap of these heavy atoms.[133]

A unique series of manganese complexes has been prepared containing bridging chalcogenides which clearly display multiple bonding to more than one metal center. They have been made by the reaction of an unsaturated Cp carbonyl complex with H_2Te generated in situ (eqs 124 and 125).[134] These compounds all contain short Mn–Te bonds (less than 2.5 Å), suggesting distinct multiple bonding character. Their reactivity also reflects this multiple bonding as the molecules readily undergo reactions with carbene reagents to generate bridging alkenetellurolates (eq 126).[135] If the



$$CpMn(CO)_2(THF) + H_2Te \longrightarrow [Cp(CO)_2Mn]_2Te{=}Mn(CO)_2Cp \quad (124)$$



$$Cp^*Mn(CO)_2(THF) + H_2Te \longrightarrow Cp^*(CO)_2Mn{=}Te{=}Mn(CO)_2Cp^* \quad (125)$$

$$Cp^*_2Mn_2(CO)_4(\mu\text{-}Te) + CH_2N_2 \rightarrow Cp^*_2Mn_2(CO)_4(\mu,\eta^2\text{-}CH_2Te) \quad (126)$$

analogous reactions are performed on the rhenium complex, multiple bonding is not observed, but an equally rich chemistry emerges.[13] Four new compounds can be isolated, all of which have been structurally characterized. These include $Cp^*Re(CO)_2H(TeH)$, $Cp^*_2Re_2(CO)_4(\mu\text{-}Te)$, $Cp^*_2Re_2(CO)_4(\mu\text{-}Te)_2$, and $Cp^*_2Re_2(CO)_4(\mu\text{-}\eta^2\text{-}Te_2)$. The first complex is a direct result of oxidative addition of H_2Te across the unsaturated metal center and is the only example to date of a terminal HTe^- ligand. All of the other compounds contain a variety of bridging tellurides and have sulfur or selenium analogs in related systems.

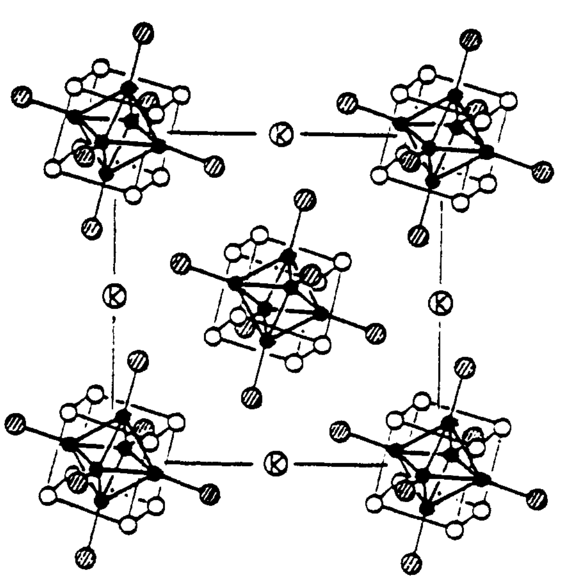


Figure 32. $KRe_6Se_5Cl_9$ (reprinted from ref 136a; copyright 1988 CNRS-Gauthier-Villars).

An interesting class of solid-state rhenium chalcogenide compounds has been reported recently. These all contain octahedra of Re(III) with face-capping μ_3-selenides as well as other ligands such as halides and hydroxides. The halides generally serve as bridging groups linking the octahedra together to form extended solids, making them structural relatives to the Chevrel phases.[136] The compounds are usually prepared by high-temperature reactions of higher valent rhenium halides with elemental rhenium and selenium (eq 127 and Figure 32). These solids are also intriguing because

$$ReCl_5 + Re + Se + KCl \rightarrow KRe_6Se_5Cl_9 \quad (127)$$

the bonding within the rhenium octahedra is very strong, allowing it to stay intact throughout a variety of chemical manipulations. However, the bonds linking the octahedra are fairly weak. Thus under the proper circumstances, the bridging linkages can be disrupted and the clusters solubilized.[137] Once in solution, they can be subjected to a variety of chemical reactions leading to the formation of new clusters. This area is one of vast potential, and many more results are anticipated in the near future.

3.5. Group 8

The chemistry of iron selenides and tellurides resembles that of the sulfides, in that several areas are extremely well-developed with an extensive descriptive chemistry, along with detailed spectroscopic and mechanistic investigations. However, in other areas even the most basic reactions have not been carried out. In the case of sulfides, this situation is rooted in the considerations of bioinorganic signifance, whereas for selenides and tellurides, it is again driven by availability of starting materials.

There are two binary selenides known. The first, $[Fe_2(\mu\text{-}Se)_2(Se_5)_2]^{2-}$, containing two Fe(III) centers tetrahedrally coordinated by selenides (Figure 33), has been known for some time. It has a well-known sulfur analog and can be prepared by several methods (eqs 128 and 129).[138,139] It should be noted that in both cases

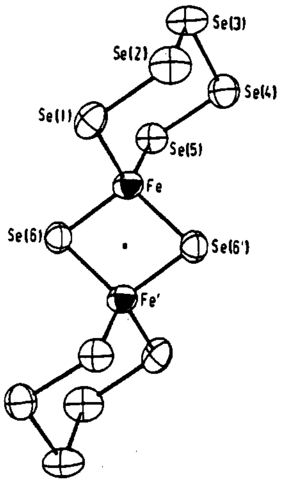


Figure 33. $[Fe_2(\mu\text{-}Se)_2(Se_5)_2]^{2-}$ (adapted from ref 139; copyright 1991 Zeitschrift fur Naturforschung).

$$2FeCl_2 + 12Se + 6Na \rightarrow [Fe_2(\mu\text{-}Se)_2(Se_5)_2]^{2-} \quad (128)$$

$$2CpFe(CO)_2I + 4Se_n^{2-} \rightarrow [Fe_2(\mu\text{-}Se)_2(Se_5)_2]^{2-} \quad (129)$$

it is necessary for polyselenide to act as an oxidizing agent, converting the iron centers from a lower valent state to Fe(III). This tendency of polychalcogenides to oxidize lower valent metal centers is rapidly becoming an important thematic consideration in this type of chemistry.

The other binary iron selenide reported is an incredible cluster having the formula $[Na_9Fe_{20}Se_{38}]^{9-}$.[140] This is made from the reaction of $FeCl_3$ and Li_2Se in ethanol, but a key ingredient is sodium acetanilide. Without this anion, rapid precipitation of amorphous powders results upon combination of the selenides and metal salt. However, the addition of the organic anion inhibits precipitation, probably by complexing to the metal center and slowing the nucleation process, allowing controlled oligomerization to occur followed by crystallization.[141] This clever synthetic gambit may be of general use, leading to the formation of characterizable clusters in a number of systems which have been previously investigated without success.

The $[Na_9Fe_{20}Se_{38}]^{9-}$ cluster itself is an extraordinary structure consisting mostly of Fe(III) centers tetrahedrally coordinated by bridging selenides with no polyselenide ligands (Figure 34). The formal charge distribution consists of 18 trivalent and two divalent iron centers. There are three chains linked at two ends, and nine sodium atoms appear to help hold the cluster together. The isolation of this structure and several related sulfur-containing clusters (Figure 35) suggests that there is a large class of higher nuclearity metal chalcogenides awaiting discovery.[141] There have been no reported binary iron tellurides in the refereed literature, but workers in our laboratory have isolated a cluster of the formula $[Fe_{14}Te_{22}]^{6-}$ having structural features similar to the large iron sulfides and selenides (Figure 36).[142] We have been unable to reproduce the synthesis of this molecule in good yield, but its isolation suggests that large binary tellurides of iron are also stable.

There are a number of other nonorganometallic iron selenides and tellurides which are almost invariably cubanes. They have been prepared by a number of methods (eqs 130,[143] 131,[144] 132,[145] 133,[146] and 134[147]).

$$[Fe_3(\mu\text{-}Se)_4(SEt)_4]^{3-} + Ni(PPh_3)_3 \rightarrow [Fe_3Ni(\mu_3\text{-}Se)_4(SEt)_4]^{3-} \quad (130)$$

$$[Fe(TePh)_4]^{2-} + HTe^- \rightarrow [Fe_4(\mu_3\text{-}Te)_4(TePh)_4]^{3-} \quad (131)$$

$$[Fe(SPh)_4]^{2-} + Te^{2-} \rightarrow [Fe_4(\mu_3\text{-}Te)_4(SPh)_4]^{3-} \quad (132)$$

$$4Fe(COT)_2 + Te{=}PEt_3 \rightarrow (Et_3P)_4Fe_4(\mu_3\text{-}Te)_4 \quad (133)$$

$$Fe + Cs_2CO_3 \xrightarrow{H_2,\,Te,\,1050\text{ K}} Cs_7Fe_4Te_8 \quad (134)$$

All are quite stable compounds containing tetrahedral metal atoms and the chalcogenide sitting either at the corner of the cube or face capping an iron tetrahedron, depending on the individual cluster. They are usually severely distorted from pure cubane symmetry, nearer to D_{2d} symmetry, and contain a significant amount of iron–iron bonding. It is difficult to determine the exact degree of Fe–Fe interaction based on the large amount of structural data collected for the sulfur systems, because the large size of the heavier chalcogenides causes considerable distortion of bond distances. However, it is clear that some metal–metal interaction is usually present. Magnetic investigations of some of these clusters demonstrate a reasonable amount of antiferromagnetic coupling between the mixed valent iron centers.[145]

Most of the other iron selenide and -telluride complexes are organometallic in nature, usually derived from either carbonyl or cyclopentadienyl starting materials. There are a number of classical bridging species such as $Cp_2Fe_2(CO)_4(\mu\text{-}Se)$, which can be prepared using well-known reactions (eq 135).[148] The

$$[CpFe(CO)_2]^- + Se_2Cl_2 \rightarrow Cp_2Fe_2(CO)_4(\mu\text{-}Se) \quad (135)$$

product of eq 135, like most other organometallic chalcogenide complexes, is susceptible to attack at the bridging selenium atom by a wide variety of electrophiles, including H^+, CH_3^+, and red selenium (eqs 136,[148] 137,[149] and 138[150]). Steigerwald has used tellurium atom

$$Cp_2Fe_2(CO)_4(\mu\text{-}Se) + X^+ \rightarrow Cp_2Fe_2(CO)_4(\mu\text{-}SeX)^+ \quad (136)$$

$$Cp_2Fe_2(CO)_4(\mu\text{-}Se) + Se_8 \rightarrow Cp_2Fe_2(CO)_4(\mu\text{-}Se_2) \quad (137)$$

$$Cp_2Fe_2(CO)_4(\mu\text{-}Se) + [Re(CO)_5]^+ \rightarrow [Cp_2Fe_2(CO)_4(\mu\text{-}Se)Re(CO)_5]^+ \quad (138)$$

transfer reactions to prepare several bridging tellurides as well (eq 139).[151] These compounds have not been

$$Cp_2Fe_2(CO)_3(PEt_3) + nTe{=}PEt_3 \rightarrow [CpFe(CO)(PEt_3)]_2(\mu\text{-}Te_n) \quad n = 1, 2 \quad (139)$$

subjected to extensive reactivity studies, but they have been characterized fully by multinuclear NMR. It was

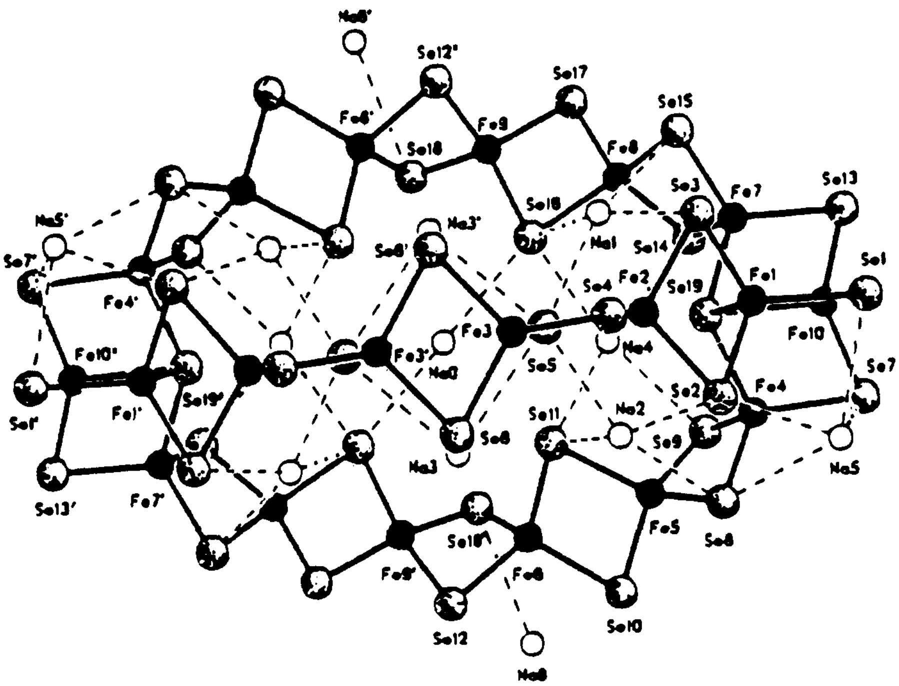


Figure 34. $[Na_9Fe_{20}Se_{38}]^{9-}$ (reprinted from ref 140; copyright 1991 American Chemical Society).

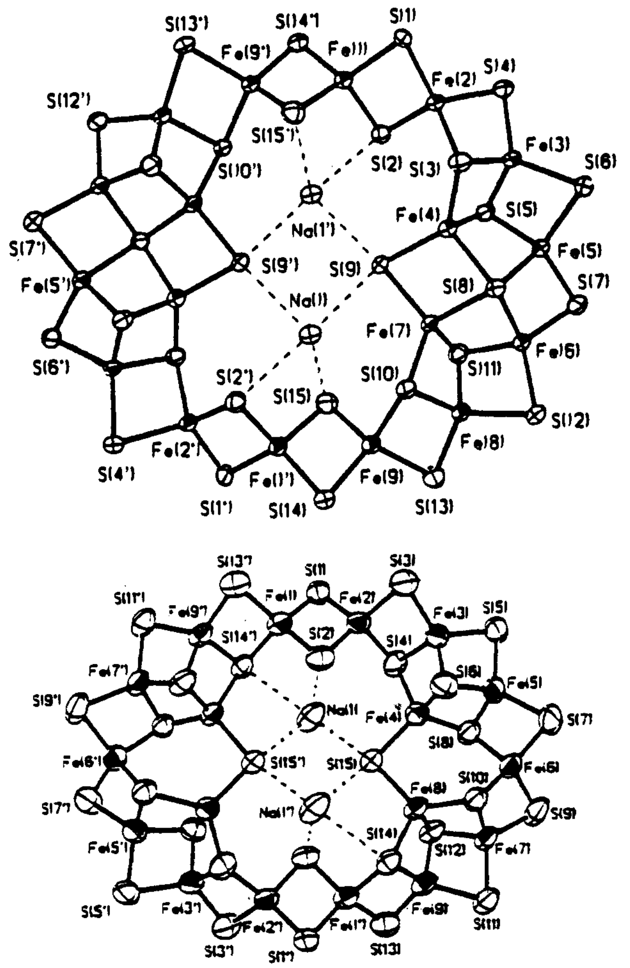


Figure 35. $[\alpha\text{-}Na_2Fe_{18}S_{30}]^{8-}$ and $[\beta\text{-}Na_2Fe_{18}S_{30}]^{8-}$ (reprinted from ref 141; copyright 1992 American Chemical Society).

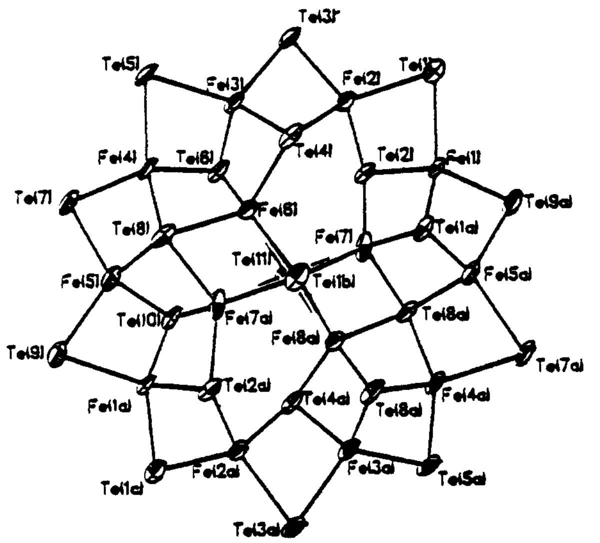


Figure 36. $[Fe_{14}Te_{22}]^{6-}$.

found that they can be pyrolyzed to form FeTe and $FeTe_2$ in good yield.

Neutral iron carbonyl complexes have an extremely rich reaction chemistry with various polytellurides. It was found that a labile iron carbonyl derivative will react with Te_4^{2-} in ethylenediamine in the presence of crypt to generate a dimer containing a very unusual $(\mu_2,\eta^1\text{-}Te_2)^{2-}$ ligand (eq 140 and Figure 37).[152] The

$$\mathrm{Fe(CO)_3(\eta^4\text{-}C_4H_6) + K_2Te_4 \xrightarrow{\text{crypt/en}} [K\cdot crypt]_2[Fe_2(CO)_6(\mu\text{-}Te)(\mu_2,\eta^1\text{-}Te_2)]} \quad (140)$$

reaction of various polytellurides with excess $Fe(CO)_5$ leads to a different series of unusual iron carbonyl telluride dianions, depending on the nature and amount of the polytelluride. Use of Na_2Te, which contains no Te–Te bonds and thus is incapable of oxidizing the iron center, generates clusters containing zero-valent iron (eqs 141 and 142 and Figure 38).[153] Reactivity

$$\mathrm{3Fe(CO)_5 + Te^{2-} \rightarrow [Fe_3(CO)_9(\mu^3\text{-}Te)]^{2-}} \quad (141)$$

$$\mathrm{3Fe(CO)_5 + Te^{2-} + O_2 \rightarrow [(Fe(CO)_4)_4(\mu_4\text{-}Te)]^{2-}} \quad (142)$$

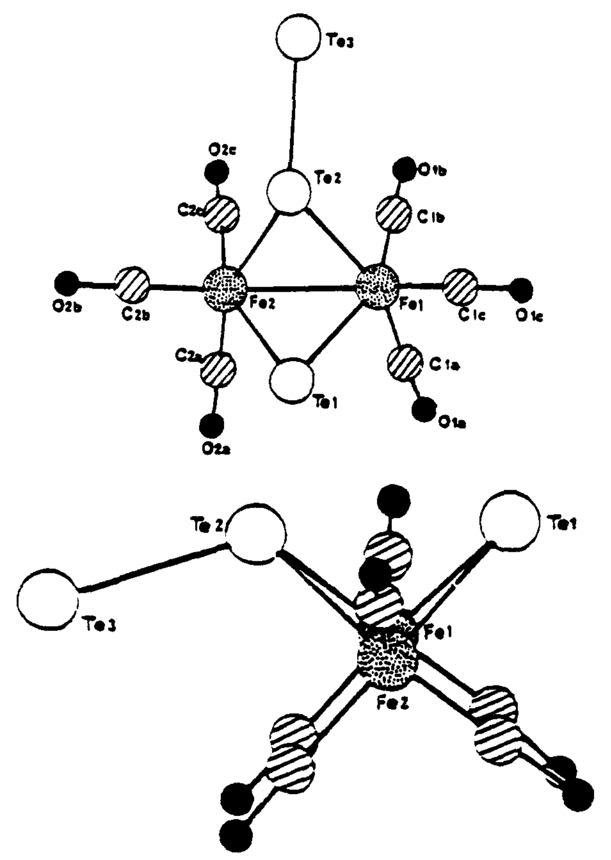


Figure 37. Two views of the $[Fe_2Te_3(CO)_6]^{2-}$ ion (reprinted from ref 152; copyright 1990 American Chemical Society).

studies of $[Fe_3(CO)_9(\mu_3\text{-}Te)]^{2-}$ toward electrophiles reveal a distinct lack of reactivity at the exposed telluride, as virtually all electrophiles (H^+, NO^+, $PhHg^+$, PPh_3Au^+) studied bridge an Fe–Fe bond (Figure 39).[153]

If longer chain polytellurides are used as reactants with $Fe(CO)_5$, they induce oxidation of the metal center, leading to clusterification. Thus some extremely unusual compounds can be isolated (eqs 143,[154] 144,[154] and 145[155]). In these molecules, the polytellurides have

$$3Fe(CO)_5 + Te_4^{2-} \rightarrow [Fe_5Te_4(CO)_{14}]^{2-} \quad (143)$$

$$3Fe(CO)_5 + Te_4^{2-} + Te\ (\text{excess}) \rightarrow [Fe_8Te_{10}(CO)_{20}]^{2-} \quad (144)$$

$$3Fe(CO)_5 + Te_3^{2-} \rightarrow [Fe_6Te_6(CO)_{16}]^{2-} \quad (145)$$

oxidized the zero-valent iron centers to a mixture of Fe(I) and Fe(II), or all Fe(II), along with reduction of the polytelluride to form Te^{2-} and Te_2^{2-}. The shapes of the molecules are quite unusual, but the structural features are normal (Figure 40). There are clearly Fe(I)–Fe(I) bonds in several of the molecules, and the telluride ligands have similar distances and angles as in other iron telluride complexes.

There has been very little work reported concerning iron carbonyls and polyselenides, but preliminary investigation indicates that the area has the potential to be as rich as that of the tellurides. For example we have recently found that excess $Fe(CO)_5$ reacts with Se^{2-} and Se_2^{2-} to form $[Fe_3(CO)_9(\mu_3\text{-}Se)]^{2-}$ and $[Fe_5(CO)_{15}(\mu_3\text{-}Se)_2]^{2-}$, respectively (Figure 41).[156] Similarly a mononuclear iron tetraselenide can be formed via oxidative decarbonylation of $Fe(CO)_5$ by elemental selenium in *N*-methylimidazole (eq 146 and Figure 42).[157] Excess iron carbonyl also reacts with $[P_2Se_8]^{2-}$

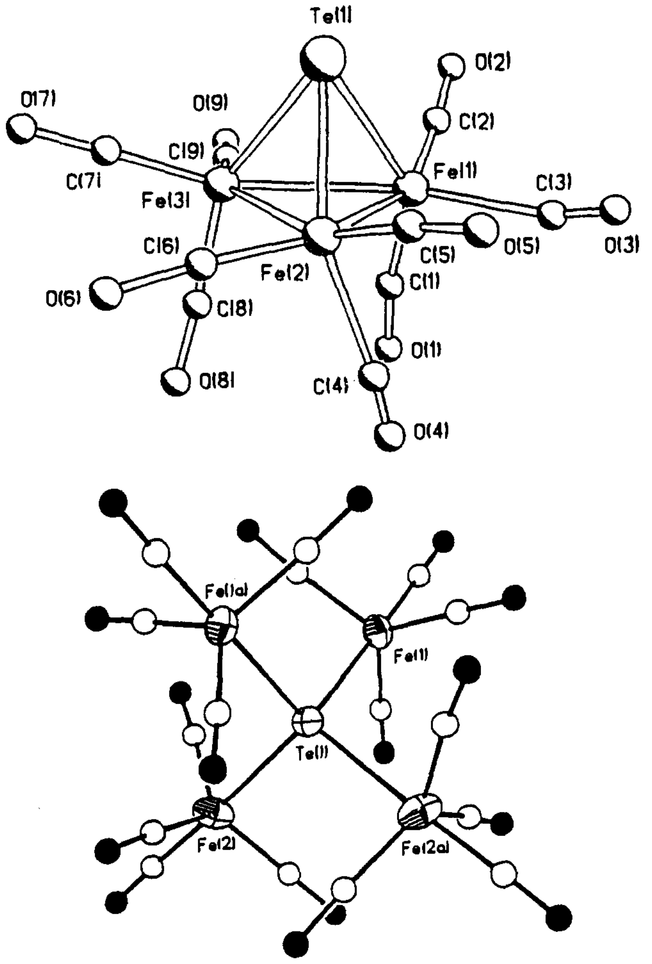


Figure 38. $[Fe_3(CO)_9(\mu_3\text{-}Te)]^{2-}$ and $[(Fe(CO)_4)_4(\mu_4\text{-}Te)]^{2-}$.

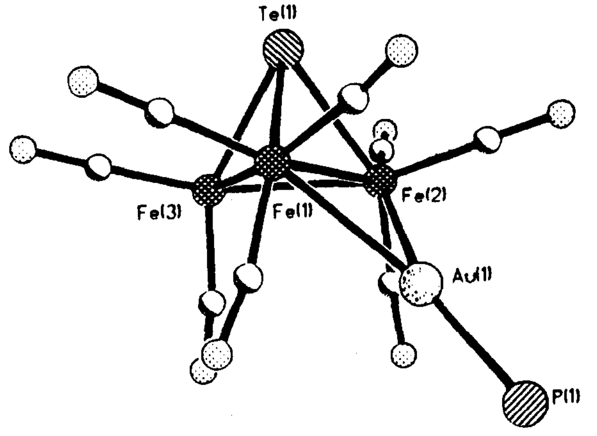


Figure 39. $[PPh_3AuFe_3(CO)_9(\mu_3\text{-}Te)]^-$.

$$Fe(CO)_5 + 4Se \xrightarrow{N\text{-MeIm}} [Fe(CO)_2(Se_4)_2]^{2-} \quad (146)$$

to form a novel dimer containing the new PSe_5^{3-} ligand (Figure 43).[158] A cationic complex $\{[(C_5H_5)Fe(CO)_2]_3(Se_2)\}^+$ has also been prepared (eq 148).[150]

$$3Fe(CO)_5 + P_2Se_8^{2-} \rightarrow [Fe_2(CO)_4(PSe_5)_2]^{2-} \quad (147)$$

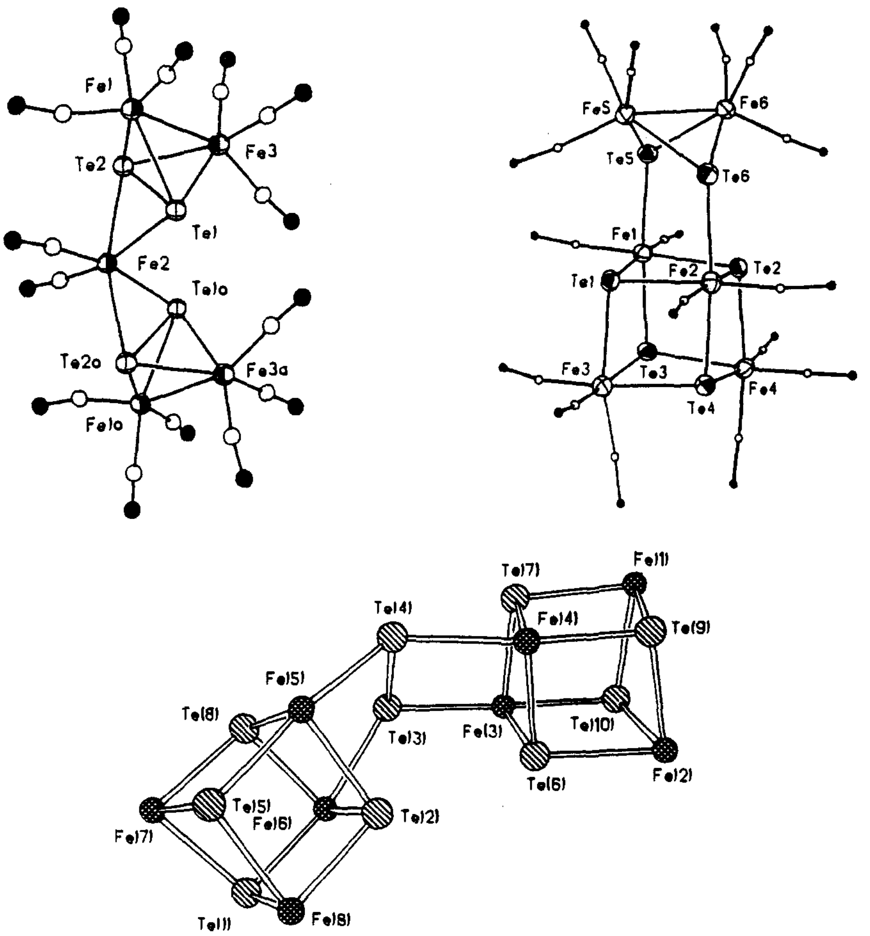


Figure 40. $[Fe_5Te_4(CO)_{14}]^{2-}$, $[Fe_6Te_6(CO)_{16}]^{2-}$, and $[Fe_8Te_{10}(CO)_{20}]^{2-}$ (reprinted from ref 154; copyright 1992 VCH Verlagsgellschaft mbH).

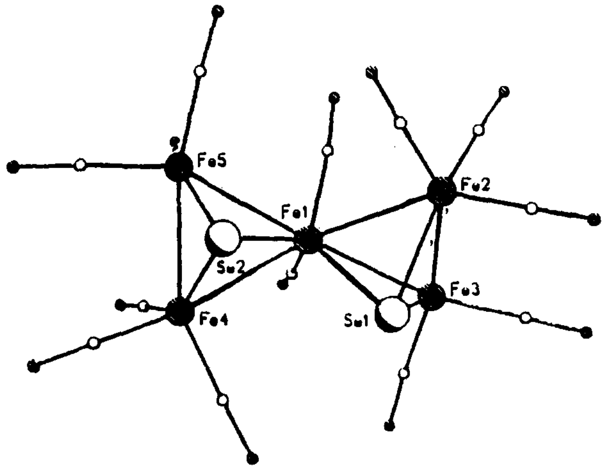


Figure 41. $[Fe_5Se_2(CO)_{14}]^{2-}$.

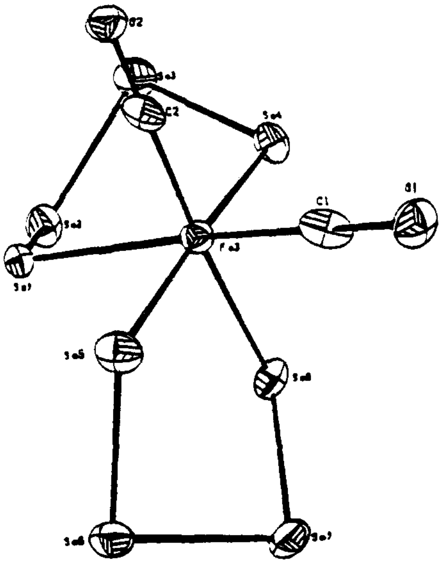


Figure 42. $[Fe(CO)_2(Se_4)_2]^{2-}$ (reprinted from ref 157; copyright 1992 American Chemical Society).

$$Cp_2Fe_2(CO)_4(Se_2) + CpFe(CO)_2^+ \rightarrow \{[(C_5H_5)Fe(CO)_2]_3(Se_2)\}^+ \quad (148)$$

Unquestionably the most extensive chemistry has been done with the neutral iron carbonyl telluride clusters. This is fitting as these are the oldest metal chalcogenide clusters, having been prepared by Walter Hieber and co-workers in the mid-1950s by the reduction of tellurium oxyanions with iron carbonyl anions (eq 149).[40] The three basic building blocks, $Fe_2(CO)_6Te_2$

$$HFe(CO)_4^- + TeO_3^{2-} \rightarrow Fe_3(CO)_9Te_2 \quad (149)$$

and $Fe_3(CO)_nTe_2$ (n = 9, 10), are all prepared approximately the same way and are interconvertible. Perhaps the most well-known is $Fe_3(CO)_9Te_2$, which can be prepared very simply by the route described above.[159] A similar route provides $Fe_3(CO)_{10}Te_2$, which can be separated from the nonacarbonyl by differences in solubility. The trinuclear cluster $Fe_3(CO)_9Te_2$ was one of the first metal telluride clusters whose reactions and mechanisms have been studied on a systematic basis. The two apical tellurides are counted as four-electron

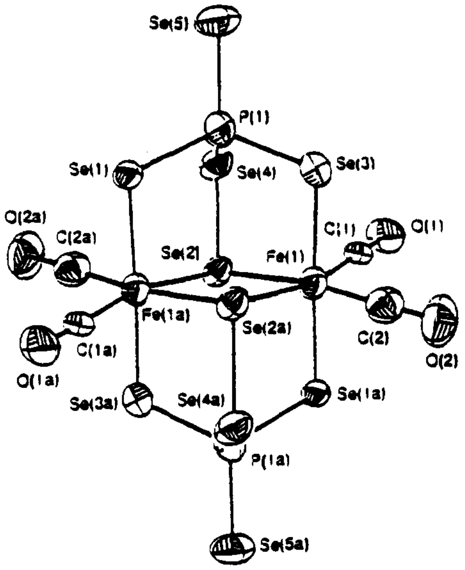


Figure 43. $[Fe_2(CO)_6(PSe_5)_2]^{2-}$ (reprinted from ref 158; copyright 1992 Royal Society of Chemistry).

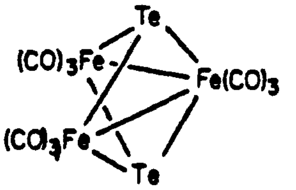


Figure 44. $Fe_3(CO)_9Te_2$ (reprinted from ref 162; copyright 1982 American Chemical Society).

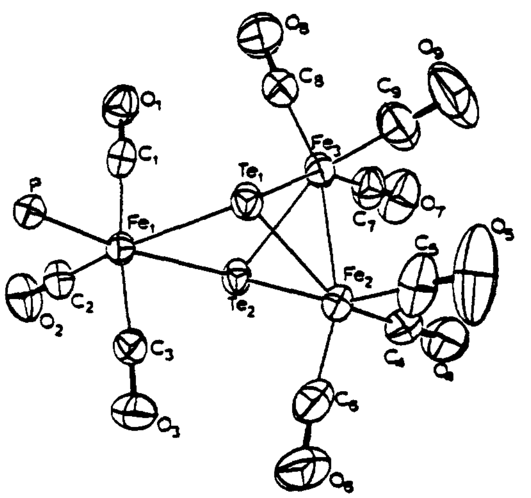


Figure 45. $Fe_3(\mu_3\text{-}Te)_2(CO)_9PPh_3$ (reprinted from ref 162; copyright 1982 American Chemical Society).

donors, making the cluster a 50-electron system. Accordingly, it is not a closed tetrahedron, but rather contains one open edge with only two Fe–Fe bonds (Figure 44).[160] Upon addition of a nucleophile such as CO or PPh_3, the adduct $Fe_3(CO)_9LTe_2$ is formed, resulting in a 52-electron system and the opening of a second Fe–Fe edge (eq 150 and Figure 45). This results

$$Fe_3(CO)_9Te_2 + L \rightarrow Fe_3(CO)_9LTe_2 \qquad L = CO, PR_3, t\text{-BuNC} \tag{150}$$

in a cluster with only one Fe–Fe bond. Thermal or chemical labilization of a coordinated carbonyl causes conversion back to a 50-electron system with formation of another Fe–Fe bond (eq 151).[161,162] Either of these

$$Fe_3(CO)_9LTe_2 + \Delta \text{ or } Me_3NO \rightarrow Fe_3(CO)_8LTe_2 \tag{151}$$

compounds can be converted into $Fe_2(CO)_6Te_2$ in good yield by decomposition in base followed by acidification.[42] Another neutral iron carbonyl telluride cluster has been reported, $Fe_4(CO)_{12}Te_4$, which is prepared by thermolytic dimerization of $Fe_2(CO)_6Te_2$.[42] It is presumed to be a cubane like its sulfur and selenium analogs,[163] but its structure has not been determined.

With these reagents so readily available, a large amount of exploratory chemistry has been carried out with them, particularly in regard to cluster buildup and modification. One reaction which has led to a large number of new clusters is the oxidative addition of the chalcogen–chalcogen bond of $Fe_2(CO)_6E_2$ (E = S, Se, Te) across a low-valent transition-metal center, leading to heteronuclear cluster expansion. This reaction was first demonstrated by Rauchfuss and co-workers for selenium and tellurium (eq 152 and Figure 46).[164] It

$$Fe_2(CO)_6E_2 + Pt(PPh_3)_2(C_2H_4) \rightarrow (CO)_6Fe_2(\mu_3\text{-}E)_2Pt(PPh_3)_2 \tag{152}$$

was later extended to a wide variety of other metals by Mathur and co-workers.[165] The telluride complex will even oxidatively add across the metal–metal bond of an osmium cluster, which, after rearrangement and extrusion of iron, leads to the osmium telluride $Os_3(CO)_9Te_2$ (eq 153).[166] When a similar reaction is

$$Fe_2(CO)_6Te_2 + Os_3(CO)_{10}(CH_3CN)_2 \rightarrow Os_3(CO)_9Te_2 \tag{153}$$

carried out with $Ru_3(CO)_{12}$, an intermediate can be isolated with an unusual structure (eq 154 and Figure 47).[167] Interestingly, when tungsten carbonyl is used

$$Fe_2(CO)_6Te_2 + Ru_3(CO)_{12} \rightarrow [\{Fe_2(CO)_6\}(\mu_4\text{-}Te)(\mu_3\text{-}Te)\{Ru_3(CO)_{11}\}] \tag{154}$$

as a substrate, the expected oxidative addition does not occur, but rather, the tungsten atom inserts into the Fe–Fe bond, generating a new mixed cluster (eq 155 and Figure 48).[168] There have also been several

$$Fe_2(CO)_6Te_2 + W(CO)_5THF \rightarrow Fe_2W(CO)_{10}(\mu_3\text{-}Te)_2 \tag{155}$$

innovative variations developed on this theme. For example, it was shown that reaction of $Fe_2(CO)_6Te_2$ with reducing agents cleaves the Te–Te bond[169] and generates the telluride centered dianion identical to the well-known sulfide dianion.[170] This dianion behaves as a strong nucleophile leading to more heterometallic clusters (eqs 156 and 157). Another unusual variation

$$Fe_2(CO)_6Te_2 + LiEt_3BH \text{ (excess)} \rightarrow [Fe_2(CO)_6(\mu\text{-}Te)_2]^{2-} \tag{156}$$

$$[Fe_2(CO)_6(\mu\text{-}Te)_2]^{2-} + Cp_2TiCl_2 \rightarrow [Fe_2(CO)_6(\mu_3\text{-}Te)_2TiCp_2] \tag{157}$$

is based on the recent report that mixtures of SeO_3^{2-} and TeO_3^{2-} lead to the mixed chalcogenide clusters $Fe_3(CO)_9(\mu_3\text{-}Te)(\mu_3\text{-}Se)$ and $Fe_2(CO)_6(\mu\text{-}SeTe)$. These

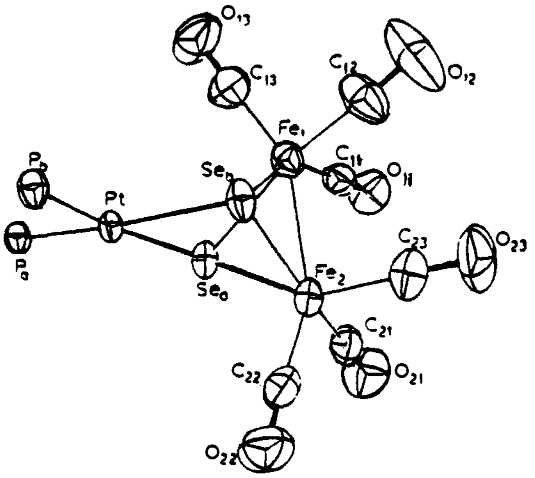


Figure 46. $(CO)_6Fe_2(\mu_3\text{-}Se)_2Pt(PPh_3)_2$ (reprinted from ref 164; copyright 1982 American Chemical Society).

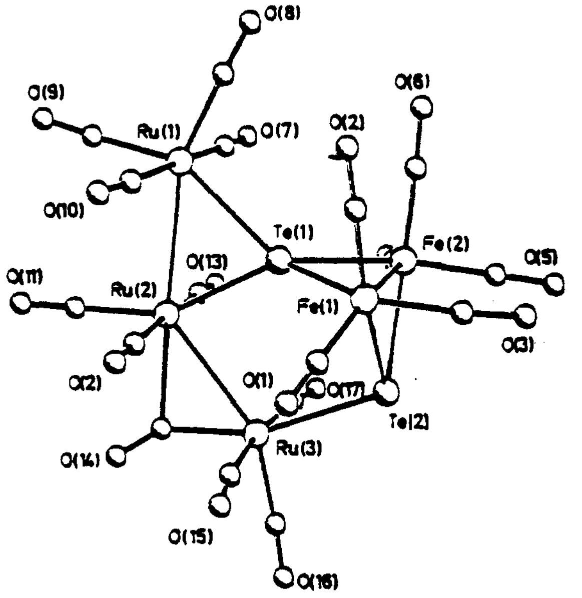


Figure 47. $[\{Fe_2(CO)_6\}(\mu_4\text{-}Te)(\mu_3\text{-}Te)\{Ru_3(CO)_{11}\}]$ (reprinted from ref 167; copyright 1989 Royal Society of Chemistry).

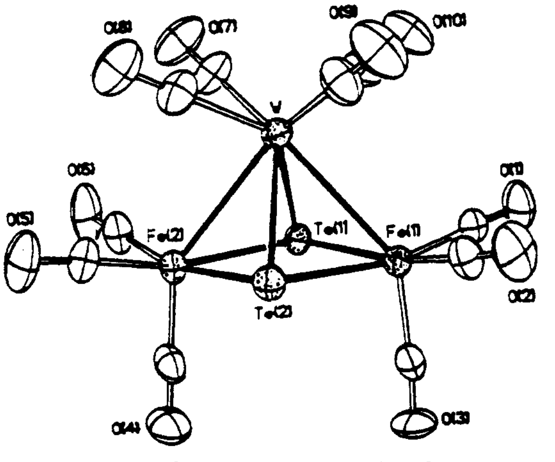


Figure 48. $Fe_2W(CO)_{10}(\mu_3\text{-}Te)_2$ (reprinted from ref 168; copyright 1992 American Chemical Society).

can then be used in the same manner as the homonuclear clusters to generate higher nuclearity mixed clusters.[171]

The telluride carbonyl clusters will also undergo metal replacement reactions. For example, $Fe_3(CO)_9Te_2$ will react with $Co_2(CO)_8$ to form $Co_2Fe(CO)_9Te$ and eventually go all the way to $Co_4(CO)_{11}Te_2$.[42] Similar reactions take place with ruthenium clusters (eq 158 and Figure 49).[172] Rauchfuss was able to prepare an interesting series of iron molybdenum telluride clusters by this transmetalation reaction (eq 159 and Figure 50).[173] The role of tellurium in cluster assemblies has been discussed and several other reactions have been performed with these mixed clusters to probe their reactivity.[174] One interesting reaction is the reaction with bromine, which results in oxidation of the ditelluride fragment and formation of a hypervalent coordinated tellurium (eq 160).[175] This functionalized molecule can then undergo substitution reactions leading to several derivatives (eqs 161 and 162).

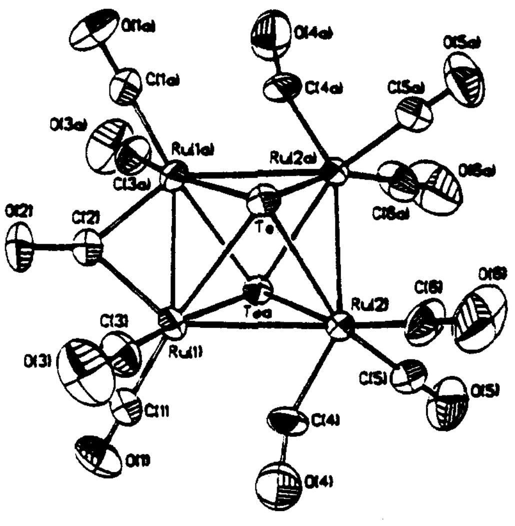


Figure 49. $Ru_4(CO)_{11}(\mu_4\text{-}Te)_2$ (reprinted from ref 172; copyright 1990 American Chemical Society).

$$Fe_3(CO)_9Te_2 + Ru_3(CO)_{12} \rightarrow Ru_4(CO)_{11}(\mu_4\text{-}Te)_2 \qquad (158)$$

$$Fe_3(CO)_9Te_2 + Cp_2Mo_2(CO)_6 \rightarrow CpMoFe_x(CO)_7Te_2 \quad x = 1, 2 \qquad (159)$$

$$CpMoFe(CO)_7Te_2 + Br_2 \rightarrow CpMoFe(CO)_7(\mu_2,\eta^2\text{-}Te_2Br) \qquad (160)$$

$$CpMoFe(CO)_7(Te_2Br) + AgSbF_6 \rightarrow AgBr + [CpMoFe(CO)_7(Te_2)]SbF_6 \qquad (161)$$

$$[CpMoFe(CO)_7(Te_2)]^+ + NaS_2CNEt_2 \rightarrow CpMoFe(CO)_7(\mu_2,\eta^2\text{-}Te_2S(S)CNEt_2) \qquad (162)$$

Unsaturated organic compounds will also add across the Te–Te bond to generate novel bridging organotelluride clusters. Some examples are given below (eqs 163[176] and 164[177]). There are also a series of mixed phosphido telluride clusters prepared by tellurium atom transfer using $TeCN^-$ as the transfer reagent.[178a] These undergo many of the same types of cluster transfor-

$$Fe_3(CO)_9Te_2 + CH_2N_2 \rightarrow Fe_2(CO)_6(\mu\text{-}TeCH_2Te) \qquad (163)$$

$$Fe_3(CO)_9Te_2 + PhC{=}CH \rightarrow Fe_2(CO)_6(\mu\text{-}TeCPh{=}CHTe) \qquad (164)$$

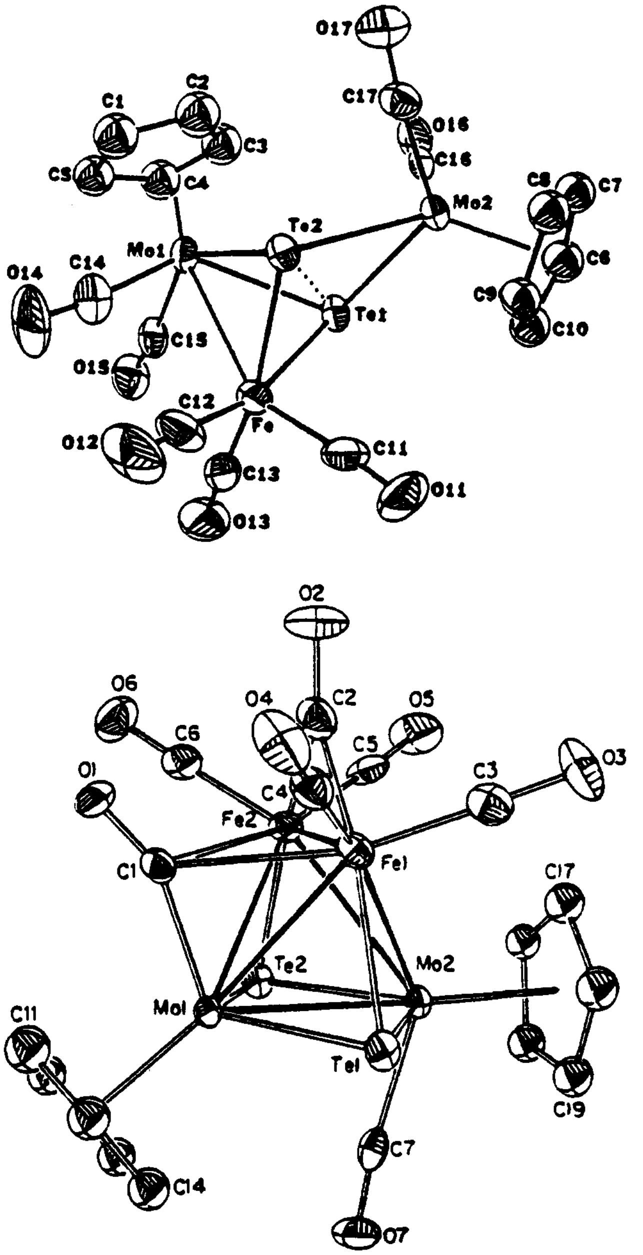


Figure 50. $Cp_2Mo_2Fe(CO)_7Te_2$ and $Cp_2Mo_2Fe_2(CO)_7Te_2$ (reprinted from ref 173; copyright 1985 American Chemical Society).

mations as the tellurides (eq 165).[178] The tellurocyanide

$$Fe_3(CO)_{10}(\mu_3\text{-PR}) + TeCN^- \rightarrow Fe_3(CO)_9(\mu_3\text{-PR})(\mu_3\text{-Te}) \quad (165)$$

is not well-known but can be simply prepared by refluxing NaCN and tellurium powder in acetonitrile. Its properties as a ligand and synthetic reagent are poorly developed but its ease of preparation makes it a promising synthon.

A related series of compounds (although not strictly organometallic) are the selenium and tellurium derivatives of Roussin's red salt $[Fe_2(CO)_4(\mu\text{-E})_2]^{2-}$ (E = S, Se, Te).[179] These salts can be prepared in good yield by the reaction of $Fe_2(NO)_4I_2$ with chalcogenide dianions. Not much chemistry has been done with them, but they can be alkylated with organohalides, and in general behave much like the analogous carbonyl dianions.

It is clear that iron carbonyls will support an enormous amount of chemistry with chalcogenide ligands. The stability and ease of preparation of several neutral iron chalcogenide clusters has made them excellent reagents for systematic development. Still, large areas lie unexplored. The chemistry of the new mixed clusters is only slightly explored, as is the further modification of coordinated chalcogenide fragments. Reactions with selenide clusters have been nearly untouched even though their classical clusters are just as accessible as those of the tellurides.[180] Our recent discovery of large anionic carbonyl clusters made from polytellurides suggests that there is an enormous amount of chemistry waiting to be discovered via this methodology. Use of these compounds in organic transformations is unexplored. Recent results show that the coordinated chalcogenide fragments can be modified with organic reagents. The catalytic or stoichiometric use of these compounds to make new unsaturated heterocycles and related compounds is certainly a future growth area.

In contrast to the well-developed iron chemistry, almost nothing is known about the chemistry of ruthenium and osmium selenides and tellurides. This situation mirrors that of the sulfides, where almost no ruthenium sulfide work has been reported until recently, despite the fact that RuS_2 is one of the best hydrodesulfurization catalysts known. In the last few years, several metal chalcogenides have been reported. Rauchfuss has shown that thermolysis of $CpRu(PPh_3)_2(SeH)$ generates the cubane $Cp_4Ru_4Se_4$ in good yield.[181] More detailed work has revealed that a set of dimers containing bridging diselenides can be prepared through a series of redox interconversions (Figure 51). These molecules all contain diselenides in a series of different bridging motifs seen in previous metal complexes, which ultimately decompose to the $Cp_4Ru_4Se_4$ cubane.[182]

Recently it has been shown that an oxidative decarbonylation reaction could be used to make $[Ru(CO)_2(Se_4)_2]^{2-}$ with ruthenium oxidized from Ru(0) to Ru(II). The metal is in a pseudo-octahedral geometry, with the now-common tetraselenide chelating ligand (eq 166 and Figure 52).[26] Several other ruthenium selenide clusters

$$Ru_3(CO)_{12} + Se_5^{2-}\ (\text{excess}) \rightarrow [Ru(CO)_2(Se_4)_2]^{2-} \quad (166)$$

have been prepared, each containing edge- or face-bridging selenides helping to hold an organometallic cluster together, but no chemistry has been reported with them (eqs 167[183] and 168[184] and Figure 53). The

$$(\text{arene})_2Ru_2Cl_4 + Zn + Se_8 \rightarrow [(\text{arene})_3Ru_3(\mu_3\text{-Se})_2]^{2+} \quad (167)$$

$$Ru_3(CO)_{12} + Ph_2Se_2 \xrightarrow{185\ ^\circ C} Ru_4(\mu_4\text{-Se})_2(CO)_{11} \quad (168)$$

very interesting $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ has been recently prepared from ruthenium carbonyl and polytelluride in water at 110 °C in a sealed tube.[185] The insolubility of the cluster allows for isolation of a good yield of the product (eq 169). The framework of the molecule

$$Ru_3(CO)_{12} + 5Na_2Te_2 + 6(PPh_4)Br \xrightarrow{110\ ^\circ C} [PPh_4]_2[Ru_6(Te_2)_7(CO)_{12}] \quad (169)$$

consists of a series of ruthenium carbonyl fragments

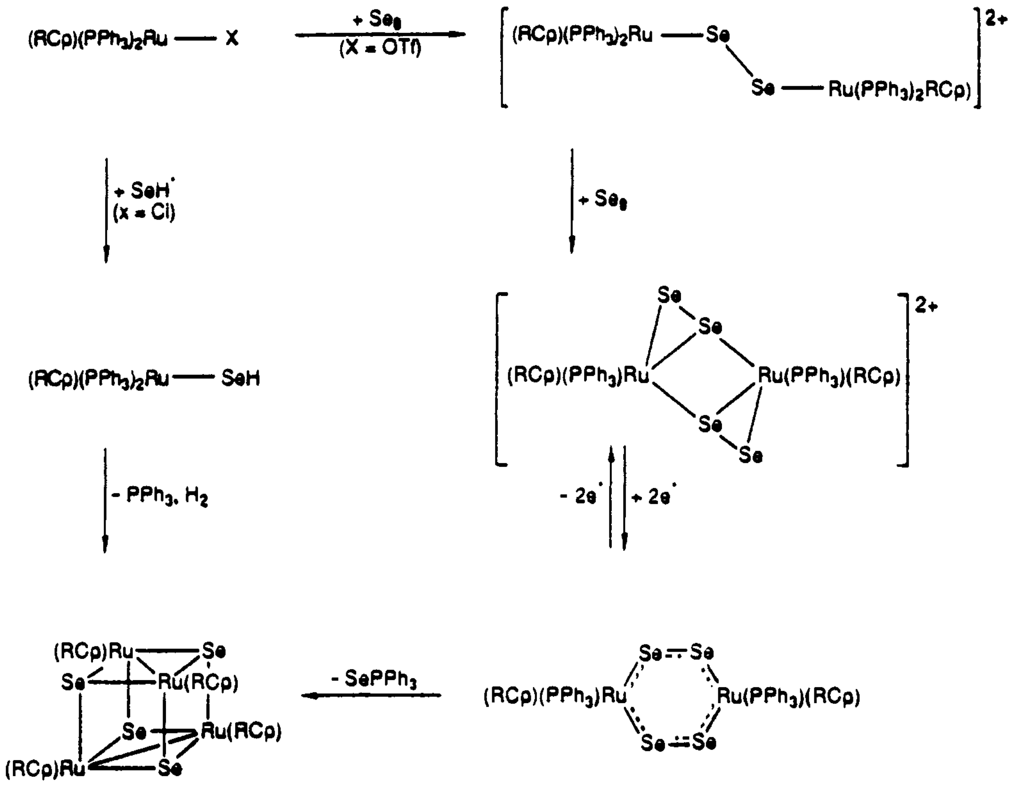


Figure 51. Reaction scheme showing the synthetic studies on the CpRu-PPh$_3$(Se$_2$) system (reprinted from ref 182; copyright 1992 American Chemical Society).

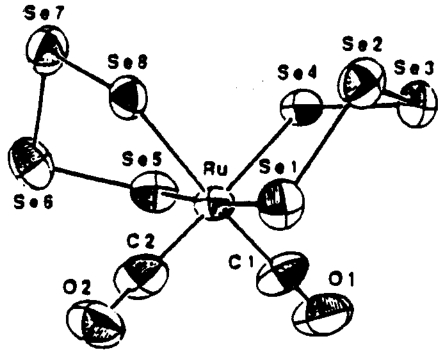


Figure 52. $[Ru(CO)_2(Se_4)_2]^{2-}$ (reprinted from ref 25; copyright 1990 American Chemical Society).

chelated by seven ditellurides (Figure 54) and is similar to that of $RuTe_2$, which has a pyrite structure.

The coordination chemistry of the osmium selenides and tellurides is very undeveloped. Mathur has made one of the parent tellurides via a thermolysis reaction (eq 170),[186] but it has not been put through its paces

$$\mathrm{HOs_3(CO)_{10}(\mu\text{-}TePh)} \xrightarrow{\Delta} \mathrm{Os_3(CO)_9(\mu\text{-}Te)_2} \qquad (170)$$

as the iron complexes have been. Another potential building block, $H_2Os_3(CO)_9(\mu_3\text{-}Te)$, can be prepared in good yield via the reaction of $Os_3(CO)_{10}(CH_3CN)_2$ and H_2Te generated in situ.[187] No reaction chemistry has been reported using these potentially useful starting materials, nor have any other simple complexes been reported. Roper and co-workers have used a labile Os complex to make a compound containing a side-bonded diselenide which can be methylated at selenium by methyl triflate, but extrudes all selenium in the presence of oxidants (eq 171).[188]

$$\mathrm{Os(CO)_2(PPh_3)_3 + Se_8 \rightarrow Os(CO)_2(PPh_3)_2(\eta^2\text{-}Se_2)} \qquad (171)$$

The chalcogenide chemistry of the heavier group 8 elements has thus far been somewhat elusive. There are no binary molecular species, and very few reactions, focusing on the chemistry of the chalcogenide ligand, nor have many complex structural transformations been effected using simple two- or three-metal building blocks as with iron. Cost of the starting materials notwithstanding, investigators are only now turning to the chalcogen chemistry of the noble metals. The increasing stability of metal–metal bonds and substantially altered redox properties of the heavier metals is sure to lead to a reaction chemistry substantially different than that of iron.

3.6. Group 9

Cobalt is another element whose selenium and tellurium coordination chemistry is extremely scant (as is the corresponding sulfide chemistry), particularly when compared to the enormous amount of general cobalt coordination chemistry. This is especially surprising considering that there are readily available, stable but reactive starting materials available for derivatization, such as cobalt carbonyls and various cobalt phosphine halides. Thus it is anticipated that this area will see rapid growth in the near future.

There has been one binary cobalt chalcogenide prepared recently by Dehnicke and co-workers,[139] which has a structure similar to the corresponding Cr(III) trimer reported earlier (eq 172).[22] Each metal center

$$\mathrm{CoCl_2{\cdot}6H_2O + Li_2Se_n\ (excess) \rightarrow [Co_3(Se_4)_6]^{3-}} \qquad (172)$$

is octahedrally coordinated by bridging chelating tetraselenide fragments (Figure 55). Note that this compound again relies on oxidation of the metal center (presumably by the polyselenide) from Co(II) to Co(III).

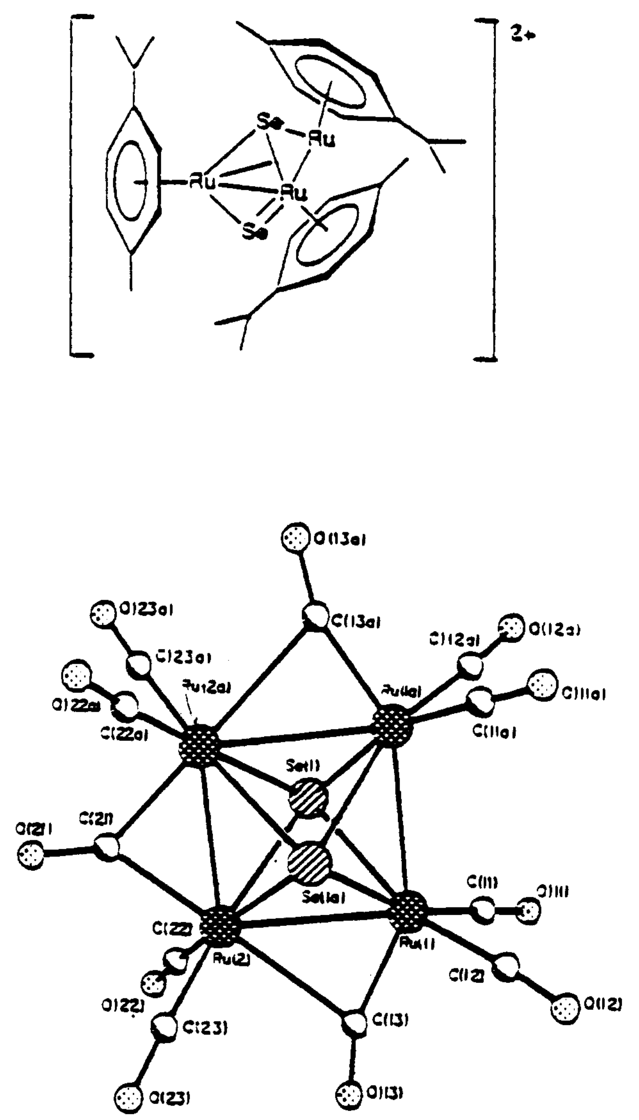


Figure 53. [(arene)$_3$Ru$_3$(μ_2-Se)(μ_3-Se)] (reprinted from ref 183; copyright 1990 Royal Society of Chemistry) and Ru$_4$(μ_4-Se)$_2$(CO)$_{11}$ (reprinted from ref 184; copyright 1992 Elsevier Sequoia S.A.).

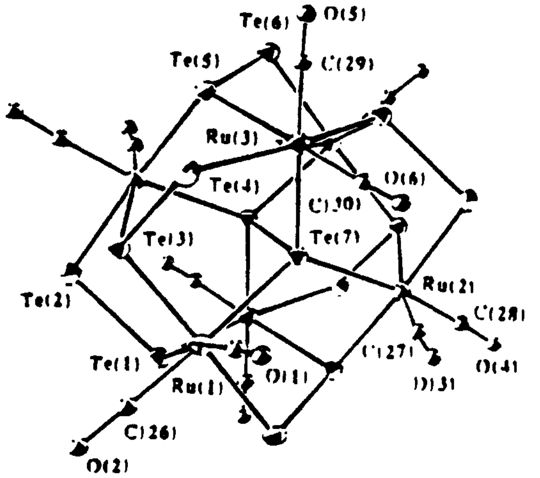


Figure 54. [Ru$_6$(Te$_2$)$_7$(CO)$_{12}$]$^{2-}$ (reprinted from ref 185; copyright 1992 American Chemical Society).

There has also been an octahedral Co(II) cluster isolated in which each face of the cluster is capped by a μ_3 selenide (eq 173).[189] The cluster is robust enough to

$$(Ph_3P)_2CoBr_2 + Na_2Se \rightarrow Co_6Se_8(PPh_3)_6 \quad (173)$$

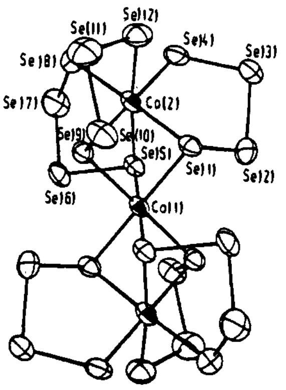


Figure 55. [Co$_3$(Se$_4$)$_6$]$^{3-}$ (reprinted from ref 139; copyright 1991 Zeitschrift fur Naturforschung).

undergo two successive reversible oxidations, presumably forming the octahedral dication. The overall lack of reported results involving cobalt is not surprising in that the sulfides of cobalt have not been developed very well either. In fact there are only very brief reports of any binary sulfides of these elements.[1a]

As with many of the transition metals, most of the heavy chalcogenide chemistry of cobalt occurs with organometallic auxiliary ligands present. A stable cluster was reported relatively early via reaction of cobalt carbonyl with H$_2$Se, along with several mixed cobalt iron derivatives (eq 174).[190] However, little

$$Co_2(CO)_8 + H_2Se \rightarrow Co_3(CO)_9Se \quad (174)$$

further use has been made of this potential building block. Given the fairly rich chemistry of cobalt carbonyl sulfides, it may be anticipated that further cobalt carbonyl selenide and telluride chemistry will appear in the near future. Several other cobalt complexes have been reported containing soft ligands like organophosphines and cyclopentadienyl. For example, elemental chalcogenides will add across Co–Co bonds, forming bridging complexes which are then susceptible to attack by the usual strong electrophiles (eqs 175 and 176).[191]

$$Cp_2Co_2(\mu\text{-}PMe_2)_2 + E \rightarrow Cp_2Co_2(\mu\text{-}PMe_2)_2(\mu\text{-}E) \quad E = S, Se, Te \quad (175)$$

$$Cp_2Co_2(\mu\text{-}PMe_2)_2(\mu\text{-}E) + X^+ \rightarrow [Cp_2Co_2(\mu\text{-}PMe_2)_2(\mu\text{-}EX)]^+ \quad X = H, CH_3 \quad (176)$$

A very thermodynamically stable complex, (PMe$_3$)$_3$Co(μ-Te)$_2$Co(PMe$_3$)$_3$, has been identified, whereby virtually any cobalt phosphine halide will react with nearly any tellurium source to produce this complex in good yield.[192] This reaction also appears to work equally well for selenides and sulfides.[192]

Steigerwald and co-workers have exploited the mild tellurium transfer reagent Te=PEt$_3$ to generate a series of cobalt carbonyl phosphine tellurides (eq 177).[193]

$$Co_2(CO)_8 + Te{=}PEt_3 \rightarrow (Et_3P)_4(CO)_6Co_4(\mu_4\text{-}Te)_2 \quad (177)$$

Three interconvertible complexes have been isolated, (Et$_3$P)$_4$(CO)$_4$Co$_2$(μ-Te$_2$), (Et$_3$P)$_4$(CO)$_6$Co$_4$(μ_4-Te)$_2$, and (Et$_3$P)$_6$Co$_6$(μ_3-Te)$_8$, depending on the conditions and relative stoichiometries used in each reaction. The first complex is a ditelluride bridged dimer almost directly

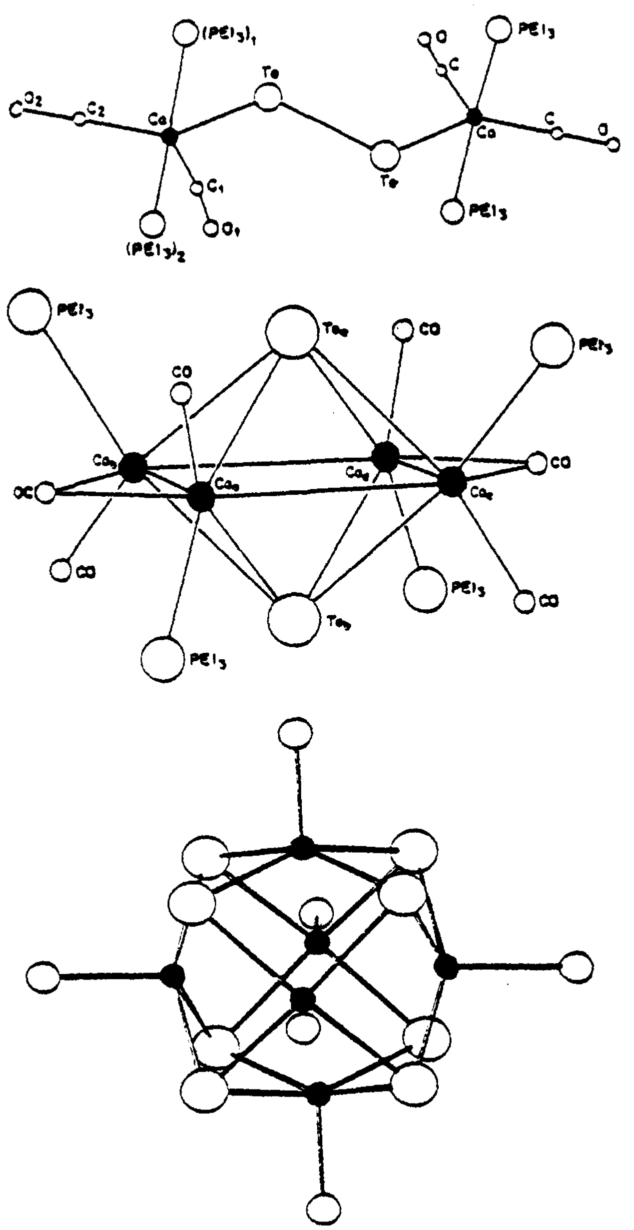


Figure 56. $(Et_3P)_4(CO)_4Co_2(\mu\text{-}Te_2)$, $(Et_3P)_4(CO)_6Co_4(\mu_4\text{-}Te)_2$, and $(Et_3P)_6Co_6(\mu_3\text{-}Te)_8$ (reprinted from ref 194; copyright 1991 American Chemical Society).

analogous to similar iron and manganese clusters. The second contains a square of metal atoms capped on top and bottom with μ_4 tellurides and is isostructural with $Co_4(CO)_{10}(\mu_4\text{-}Te)_2$ reported earlier by Dahl.[194] The third is the ubiquitous face capping octahedral structure (Figure 56). All three can ultimately be converted to CoTe upon thermolysis.

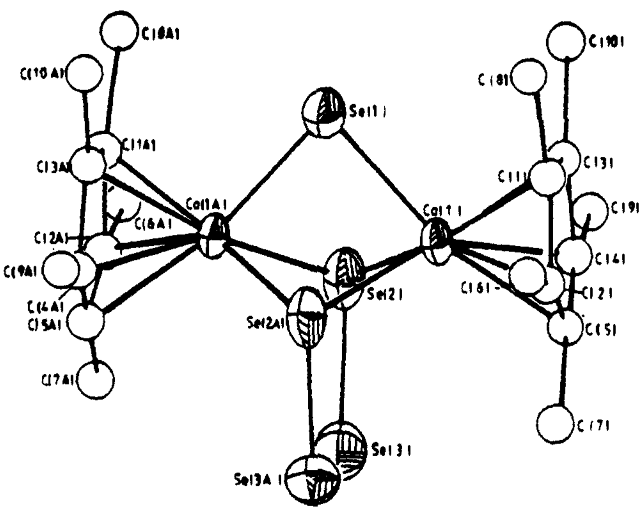


Figure 57. $Cp'_2M_2(\mu\text{-}Se)(\mu_2,\mu_2\text{-}Se_4)$ (reprinted from ref 195a; copyright 1988 Elsevier Sequoia S.A.).

$$Cp^*_2M_2(CO)_2 + Se_8 \rightarrow Cp^*_2M_2(CO)_2(\mu\text{-}Se) \quad (178)$$

$$Cp^*_2M_2(CO)_2(\mu\text{-}Se) + Se_8 \rightarrow Cp^*_2M_2(CO)_2(\mu\text{-}Se)_2 \quad (179)$$

$$Cp^*_2M_2(CO)_2(\mu\text{-}Se)_2 + Se_8 \rightarrow Cp^*_2M_2(\mu\text{-}Se)(\mu_2,\eta_2\text{-}Se_4) \quad (180)$$

Wachter and co-workers have prepared an extensive series of cyclopentadienyl carbonyl cobalt and rhodium dimers containing various selenide and telluride fragments in different bridging positions. They found that selenium in particular will react with the double bonded dimer $Cp^*_2M_2(CO)_2$ to generate a selenide bridged dimer. This dimer further combines with more Se_8 to provide selenium rich products, including one containing the very unusual $\mu_2,\mu_2\text{-}Se_4$ fragment (eqs 178–180 and Figure 57).[195] This novel structural motif was first observed in the corresponding sulfide.[1d] Thermal decomposition of these dimers ultimately leads to the cubane $Cp^*_4M_4Se_4$. This chemistry also takes place with the mixed Co/Rh dimer.[196] A unique electrophilic attack by SO_3 upon $Cp^*_2Rh_2(CO)_2(\mu\text{-}Se)$ involves simple adduct formation at the bridging selenide, rather than the expected oxidation (eq 181).[197]

$$Cp^*_2Rh_2(CO)_2(\mu\text{-}Se) + py{\cdot}SO_3 \rightarrow Cp^*_2M_2(CO)_2(\mu\text{-}SeSO_3) \quad (181)$$

Some interesting work has been done using the tripodal polyphosphine ligand tris(2-(diphenylphosphino)ethyl)phosphine (pp_3), to support rhodium complexes of various selenides and tellurides. For example the dicationic complex $[(pp_3)_2Rh_2(\mu_1,\eta^2\text{-}Se_2)_2]^{2+}$, containing side-bonded, bridging diselenides can be prepared via the novel route of decomposition of a coordinated diselenocarbonate.[198] The labile $[pp_3Rh(COD)]^+$ undergoes nucleophilic attack by HE^- (E = S, Se, Te) to from the adduct pp_3RhEH.[199] Similarly, cationic precursors are attacked by anionic tellurides to form a bridging ditelluride complex (eq 182).[200] All

$$[pp_3Rh]^+ + Te_n^{2-} \rightarrow pp_3Rh{-}Te{-}Te{-}Rhpp_3 \quad (182)$$

of these complexes have been subjected to very detailed multinuclear NMR investigations which suggest that the behavior in solution is not always reconcilable with the products isolated in the solid state.

A large number of cobalt phosphine selenide clusters has been prepared by Fenske and co-workers by the reaction of TMS_2Se with various cobalt phosphine halides. These structures are all cobalt–cobalt bonded clusters with face-capping selenides. For example, the reaction shown in 183 affords three products. The

$$CoCl_2(PPh_3)_2 + TMS_2Se \rightarrow Co_4(\mu_3\text{-}Se)_4(PPh_3)_4 + Co_6(\mu_3\text{-}Se)_8(PPh_3)_6 + Co_9(\mu_3\text{-}Se)_{11}(PPh_3)_6 \quad (183)$$

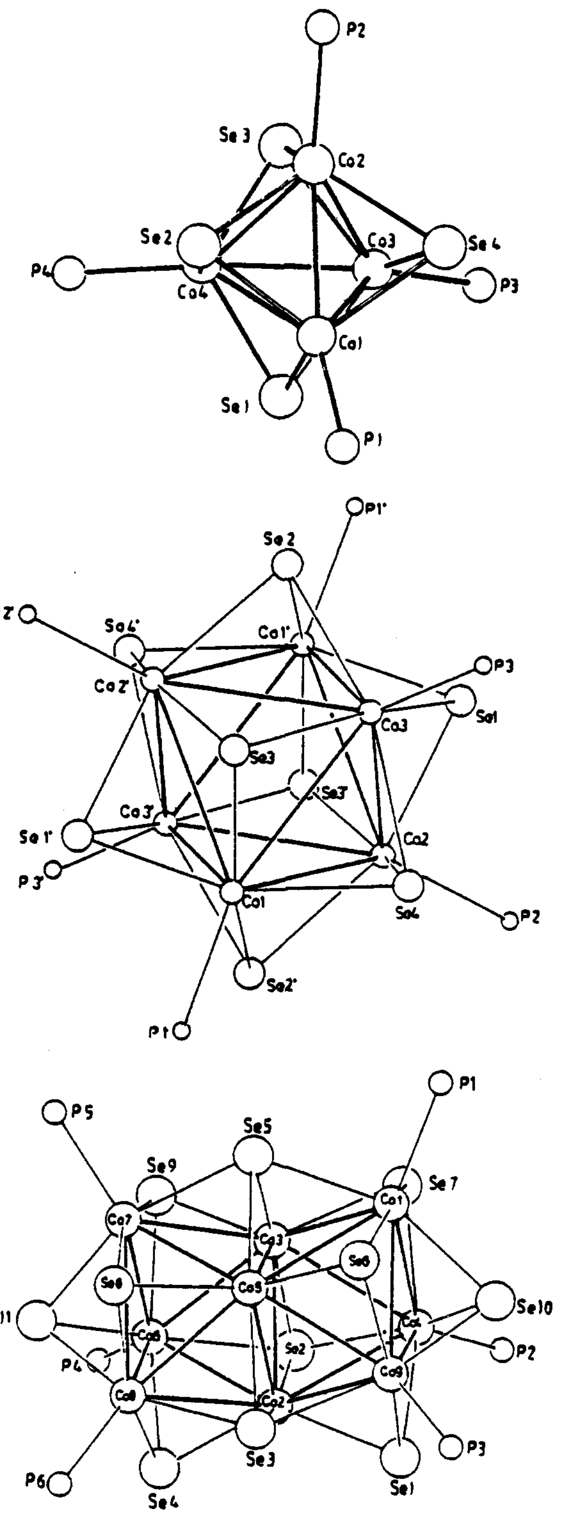


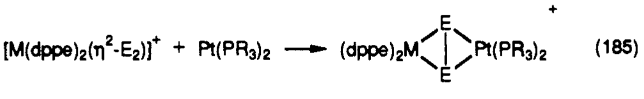
Figure 58. $Co_4(\mu_3\text{-}Se)_4(PPh_3)_4$, $Co_6(\mu_3\text{-}Se)_8(PPh_3)_6$, and $Co_9(\mu_3\text{-}Se)_{11}(PPh_3)_6$ (reprinted from ref 201; copyright 1985 VCH Verlagsgesellschaft mbH).

shapes range from face-capped tetrahedra in $Co_4(\mu_3\text{-}Se)_4(PPh_3)_4$, through edge-sharing square prisms in $Co_8(\mu_3\text{-}Se)_8(PPh_3)_6$, to face-sharing octahedra in $Co_9(\mu_3\text{-}Se)_{11}(PPh_3)_6$ (Figure 58).[201] Use of other phosphines and other conditions generates different but related products.[38] Many, but not all, of these have sulfur analogs and also bear structural similarity to related nickel clusters (vide infra).

In somewhat earlier work, Ginsberg and co-workers showed that cationic phosphine complexes of Rh and Ir react cleanly with Se_8 or S_8 to form monocations with side-bonded dichalcogenide fragments.[202] If dmpe is

$$[M(dppe)_2]^+ + E_8 \rightarrow [M(dppe)_2(\eta^2\text{-}E_2)]^+ \quad E = S, Se \quad (184)$$

used as a ligand in the presence of excess selenium, the chelating tetraselenide complex $[M(dmpe)_2(E_4)]^+$ can be isolated.[203] This family of complexes was subjected to a very detailed bonding and reactivity study. It was found that the diselenide fragments could be cleanly abstracted in the presence of such selenophiles as phosphines and Hg metal. However they will oxidatively add to low valent metal centers to form heterometallic dimers with bridging selenides (eq 185).[202]


$$[M(dppe)_2(\eta^2\text{-}E_2)]^+ + Pt(PR_3)_2 \longrightarrow [(dppe)_2M(\mu\text{-}E)_2Pt(PR_3)_2]^+ \quad (185)$$

3.7. Group 10

With the exception of groups 6 and 11, the nickel triad probably has the richest binary coordination chemistry of any of the transition-metal groups. This is fitting in that the first binary metal polychalcogenide complex ever reported is the venerable $[Pt(S_5)_3]^{2-}$.[204] Thus it would be expected that group 10 polyselenides and -tellurides would be stable as well, and indeed this is the case.

An attempt to prepare the direct selenium analog of the platinum sulfide complex results instead in the tris-tetraselenide chelate $[Pt(Se_4)_3]^{2-}$ as the tetraphenylphosphonium salt.[205] Again this reaction involves an oxidation of the metal center from Pt(II) to Pt(IV) by the polyselenide reagent (eq 186 and Figure 59). Given

$$Pt(S_2COEt)_2 + 3Se_5^{2-} \rightarrow [Pt(Se_4)_3]^{2-} \quad (186)$$

that the complex does not appear to be labile, there exists the possibility that its optical isomers may be resolved as the sulfide complex has been.[206] Far more common however, are the bis chelating tetrachalcogenido complexes $[M(Se_4)_2]^{2-}$ (M = Ni, Pd, Pt). They have all been prepared by the reaction of a metal salt, either a xanthate or a halide, with a tetraselenide anion. The complete series of selenides has been prepared and reported by several authors.[128,207,208] The compounds are essentially isostructural, with a slightly distorted square planar coordination environment around the M(II) center (Figure 60). It should be noted that the platinum complex $[Pt(Se_4)_2]^{2-}$ was also prepared as the $[PPh_4]^+$ salt by the reaction of a salt of nominal composition Se_2^{2-} with $PtCl_2$. Although the idea has not been tested, it is intriguing to speculate that the reason that $[Pt(Se_4)_3]^{2-}$ was not formed is because the shorter chain, i.e. more reduced, polyselenide (Se_2^{2-} versus Se_5^{2-}), was used as a starting material. Thus the polyselenide was not a good enough oxidant to transform the Pt(II) to the necessary Pt(IV) state to form the octahedral complex. The corresponding palladium tetratelluride complex has also been prepared (eq 187),

$$PdCl_2 + 2Te_4^{2-} \rightarrow [Pd(Te_4)_2]^{2-} \quad (187)$$

having essentially the same square planar coordination environment around the Pd(II) center.[209] A different crystallographic modification of the same salt was subsequently reported.[210]

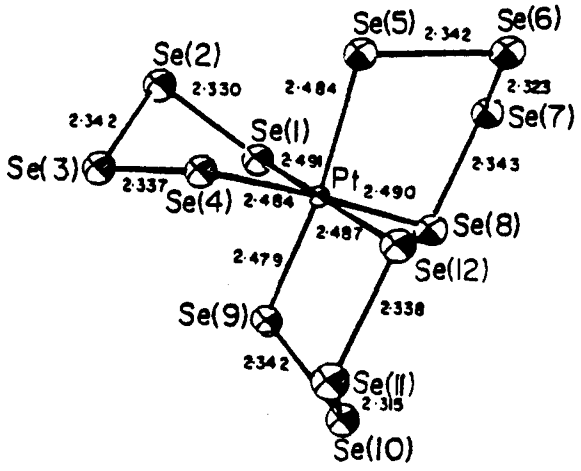


Figure 59. $[Pt(Se_4)_3]^{2-}$ (reprinted from ref 205; copyright 1989 American Chemical Society).

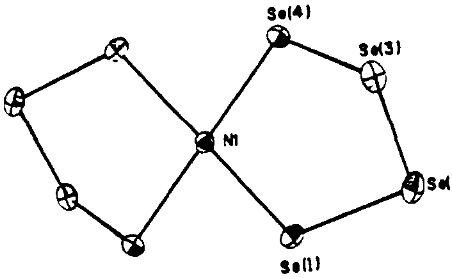


Figure 60. $[M(Se_4)_2]^{2-}$, M = Ni, Pd, Pt (reprinted from ref 128; copyright 1990 American Chemical Society).

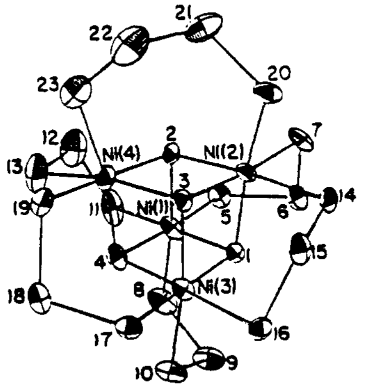


Figure 61. $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ (reprinted from ref 182; copyright 1991 American Chemical Society).

When $Ni(S_2COEt)_2$ is treated with a less than 2:1 excess of Se_4^{2-}, an unusual cubane cluster can be isolated along with the expected $[Ni(Se_4)_2]^{2-}$ (eq 188).[211] The

$$2Ni(S_2COEt)_2 + 3Se_4^{2-} \rightarrow [Ni_4(\mu_3\text{-}Se)_4(Se_3)_5(Se_4)]^{4-} \quad (188)$$

cluster consists of a regular Ni_4Se_4 cubane, but each face is diagonally bridged from nickel to nickel by a polyselenide fragment (Figure 61). Five of the bridging groups are triselenides and one is a tetraselenide chain. In addition, each nickel is in a formal Ni(IV) oxidation state, so the polyselenides again appear to have oxidized the metal center. There is a structurally analogous rhenium sulfide cluster,[212] but this is the first of this structural type for the heavier polychalcogenides. Recently a similar telluride analog has been isolated in much the same way (eq 189).[213] Again it is a Ni(IV) cubane with polytelluride fragments bridging diagonally

$$Ni(xan)_2 + Te_4^{2-} \rightarrow [Ni_4(\mu_3\text{-}Te)_4(Te_2)_2(Te_3)_4]^{4-} \quad xan = xanthate \quad (189)$$

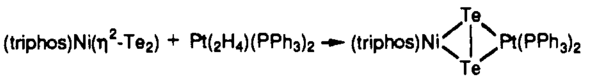
across all the faces (Figure 62), but in accordance with the larger size of tellurium, the polytelluride fragments are shorter.

A harbinger of the next generation of metal polychalcogenides has been reported recently. Kim and Kanatzidis have isolated a palladium polyselenide from a reaction done in a Carius tube in water at 110 °C.[214] The compound is a solid consisting of an infinite lattice of Pd(II) atoms bridged by either Se_4^{2-} or Se_6^{2-} chains. It is an ordered lattice consisting of two interpenetrating networks of $[Pd(Se_4)_2]^{2-}$ and $[Pd(Se_6)_2]^{2-}$. Each metal is tetrahedrally coordinated and they are tetrahedrally disposed relative to each other, so the overall effect is two interlocking adamantyl frameworks (Figure 63). This synthetic methodology of using superheated solvents has been known by geochemists for a long time as the way in which large gems are formed in the earth. Recently chemists are finding that it is an excellent way to grow crystals, often leading to very novel compounds, and rapid expansion of this technique is anticipated.

Several nickel ditelluride complexes have been isolated using various tripodal phosphines as supporting ligands.[215] In (triphos)Ni(η^2-Te_2) the ditelluride completes the 18-electron count around the metal center regardless of whether it is considered a neutral Te_2 donating two electrons to a 16-electron Ni(0) complex or Te_2^{2-} donating two lone pairs to Ni(II) (eq 190). If

$$Ni(ClO_4)_2\cdot 6H_2O + Te_2^{2-} + triphos \rightarrow (triphos)Ni(\eta^2\text{-}Te_2) \quad (190)$$

twice as much nickel starting material is used, a dinuclear complex is obtained which has the ditelluride side-bonded to two metal centers.[216] The Te–Te distance of 2.802 Å suggests that the ditelluride bond remains intact. The side-bonded ditelluride complex also reacts with other neutral unsaturated metal centers to generate heterometallic ditelluride bridged dimers.



$$(triphos)Ni(\eta^2\text{-}Te_2) + Pt(C_2H_4)(PPh_3)_2 \rightarrow (triphos)Ni(\mu\text{-}Te_2)Pt(PPh_3)_2 \quad (191)$$

The tellurium atom transfer reagent Te=PEt_3 can be used effectively to prepare several interesting metal telluride clusters in good yield. Depending on conditions and relative stoichiometries, two extremely intriguing nickel clusters can be isolated (eqs 192 and 193).[217] Both clusters have unusual closed structures

$$Ni(COD)_2 + Et_3P + Te{=}PEt_3 \rightarrow Ni_{20}Te_{18}(PEt_3)_{12} \quad (192)$$

$$2Ni(COD)_2 + Et_3P + 2Te{=}PEt_3 \rightarrow Ni_9Te_6(PEt_3)_8 \quad (193)$$

which can be related to known thermodynamic close-packed phases (Figure 64) and can be converted to NiTe upon pyrolysis. A theoretical treatment of the structure and bonding of these clusters, and the relationships between them and the simple nickel telluride phases, has recently been published.[218] Similar reactions with

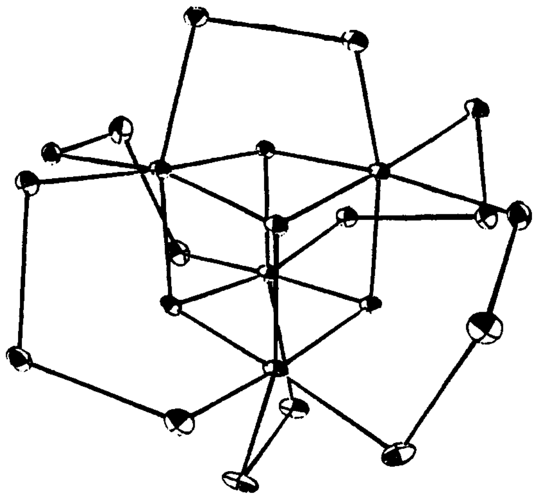


Figure 62. $[Ni_4(\mu_3\text{-}Te)_4(Te_2)_2(Te_3)_4]^{4-}$.

palladium phosphines lead to several other clusters which are somewhat smaller and more open than the nickel compounds (Figure 65) (eq 194).[219] A platinum

$$Pd(PPh_3)_4 + Te{=}PEt_3 \rightarrow Pd_6Te_6(PEt_3)_8 + Pd_2(PEt_3)_4(\mu\text{-}Te)_2 \quad (194)$$

analog to the second compound has been previously prepared using a mercury telluride cluster and $Pt(PPh_3)_4$.[209] Both palladium compounds can also be converted to PdTe upon heating.

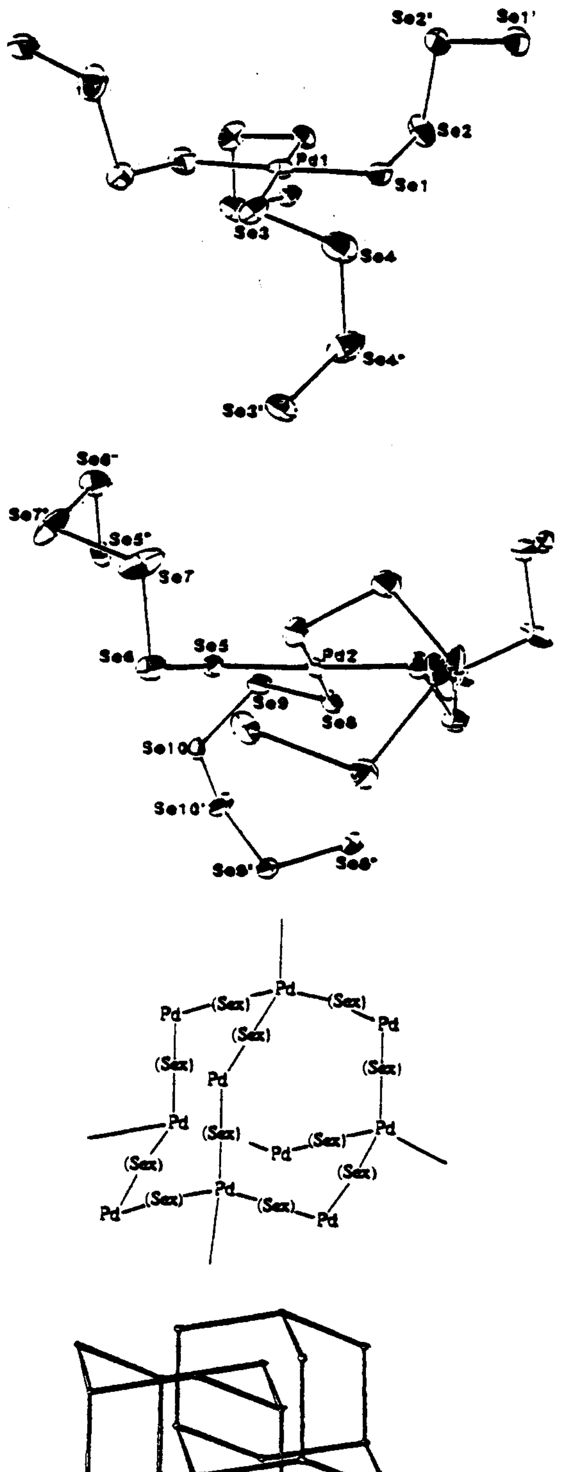


Figure 63. Views of the separate repeating units of $[Pd(Se_4)_2]^{2-}$ and $[Pd(Se_6)_2]^{2-}$ along with a view of their interpenetrating behavior (reprinted from 214; copyright 1992 American Chemical Society).

Fenske and co-workers have found that the group 10 triad provides an appropriate entry to some of their most spectacular clusters, using simple starting materials and bis(trimethylsilyl) reagents. As with many other metal complexes, small changes in the size and donor properties of auxiliary ligands like phosphines result in enormous differences in size and shape of the clusters which have been isolated.[35] This is illustrated by the system $NiCl_2P_2$, where P is various organophosphines. By simply changing ratios of starting materials and the organic group on the phosphines, six new nickel selenide phosphine complexes can be isolated and characterized.[220] In each case it appears that the size of the phosphine and the solubility that it imparts upon the cluster dictates the nature of the product. All the clusters contain terminal phosphines and bridging monoselenides in various positions (Figure 66). There is no evidence for Se–Se bond formation in any of this chemistry. The structures of many, though not all, of these clusters can be rationalized by the condensation of polyhedra through edges, faces, or vertices. For example, the series of clusters $[Ni_9S_9(PEt_3)_6]^{2+}$ to $Ni_{12}Se_{12}(PEt_3)_6$ to $Ni_{15}Se_{15}(PEt_3)_6$ are chains of two, three, and four face-sharing octahedra, respectively.[221] One cluster which has been prepared earlier by the same method (eq 195) is especially interesting because of its

$$NiCl_2(PPh_3)_2 + Se(TMS)_2 \rightarrow Ni_{34}(\mu_5\text{-}Se)_2(\mu_4\text{-}Se)_{20}(PPh_3)_{10} \quad (195)$$

enormous size (Figure 67).[201] It can be anticipated that clusters this large should begain to assume some properties of a bulk solid, even if they do not directly mimic the structures of known simple binary compounds. The size of this cluster was subsequently dwarfed by a copper selenide prepared in a similar manner (vide infra).

Changing the phosphine ligands to cyclopentadienyl leads to an entirely different series of clusters (eq 196 and Figure 68).[222] There have been several Cp nickel

$$Cp'Ni(CO)Br + Se(TMS)_2 \rightarrow Cp'_3Ni_4Se_2(CO)Br + Cp'_5Ni_6Se_4 + Cp'_8Ni_{15}Se_{10}(CO)_3 \quad (196)$$

tellurides isolated using the same technique. They have

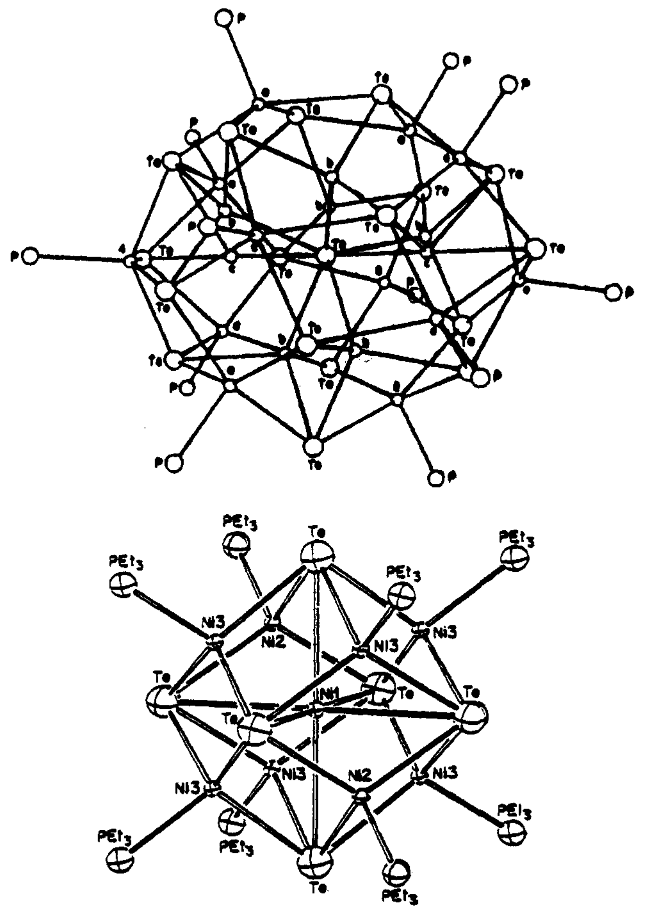


Figure 64. $Ni_{20}Te_{18}(PEt_3)_{12}$ and $Ni_9Te_6(PEt_3)_8$ (reprinted from ref 218; copyright 1989 American Chemical Society).

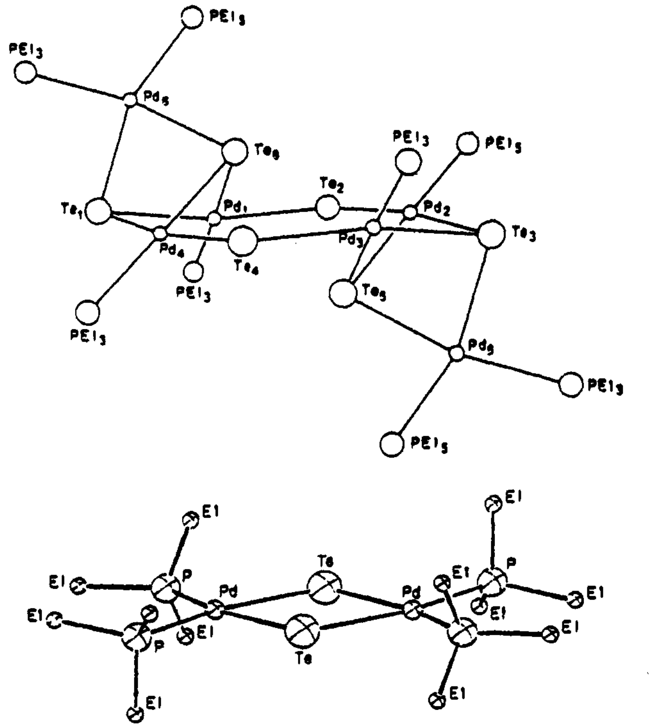


Figure 65. $Pd_6Te_6(PEt_3)_8$ and $Pd_2(PEt_3)_4(\mu\text{-}Te)_2$ (reprinted from ref 219; copyright 1990 American Chemical Society).

similar bonding characteristics, but are generally not as large as the selenides (eq 197 and Figure 69).[223] Another extensive series of palladium compounds can be prepared using the same technique (eq 198 and Figure 70).[224] These again contain various polyhedra

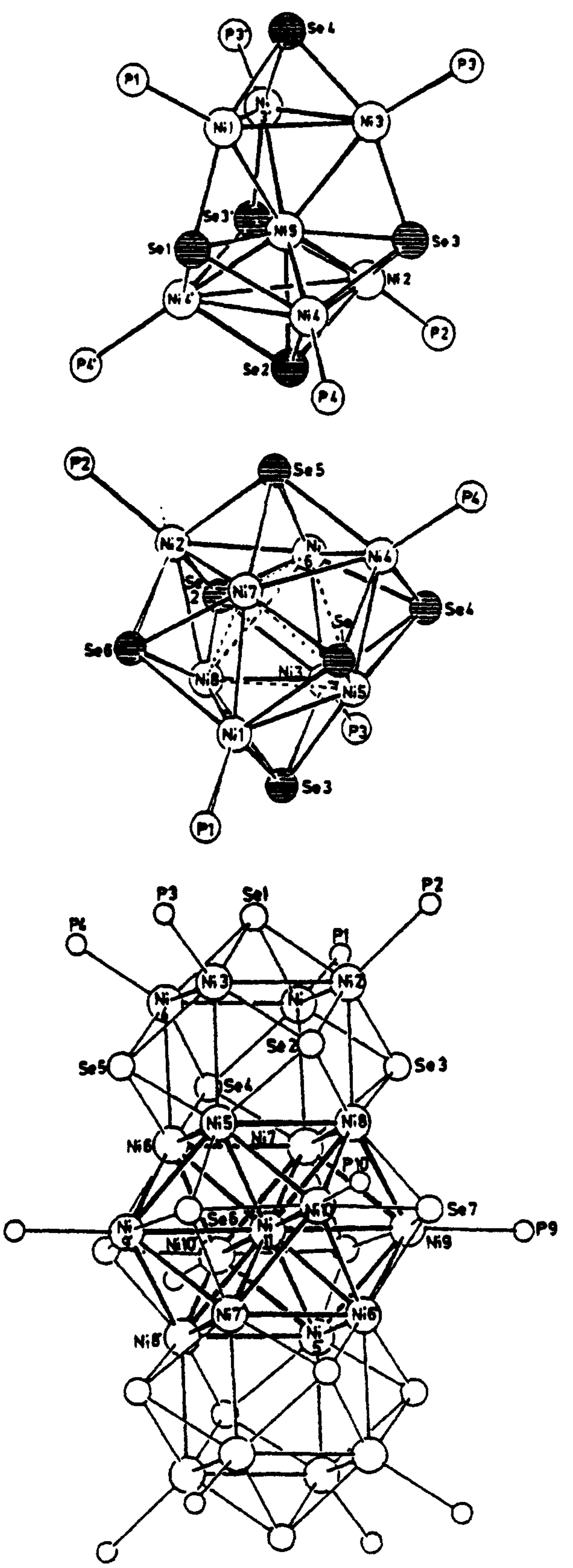


Figure 66. $[Ni_7Se_5(PiPr_3)_6]$, $[Ni_8Se_6(PiPr_3)_4]$, and $[Ni_{21}Se_{14}(PEt_2Ph)_{12}]$ (reprinted from ref 220; copyright 1992 VCH Verlagsgesellschaft mbH).

$$CpNi(PPh_3)Cl + Te(TMS)_2 \rightarrow Cp_4Ni_4(\mu_4\text{-}Te)_2 + Cp_4Ni_4(\mu_3\text{-}Te)_3(PPh_3)_2 \quad (197)$$

with metal-capping phosphine ligands and face-bridging selenides.

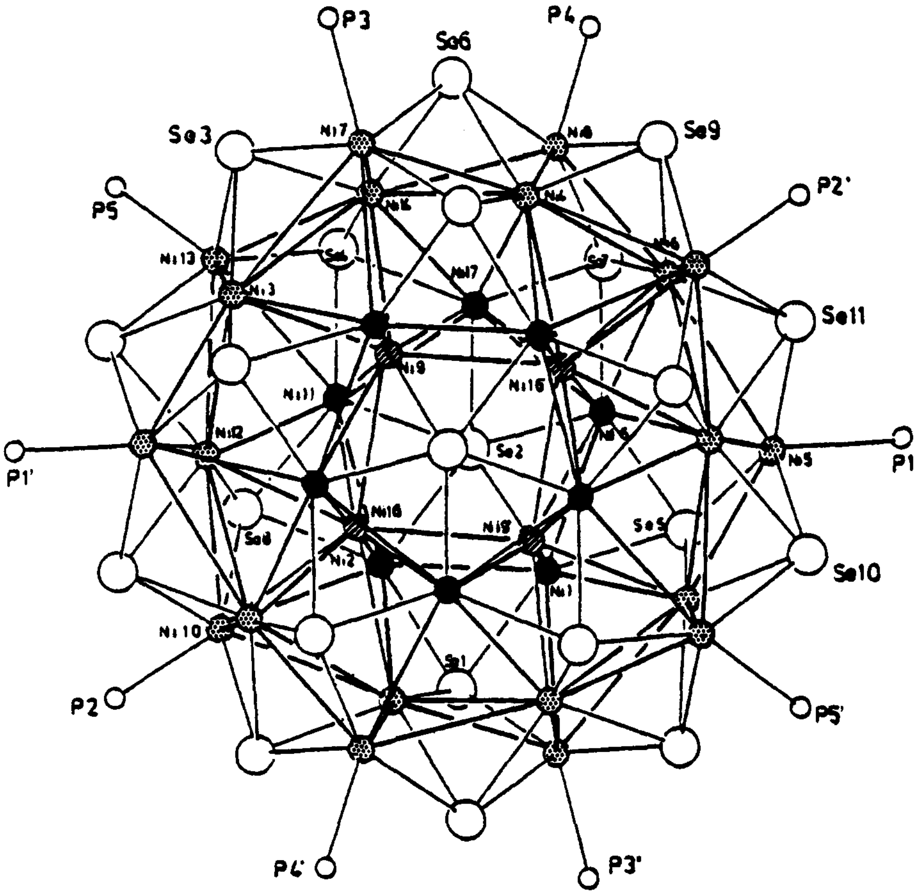


Figure 67. $[Ni_{34}(\mu_5\text{-}Se)_2(\mu_4\text{-}Se)_{20}(PPh_3)_{10}$ (reprinted from ref 201; copyright 1985 VCH Verlagsgesellschaft mbH).

$$PdCl_2(PPh_3)_2 + Se(TMS)_2 \rightarrow Pd_3Se_2(SeTMS)_2(PPh_3)_4 + Pd_5Se_5(PPh_3)_5 + Pd_8Se_8(PPh_3)_8 \quad (198)$$

3.8. Group 11

The binary selenides and tellurides of group 11 very closely resembles the sulfides. Most of the compounds are multinuclear anions linked by various bridging polychalcogenides. They are quite labile in that the compounds isolated are much more strongly dependent on the conditions of crystallization and nature of the counterion than on the identity of the starting materials. As with the sulfides, great return can be obtained from reaction of a simple metal salt with a polychalcogenide anion followed by extensive experimentation with various counterions and solvents. The chemistry is mostly that of metal polyselenides. There have been a few metal tellurides isolated, but in general more metal selenides are known which often bear a reasonable resemblance to the corresponding metal sulfides.

Several copper selenides have been synthesized by the methods described above (eqs 199[225] and 200[226]). In

$$2Li_2Se_n + CuCl \rightarrow [Cu_2(Se_4)(Se_5)_2]^{4-} \quad (199)$$

$$CuCl_2 + Na + Se \rightarrow [Cu_4(Se_4)_{2.4}(Se_5)_{0.6}]^{2-} \quad (200)$$

both cases the copper is tetrahedrally coordinated and has not been oxidized by the polyselenide from Cu(I) to Cu(II). In addition both anions are discrete clusters rather than extended polymers and have similar, if not identical, counterparts in sulfur chemistry (Figure 71).

There have also been several ternary copper selenide and telluride compounds isolated from the reaction of copper metal with molten alkali polychalcogenides. These are often infinite chains of metal polychalcogenide complexes with the alkali metals occupying voids in the lattice. This is the case for α-$KCuSe_4$, which consists of an infinite chain of Cu(I) atoms tetrahedrally coordinated by Se_4^{2-} groups in an unusual triply bridging mode (eq 201 and Figure 72).[227] There have also been

$$Cu + K_2Se_4 \xrightarrow{250\ ^\circ C} \alpha\text{-}KCuSe_4 \quad (201)$$

several copper telluride compounds, namely $K_4Cu_8Te_{11}$ and $K_2Cu_5Te_5$, made in essentially the same way, but these have considerably more complex structures.[228,229] The $K_2Cu_5Te_5$ compound consists of infinite corrugated sheets of Cu and Te having a distorted PbO structure. The structure of the other compound is considerably more dramatic, with a complex three-dimensional lattice of fused, face-sharing copper ditelluride dodecahedra (Figure 73). These complexes contain mixed valent copper(I/II) sites, and their magnetic and conductivity properties have been measured.

There have been a number of silver selenide complexes reported, all prepared by reaction of a polyselenide with an Ag(I) salt. Kanatzidis and co-workers found that there is a large solvent and counterion dependence on the nature of the compound isolated. With PPh_4^+ as a counterion, an infinite chain of Ag(I) atoms chelated by bridging tetraselenides is formed (eq 202 and Figure 74).[230] If a small counterion,

$$AgNO_3 + 2Se_5^{2-} + PPh_4^+ \rightarrow [(PPh_4)Ag(Se_4)] \quad (202)$$

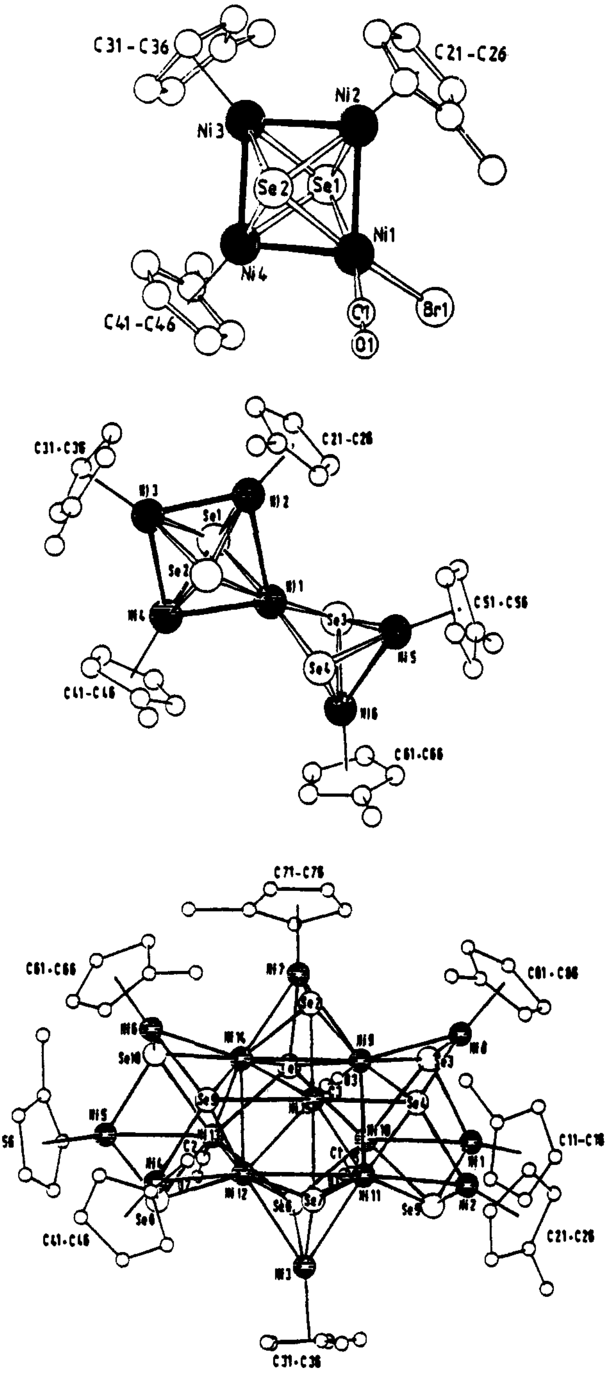


Figure 68. $Cp'_3Ni_4Se_2(CO)Br$, $Cp'_5Ni_6Se_4$, and $Cp'_8Ni_{15}Se_{10}(CO)_3$ (reprinted from ref 222; copyright 1989 VCH Verlagsgesellschaft mbH).

$(Me_4N)^+$, is used, a different polymer is isolated with bridging pentaselenides. Finally, if larger ammonium salts are used, discrete clusters are observed (eqs 203–205).[231] All of these compounds contain three- or four-

$$AgNO_3 + 2Se_5^{2-} + Me_4N^+ \rightarrow [(Me_4N)Ag(Se_5)]_n \quad (203)$$

$$AgNO_3 + 2Se_5^{2-} + Et_4N^+ \rightarrow [(Et_4N)Ag(Se_4)]_4 \quad (204)$$

$$AgNO_3 + 2Se_5^{2-} + Pr_4N^+ \rightarrow (Pr_4N)_2[Ag_4(Se_4)_3] \quad (205)$$

coordinate Ag(I) centers bridged by tetra- or pentaselenides in a variety of ways. There is no evidence of oxidation of the Ag(I) centers to higher oxidation states by the polyselenides, nor have any silver selenide ternary compounds been isolated from molten salt reactions. However, a new ternary silver selenide with a columnar structure has been prepared in supercritical ethylene-

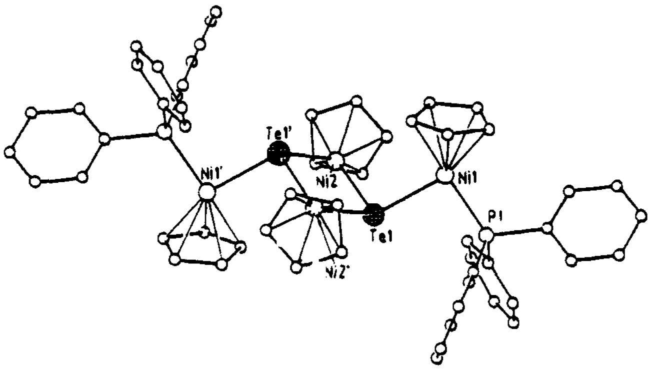


Figure 69. $Cp_4Ni_4(\mu_3\text{-}Te)_2(PPh_3)_2$ (reprinted from ref 223; copyright 1988 VCH Verlagsgesellschaft mbH).

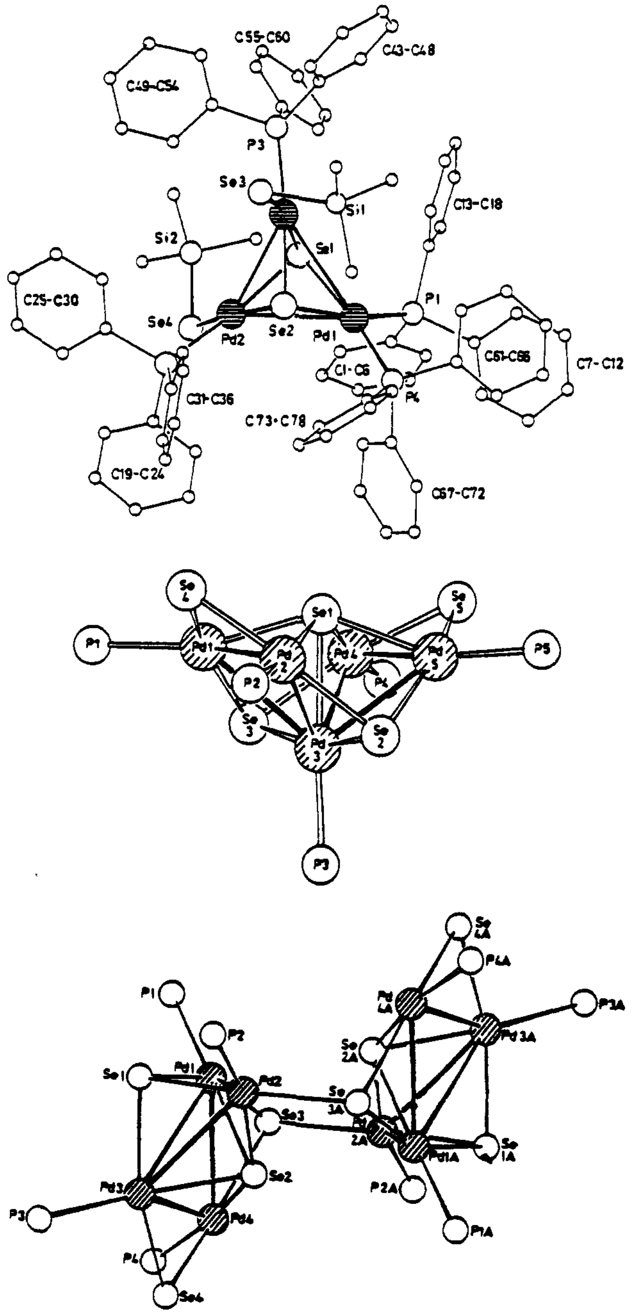


Figure 70. $Pd_3Se_2(SeSiMe_3)_2(PPh_3)_4$, $Pd_5Se_5(PPh_3)_5$, and $Pd_8Se_8(PPh_3)_8$ (reprinted from ref 224a,b, copyright 1990 and 1991 Zeitschrift fur Naturforschung).

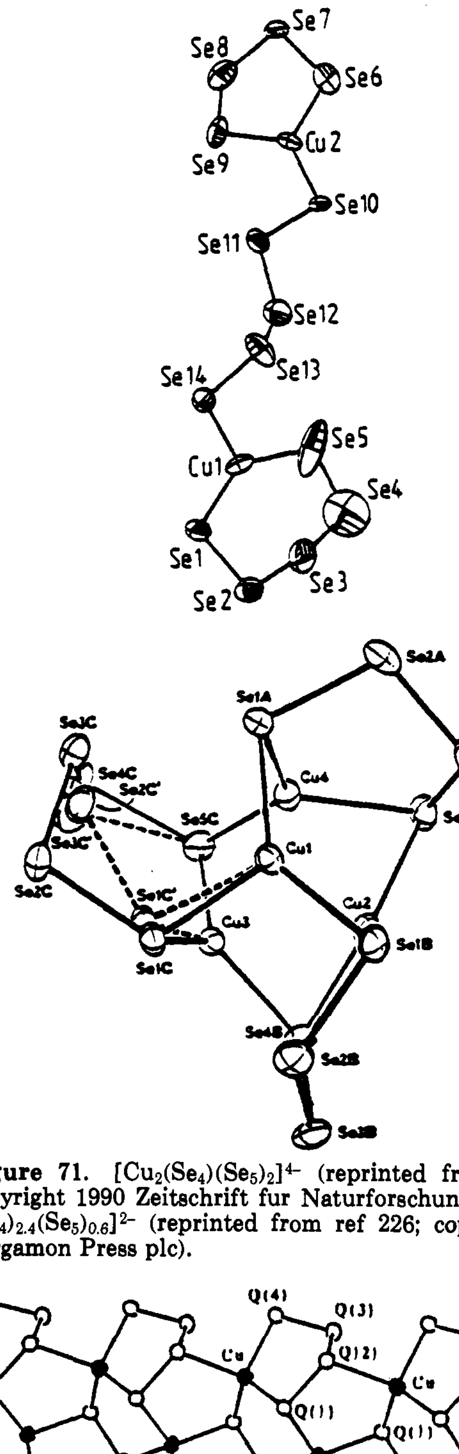


Figure 71. $[Cu_2(Se_4)(Se_5)_2]^{4-}$ (reprinted from ref 225; copyright 1990 Zeitschrift fur Naturforschung) and $[Cu_4(Se_4)_{2.4}(Se_5)_{0.6}]^{2-}$ (reprinted from ref 226; copyright 1989 Pergamon Press plc).

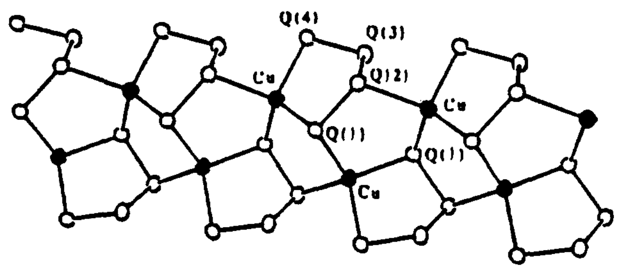


Figure 72. α-$KCuSe_4$ (reprinted from ref 50; copyright 1990 American Chemical Society).

diamine for the first time (eq 206).[232] The structure

$$K_2Se_4 + 2Se + Ag \xrightarrow{\text{en/350 °C/3500 psi}} K_2Ag_{12}Se_7 \tag{206}$$

contains a series of Ag(I) ions bridged by monoselenides forming a column of stacked 18-membered rings (Figure 75). Passing down the middle of the rings is a disordered chain of selenide ions. The stacked rings form columns which bridge to one another, creating channels containing the K^+ ions. The corresponding sulfide prepared from the equivalent reaction has a completely different structure.[233] This synthetic method is new but shows enormous promise for the synthesis of kinetically stabilized solids.

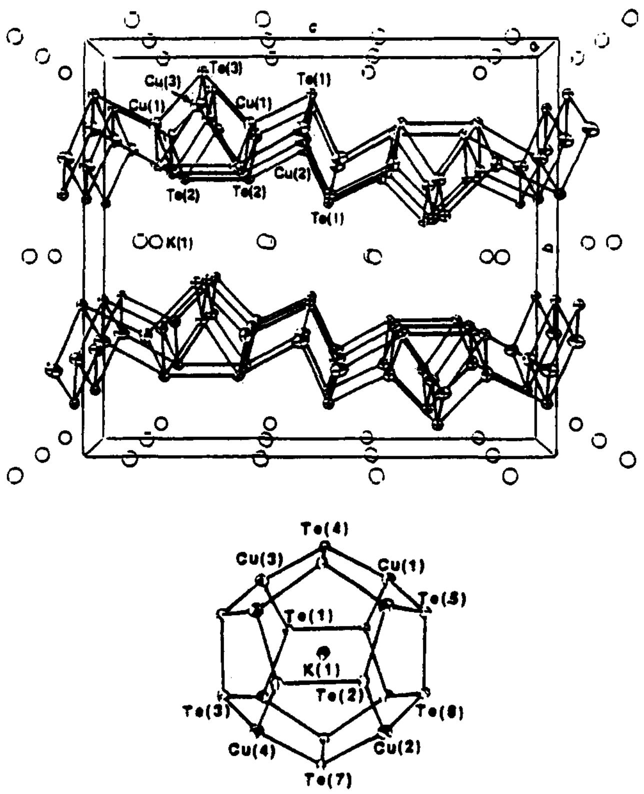


Figure 73. $K_2Cu_5Te_5$ (reprinted from ref 228; copyright 1991 VCH Verlagsgesellschaft mbH), and $K_4Cu_8Te_{11}$ (reprinted from ref 229; copyright 1991 American Chemical Society).

In contrast to the situation with silver, the solution chemistry of gold polyselenides does not show a marked countercation dependency. It does however show a distinct dependence on the nature of the polyselenide starting material (eqs 207,[234] 208,[234] and 209[235]). In the

$$AuCN + Se_n^{2-} \rightarrow [Au_2(Se_2)(Se_3)]^{2-} \quad n = 2, 3 \tag{207}$$

$$AuCN + Se_4^{2-} \rightarrow [Au_2(Se_2)(Se_4)]^{2-} \tag{208}$$

$$AuCN + Se_5^{2-} \rightarrow [Au_2(Se_2)(Se_4)_2]^{2-} \tag{209}$$

first two cases the gold centers are both Au(I) bridged by several different polyselenides. There is some Au(I)···Au(I) interaction and the bridging selenides are linear, as is often the case with gold complexes (Figure 76). However in the presence of the less reduced (more oxidizing) pentaselenide, the gold centers become oxidized to Au(III). This once again demonstrates the importance of the internal redox chemistry in metal polychalcogenide coordination compounds.

Several ternary gold polyselenides have been isolated via reaction of gold powder with molten polyselenides at 250 °C (eqs 210 and 211).[236] The first compound is

$$2K_2Se + 8Se + Au \rightarrow KAuSe_5 \tag{210}$$

$$1.8K_2Se + 8Se + Au \rightarrow K_3AuSe_{13} \tag{211}$$

a now-familiar infinite chain of Au(I) ions bridged by pentaselenides. However, the second compound contains a very unusual monodentate pentaselenide. Each

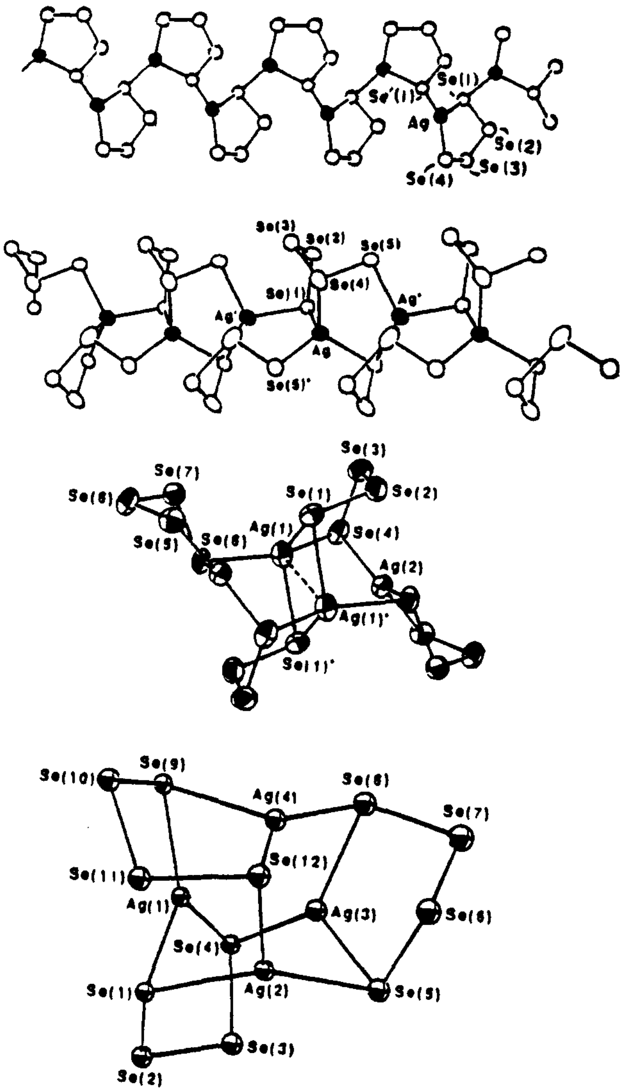


Figure 74. $[(PPh_4)Ag(Se_4)]_n$, $[(MeN_4)Ag(Se_5)]_n$, $[(Et_4N)Ag(Se_4)]_4$, and $(Pr_4N)_2[Ag_4(Se_4)_3]$ (reprinted from ref 231b; copyright 1991 American Chemical Society).

Au(I) is four coordinate and two of the ligands are Se_5^{2-} chains which are coordinated through one terminal selenium atom, while the rest of the chain meanders into the lattice and stops (Figure 77). This mode of coordination is extremely rare. Similarly, if sodium selenides are used under the same conditions, another ternary compound, Na_3AuSe_8, is obtained.[51] This consists of a polymeric chain of square planar Au(III) centers bridged by Se_2^{2-} groups with each metal also ligated by two monodentate Se_3^{2-} fragments each of which also have one end of the chain unbound.

There are several novel gold telluride clusters which have been prepared by reducing gold telluride alloys with potassium metal and extracting them into ethylenediamine or DMF (eqs 212 and 213).[237,238] The first

$$KAuTe + en \rightarrow [Au_2(Te_2)_2]^{2-} \qquad (212)$$

$$K_3AuTe_2 + en \rightarrow [KAu_9Te_7]^{4-} + [K_2Au_4Te_4]^{2-} \qquad (213)$$

of these compounds contains η^2-ditellurides (Figure 78) while the others have gold monotelluride clusters partly held together by potassium cations (Figure 79). In the case of $[KAu_9Te_7]^{4-}$ there is actually a cation encapsulated within the cluster. With $[K_2Au_4Te_4]^{2-}$ the cations serve to link the squares together to form infinite stacked sheets.

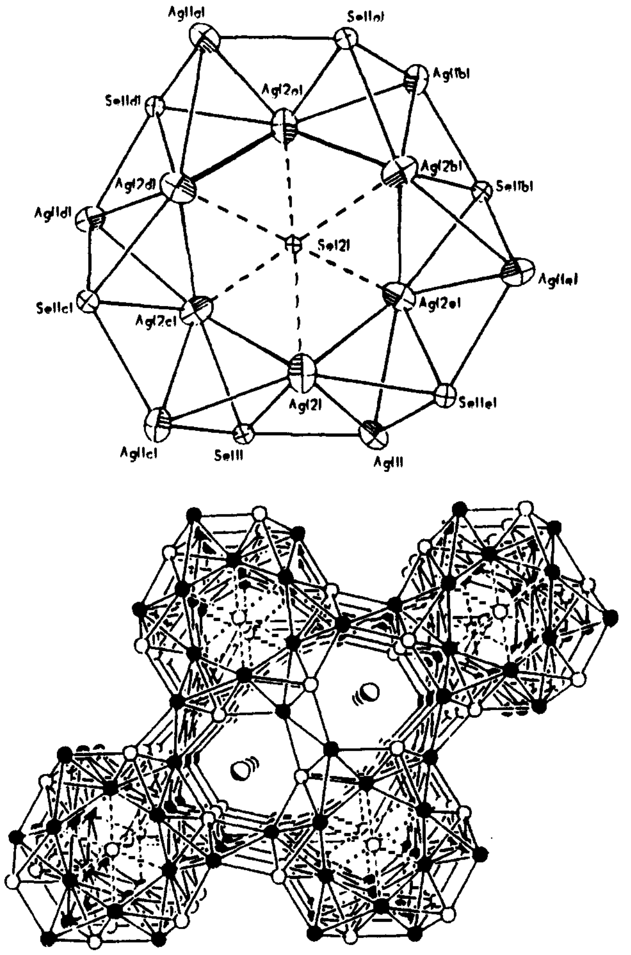


Figure 75. Molecular structure of $K_2Ag_{12}Se_7$ and its packing diagram.

Fenske and his co-workers have also been able to isolate several spectacular copper phosphine selenides using the usual strategy of reacting CuCl with $(TMS)_2Se$ in the presence of various phosphines (eqs 214 and 215).[239] These enormous clusters contain irregular

$$CuCl + Se(TMS)_2 + i\text{-}Pr_3P \rightarrow Cu_{30}Se_{15}(i\text{-}Pr_3P)_{12} + Cu_{29}Se_{15}(i\text{-}Pr_3P)_{12} \qquad (214)$$

$$CuCl + Se(TMS)_2 + t\text{-}Bu_3P \rightarrow Cu_{36}Se_{18}(t\text{-}Bu_3P)_{12} \qquad (215)$$

geometries with a continuum of Cu–Cu and Cu–Se bonds (Figure 80). However, they are dwarfed by the compound which forms when a smaller phosphine is used (eq 216).[240] This enormous cluster is probably

$$CuCl + Se(TMS)_2 + Et_3P \rightarrow Cu_{70}Se_{35}(Et_3P)_{22} \qquad (216)$$

the largest discrete metal chalcogenide molecule characterized to date (Figure 81). Its scale begins to approach that of nanoscale particles. Thus it may be used to study the onset of properties attributed to the quantum confinement effect. However, no reaction chemistry or physical measurements on these important molecules have been reported yet.

3.9. Group 12

There have been several interesting group 12 polyselenides and tellurides prepared, and in fact, their

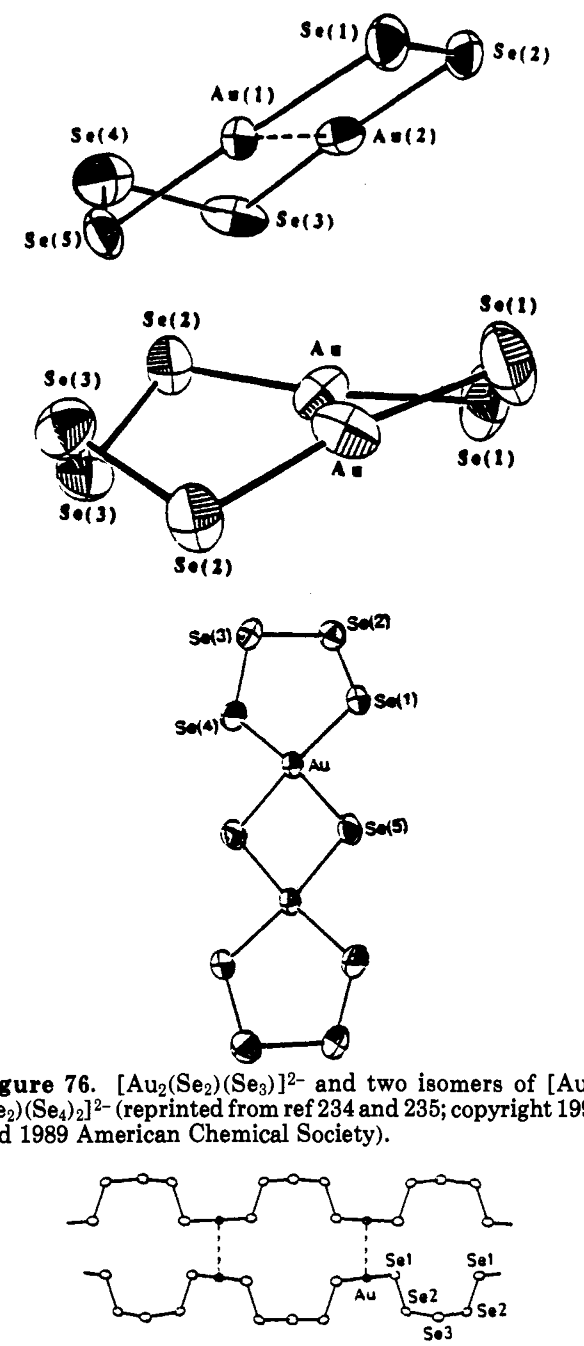


Figure 76. $[Au_2(Se_2)(Se_3)]^{2-}$ and two isomers of $[Au_2(Se_2)(Se_4)_2]^{2-}$ (reprinted from ref 234 and 235; copyright 1991 and 1989 American Chemical Society).

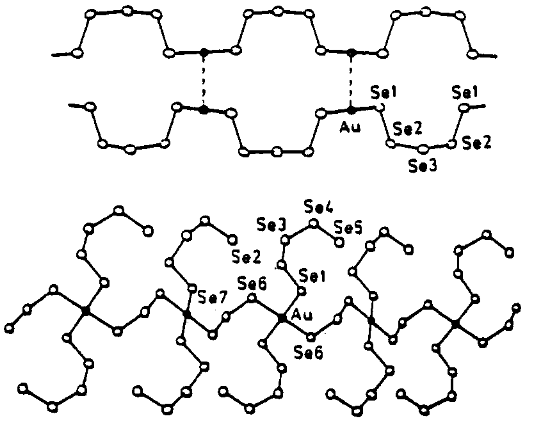


Figure 77. $KAuSe_5$ and K_3AuSe_{13} (reprinted from ref 236; copyright 1990 VCH Verlagsgesellschaft mbH).

number and novelty approaches or even exceeds those of the metal sulfides. Most of the known group 12 polyselenides and sulfides are binary anions. There have been relatively few complexes reported which contain other ligands. The simplest compounds are $[M(Se_4)_2]^{2-}$ (M = Zn, Cd, Hg), with the three members of the series prepared by three different groups. The complexes are formed by reaction of a metal salt with anionic polyselenides of various chain lengths, and can be isolated with several different counterions (eq

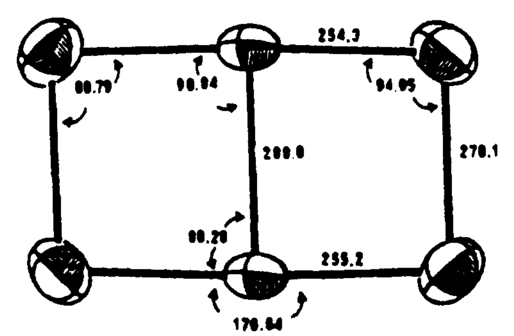


Figure 78. $[Au_2(Te_2)_2]^{2-}$ (reprinted from ref 238; copyright 1985 Elsevier Sequoia).

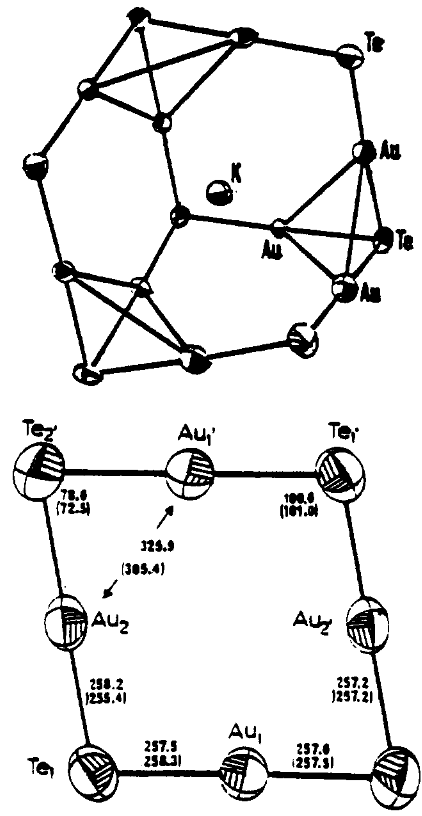


Figure 79. $[KAu_9Te_7]^{4-}$ and $[K_2Au_4Te_4]^{2-}$ (reprinted from ref 237; copyright 1985 VCH Verlagsgesellschaft mbH).

217).[128,207,241] All three compounds contain a divalent

$$MX_2 + Se_n{}^{2-} \rightarrow [M(Se_4)_2]^{2-} \quad M = Zn, Cd, Hg$$
$$X = Cl^-, (S_2COEt)^-, (CH_3CO_2)^- \qquad (217)$$

metal center tetrahedrally coordinated by the chelating tetraselenides. No further reaction chemistry has been reported for these complexes.

However, a different series of compounds can be isolated if crown ether complexes of larger alkali metal cations are used instead of quaternary organic counterions. If the reaction described above is performed with $Zn(OAc)_2$ and isolated as the 18-crown-6 complex of Rb^+, a new molecule, $[Rb(18\text{-crown-}6)]_2[Zn(Se_4)(Se_6)]$, is formed. This cluster again contains a tetrahedrally coordinated Zn(II), but is chelated by a tetraselenide and a hexaselenide. The tetraselenide is stabilized by interaction with the exposed side of the complexed Rb^+ cations.[242] If a similar reaction is done with a mercury salt and Cs^+, an entirely different multinuclear cluster is isolated (eq 218).[243] This

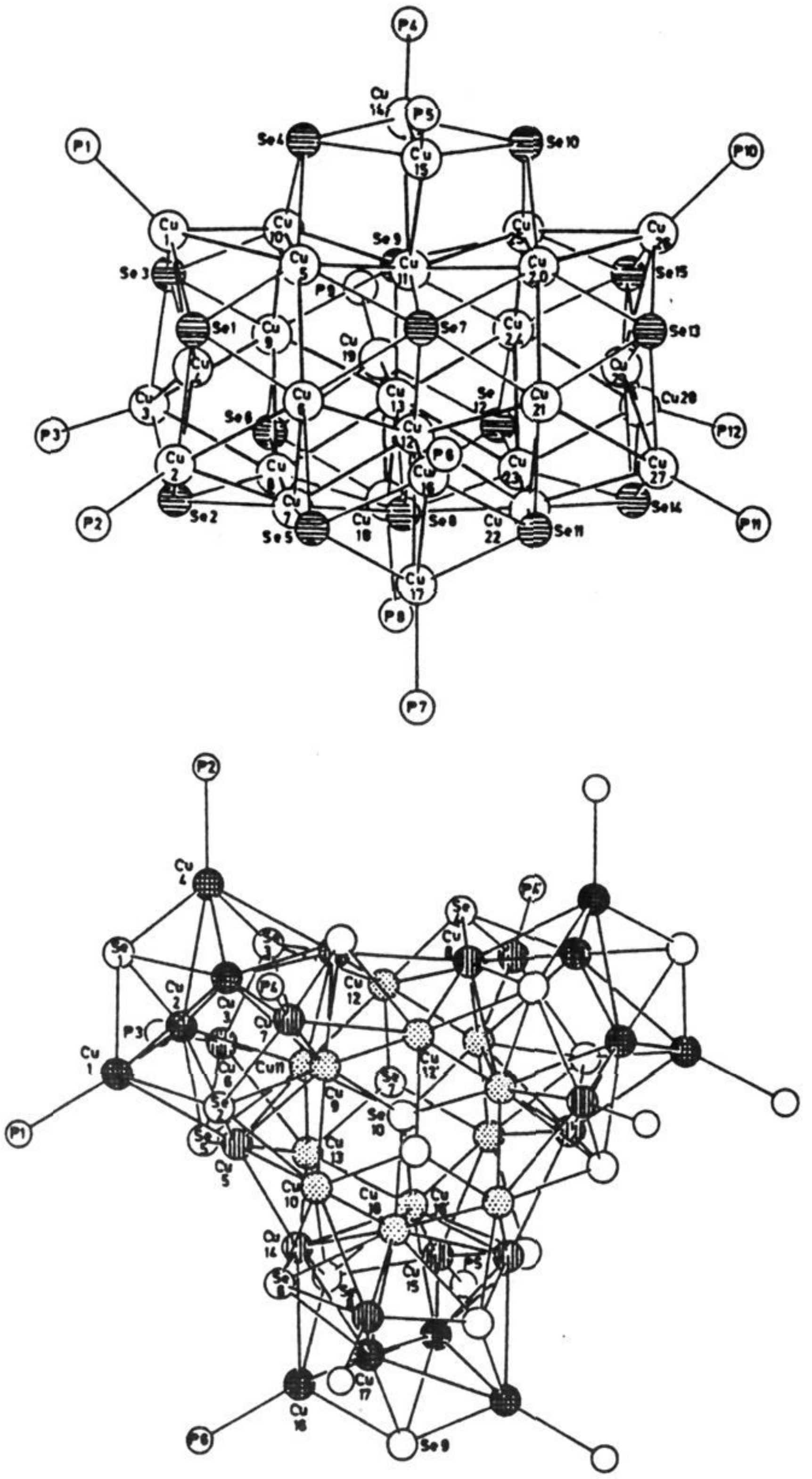


Figure 80. $[Cu_{29}Se_{15}(i\text{-}Pr_3P)_{12}]$ and $[Cu_{36}Se_{18}(t\text{-}Bu_3P)_{12}]$ (reprinted from ref 239; copyright 1990 VCH Verlagsgesellschaft mbH).

$$3Li_2Se_5 + 2CsBr + 2Hg(OAc)_2 + 2(18\text{-crown-6}) \rightarrow [Cs(18\text{-crown-6})]_2[Hg_2(Se_4)_3] \quad (218)$$

compound also contains tetrahedrally coordinated Hg(II) metal centers and the ubiquitous Se_4^{2-} chelating groups, but it is certainly not a very common structural type (Figure 82). Crown ether complexes of alkali metal countercations are not as common as quaternary phosphonium and ammonium salts, but in light of these recent results, perhaps they should be investigated more fully.

A zinc compound with a chelated tetraselenide and two terminal imidazole ligands has been characterized by Rauchfuss and co-workers.

$$Zn + Se \xrightarrow{N\text{-MeIm}/100\ °C} (N\text{-MeIm})_2Zn(Se_4)$$

It is prepared by the novel method of dissolving zinc metal and elemental selenium in the strong donor solvent *N*-methylimidazole. This technique has been recently developed and shows an enormous amount of promise.[244]

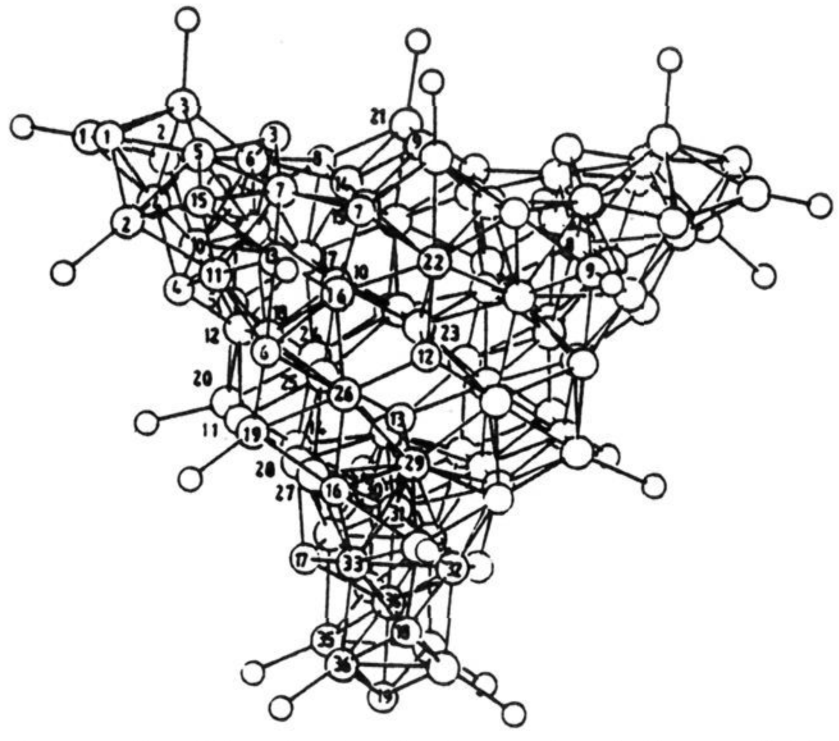


Figure 81. $[Cu_{70}Se_{35}(Et_3P)_{22}]$ (reprinted from ref 240; copyright 1990 VCH Verlagsgesellschaft mbH).

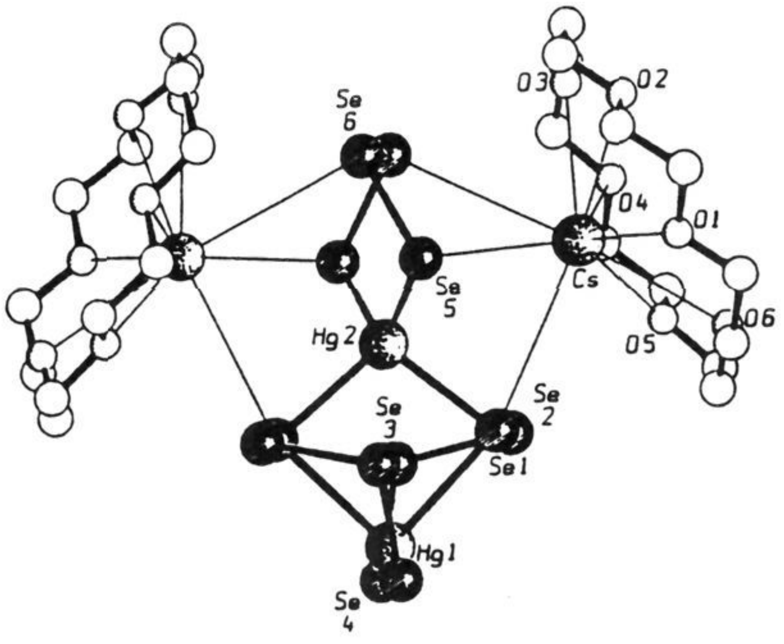


Figure 82. $[Cs(18\text{-crown-6})]_2[Hg_2(Se_4)_3]$ (reprinted from ref 241; copyright 1989 Zeitschrift fur Naturforschung).

Kanatzidis and co-workers have found that reaction of shorter chain selenide anions with mercury salts results in the formation of a more complex series of clusters (eqs 219 and 220).[245] Both complexes have been

$$2HgCl_2 + 3Na_2Se_2 \rightarrow [Hg_7(\mu_2\text{-}Se_2)(\mu_2\text{-}Se)_8]^{4-} \quad (219)$$

$$HgCl_2 + Na_2Se \rightarrow [Hg_7(Se)_9]_n^{4n-} \quad (220)$$

isolated as their Et_4N^+ salts and contain Hg(II) in two-, three-, or four-coordination environments (Figure 83). The first compound contains four distorted tetrahedral Hg(II) and three linear Hg(II) centers. The clusters are joined by weak intercluster Hg–Se interactions. The second product has an infinite layered structure, with two- and three-coordinate Hg(II) centers linked by bridging selenides to form a planar network with large holes in it. There are also several solid-state mercury selenide phases which can be prepared by the reaction of HgSe with polyselenides under molten salt conditions (eq 221).[246] The product of eq 221 has an infinite chain

$$HgSe + K_2Se_3 \xrightarrow{250\ °C} K_2Hg_3Se_4 \quad (221)$$

of selenides bridging tetrahedral Hg(II) centers, (Figure

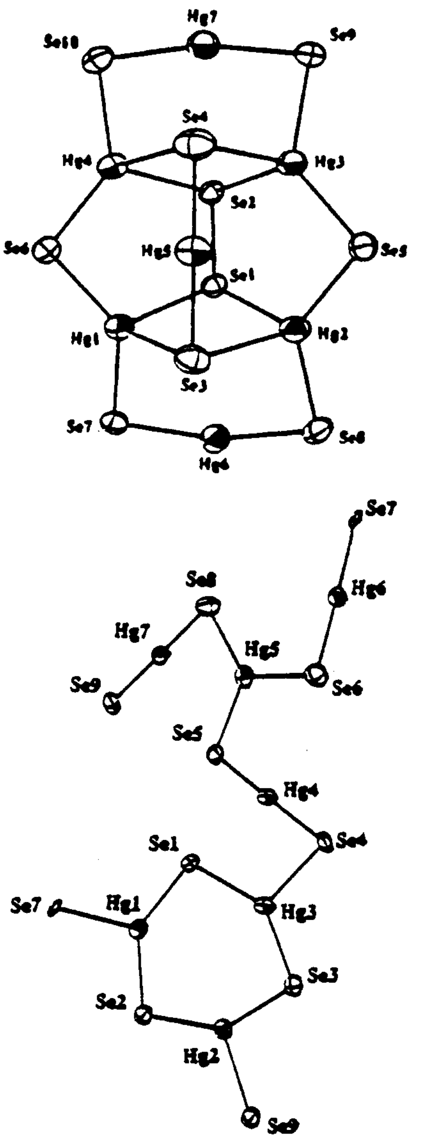


Figure 83. $[Hg_7(\mu_2\text{-}Se_2)(\mu_2\text{-}Se)_8]^{4-}$ and $[Hg_7(Se_9)]_n^{4n-}$ (reprinted from ref 244; copyright 1991 American Chemical Society).

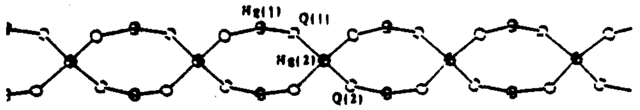


Figure 84. Structure of $[Hg_3Se_4]_n^{2n-}$ (reprinted from ref 245; copyright 1990 American Chemical Society).

84). There is evidence that there are a number of other complex lattices which can be made this way.

Mercury tellurides have been prepared by extracting a reduced mercury telluride into ethylenediamine (eq 222). The first was reported in 1981 and is a simple

$$KHgTe + 2,2,2\text{-crypt} \xrightarrow{en} [2,2,2\text{-crypt-K}]_2[HgTe_2] \qquad (222)$$

linear molecule.[247] Several other fascinating clusters were subsequently isolated by Haushalter using a similar methodology but with different counterion and solvent combinations (eqs 223 and 224).[248] The product of eq 223 is a discrete cluster with a shape similar to that of $[Hg_7Se_{10}]^{2-}$. The second complex is an infinite chain with three-coordinate Hg(II) bridged by tellurides and ditelluride fragments (Figure 85). To our knowledge there have been very few zinc or cadmium tellurides reported, though there seems to be no reason for this absence.

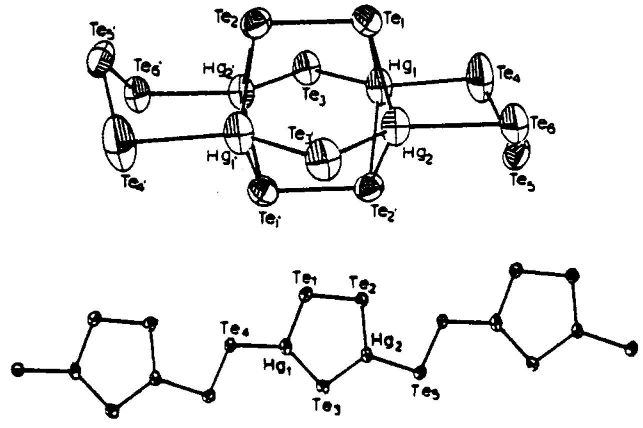


Figure 85. $[Hg_4Te_{12}]^{4-}$ and $[Hg_2Te_5]^{2-}$ (reprinted from ref 247; copyright 1985 VCH Verlagsgesellschaft mbH).

$$K_2Hg_2Te_3 + en \xrightarrow{n\text{-}Bu_4NBr/MeOH} [n\text{-}Bu_4N]_4[Hg_4Te_{12}] \qquad (223)$$

$$K_2Hg_2Te_3 + en \xrightarrow{Ph_4PBr/MeOH} [Ph_4P]_2[Hg_2Te_5] \qquad (224)$$

3.10. f Elements

The lanthanide and actinide coordination chemistry with selenide and telluride ligands is nearly undeveloped, as it also is with sulfides. The obvious reason for this slow growth is that the hard f element centers have a much lower affinity for soft donors such as polychalcogenides. Thus it is difficult to replace hard donors like halides and oxides. Also most chalcogenide ligands are most soluble in polar oxygenated solvents such as DMF. Thus the solvents often have a higher affinity for the metal centers than the erstwhile ligands. In addition, it is very difficult to dry such polar solvents completely and even traces of water can be sufficient to hydrolyze the f element complexes. Nevertheless several compounds have been reported. Phosphine selenides and tellurides will transfer chalcogen atoms to unsaturated lanthanide and actinide complexes to form bridging dimers (eqs 225 and 226).[249,250] The problems of solvent have been neatly circumvented by the reaction of uranium metal with polyselenides in molten potassium polyselenide to generate a discrete cluster in the solid state (eq 227).[50] The molecule is an eight-coordinate U(IV) complex (Figure 86) which is slightly soluble in polar solvents, paving the way for solution reactivity studies. Thus, despite the barriers described above, several new compounds have been reported, demonstrating that there is nothing inherently unstable about f element–chalcogenide bonds. As the

$$(Me_5C_5)_2Yb + E{=}PR_3 \rightarrow [(Me_5C_5)_2Yb]_2(\mu\text{-}E) \quad (E = S, Se, Te) \qquad (225)$$

$$(MeC_5H_4)_3U + E{=}PR_3 \rightarrow [(MeC_5H_4)_3U]_2(\mu\text{-}E) \qquad (226)$$

$$2K_2Se + U + 8Se \xrightarrow{300\,^{\circ}C} K_4[U(\eta^2\text{-}Se_2)_4] \qquad (227)$$

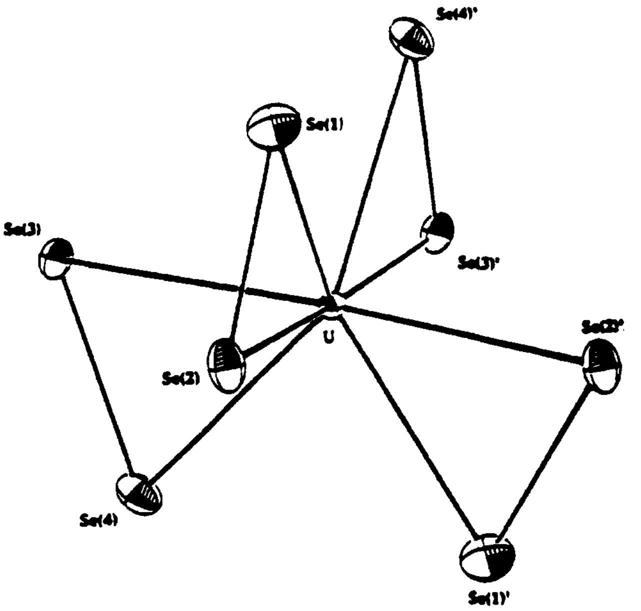


Figure 86. $K_4[U(\eta^2\text{-}Se_2)_4]$ (reprinted from ref 49; copyright 1991 American Chemical Society).

synthetic armamentarium of the chalcogenide chemist continues to grow, new methods will undoubtedly be developed for the preparation of f metal chalcogenide complexes and the area will undergo rapid expansion.

3.11. Main Group Elements

This is a somewhat dangerous region to end what is meant to be a (hopefully) comprehensive review. The lines become blurred between what are considered coordination complexes and what are actually other reagents. Even polychalcogenides themselves can be androgynous. For example Se_{11}^{2-} can be thought of as a polyselenide or a four-coordinate Se(II) chelated by two Se_5^{2-} ligands. Thus the choice of where to terminate the subject treatment becomes somewhat arbitrary.

There are several examples of compounds where a main group center is clearly ligated by polychalcogenide ligands. They are generally prepared by reaction of a metal halide and a polychalcogenide. Indium and tin form compounds that are obviously within this class (eqs 228[251] and 229[252] Figure 87). However, the vast

$$SnCl_4 + Se_5^{2-} \rightarrow [Sn(Se_4)_3]^{2-} \tag{228}$$

$$InCl_3 + Se_5^{2-} \rightarrow [In_2(Se_4)_4(\mu\text{-}Se_5)]^{4-} \tag{229}$$

majority of main group compounds can be more realistically catagorized as mixed polyanions. These compounds have formulas like $Sn_2Te_6^{4-}$, $In_4Se_{10}^{8-}$, $Pb_2Se_3^{2-}$, and so forth. There are a huge number of these which can be prepared by a wide variety of methods, and are generally classically bonded species. They contain bridging monochalcogenides and can be either discrete clusters or infinite polymers. The main group sulfides and selenides have been the subject of a classic review.[253] Since then a large number of new compounds have been made. It is our opinion that these anionic clusters are most fruitfully considered as ligands in their own right rather than as main group complexes of chalcogenides. It is interesting that despite their large numbers and ease of preparation, their reaction chemistry remains shockingly undeveloped. It is anticipated that this situation will change dramatically in the near future given the enormous potential of these mixed main group clusters.[254]

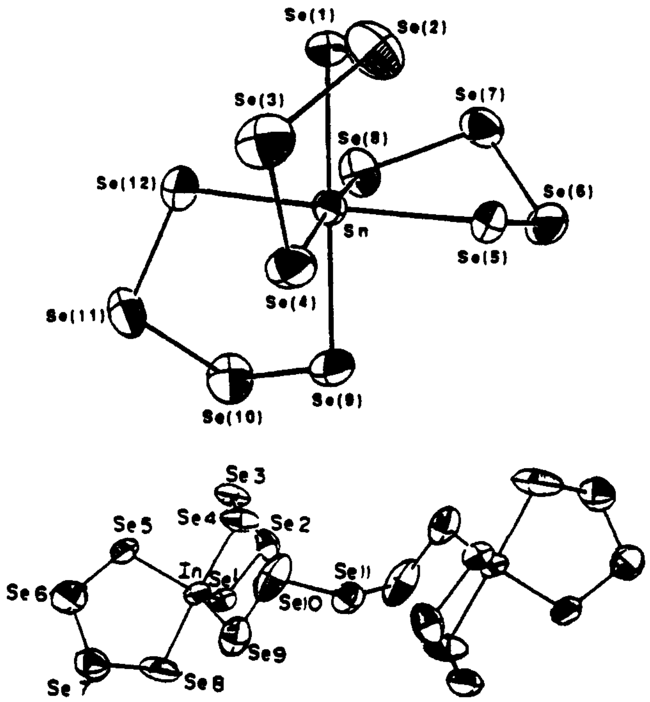


Figure 87. $[Sn(Se_4)_3]^{2-}$ (reprinted from ref 250; copyright 1990 Pergamon Press pch) and $[In_2(Se_4)_4(\mu\text{-}Se_5)]^{4-}$ (reprinted from ref 251; copyright 1989 American Chemical Society).

4. Summary and Future Directions

Even a cursory examination of the main body of the article gives a sense of the state of the metal selenide and telluride field. A large percentage of the references in this article have been published in the last 5 years, verifying that the field is expanding at an enormous rate. Most of the progress has been largely descriptive, whereby researchers combine various chalcogenide sources with simple metal complexes and analyze the products, usually by crystallography. The development of several new classes of reagents, notably soluble Zintl polynuclear anions, trimethylsilyl compounds, organophosphine chalcogenides, and molten alkali metal polychalcogenides, has allowed synthetic exploration to proceed at an ever expanding rate.

Despite the lack of maturity of the field several trends are beginning to suggest themselves. There appears to be nothing inherently unstable about metal chalcogenide bonds in any sector of the periodic table. Most of the elements investigated have yielded stable and interesting selenide and telluride complexes of various types. The most obvious gaps that do exist seem only to be a result of a lack of effort directed toward those areas. Also there seems to be no inherent instability of metal complexes containing polyselenide or -telluride ligands. Extremely stable compounds ligating di-, tri-, and tetrachalcogenides are being reported at an accelerating pace. In fact mild pyrolytic conditions are often employed to enhance reactivity and crystallization. The complexes seem to show no tendency to extrude elemental selenium or tellurium and form polymeric metal monochalcogenides. This is in marked contrast to organopolyselenides and -tellurides. The metal complexes generally do not seem to show much photochemical sensitivity either, again in contrast to organic compounds.

There are several obvious differences between the complexes of selenium and tellurium and their closest relatives, and metal sulfides. The coordinated chains of the heavier elements are somewhat shorter than those of polysulfides. Only a few coordinated pentaselenides are known, and tetratellurides are the longest coordinated tellurium chains known, unlike the polysulfides where coordinated chains of nine sulfur atoms have been reported. There are some metal selenide and telluride complexes which are direct analogs to known sulfur complexes. However, the heavier chalcogenides more often form complexes which have considerably different structural and electronic properties. This is especially so for complexes of tellurium, where its large size and diffuse orbitals often leads to complexes which are often extremely unusual. Indeed these attributes make it unlikely that sulfur analogs to compounds such as $NbTe_{10}^{3-}$ will ever be isolated.

What are the future directions of this field? It appears that the synthetic explorations will continue unabated for some time. In fact the richness of this work has made it difficult to successfully realize a termination point for this article. Many of the new synthetic techniques have simply not been applied to all the metal systems. Interestingly, there do not appear to be many "sinks" in these systems. Therefore reaction of soluble polyanions with a particular metal salt often does not lead to the same products as does reaction of trimethylsilyl reagents or organophosphine reagents with the same metal starting material. The systematic variation of counterions and solvents will also continue to lead to new products, but Goddess Fortuna can sometimes cast a baleful eye in this direction. The approach can be frustrated by the fact that simple salts of the starting materials such as Se_5^{2-} and Te_4^{2-} often crystallize far better than the desired metal complexes. A much higher success rate will be obtained as more new reagents and conditions are developed. For example, mixed polychalcogenides are only now beginning to emerge. The difference in size and electronegativity from sulfur to tellurium will lead to distinctive coordination chemistry of mixed ligands. Use of mixed 15/16 clusters as starting material further accentuates this difference and leads to even more novel coordination chemistry.

The reactivity of the new metal complexes is just beginning to be probed. The use of neutral metal carbonyl complexes in cluster building reactions has been quite rewarding. Also conversion of metal complexes to dense binary solids has begun to bear fruit. However, use of the new complexes in organic transformations and catalytic processes has been essentially ignored. An obvious use for these new complexes is their application in new materials with novel electronic, magnetic and optical properties. However, an unfortunate situation emerges here. Most of the compounds recently characterized are molecular species which can be readily crystallized by using large organic counterions, organophosphines as co-ligands, and other related techniques. However, to obtain bulk properties like those described above, these large carbon rich counterions must be eliminated. This does indeed lead to extended solids, but they are often difficult to characterize and control chemically. Therefore new synthetic strategies must be developed to lead to pure, characterizable (i.e. crystalline) bulk solids which are subject to chemical control. This desire has spawned the use of several nontraditional techniques aimed at dissolving the real and conceptual boundaries between molecules and bulk solids. These include synthesis of very large clusters (using trimethylsilyl reagents, for example), use of molten polychalcogenides as solvents and reagents, and synthesis in superheated solvents. It is techniques like these which will be responsible for the continued rapid expansion of this exciting area of coordination chemistry.

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(254) For an example of the kind of chemistry which is anticipated for these compounds, see ref 158.