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COORDINATION CHEMISTRY OF POLYCHALCOGEN ANIONS AND TRANSITION METAL CARBONYLS

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SUMMARY

This article focuses on the chemistry of heavy polychalcogenides as ligands to transition metal centers. After reviewing some of the general synthetic strategies leading to metal polyselenides and polytellurides, work from the author's labs is discussed, which involves the coordination of polychalcogenide anions to metal carbonyls. It has been found that coordination of polychalcogenide anions to metal carbonyls often results in oxidation of the metal center, with loss of some or all of the carbonyl ligands. This oxidative decarbonylation reaction provides a convenient entry to a wide variety of new and existing metal chalcogenide complexes. The scope and potential of this unusual reaction is discussed.

INTRODUCTION

The coordination chemistry of molecular transition metal polysulfides is rich and versatile. Due to the tendency of sulfur to adopt a wide variety of coordination environments, an enormous number of novel structures has been isolated and characterized (refs. 1-4). In addition, metal sulfides have applications in catalysis (refs. 5-7), as well as enzymic processes (ref. 8,9). As a result the chemistry of metal sulfides has received a large amount of attention.

In contrast, the coordination chemistry of selenides and tellurides has traditionally been almost ignored. However, there has recently been a tremendous upsurge in the study of metal selenides and tellurides (refs. 10-15) One reason for this increased interest is that the fallacy that the chemistry

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of the heavier chalcogenides is similar to metal sulfides, has been amply discredited by a variety of recent results (See refs 16-19 for example). Another is that molecular metal chalcogenides have proven to be useful precursors to novel materials (refs. 20-22).

One historical limitation to this area has been development of synthetic entries to the chemistry of metal selenides and tellurides. The most common traditional method of synthesizing molecular metal sulfides is to either react metal oxyanions directly with H_2S (eq. 1), or to prepare an aqueous polysulfide solution by combining H_2S and elemental sulfur in aqueous base and adding this to metal salts (eq. 2).

$MoO_4^{2-} + H_2S \dashrightarrow MoS_4^{2-} + H_2O$ (ref.23) (1)

$S_x^{2-} + AgNO_3 \dashrightarrow Ag_2S_{20}^{2-}$ (ref. 24) (2)

The driving force for the first method is the fact that water is formed, and for the second it is the nucleophilicity of the polysulfide toward the metal halide. Once a particular metal sulfide is isolated in reasonable yield, it can be used as a starting material and converted to a variety of derivatives. This route is particularly well exploited for the molybdenum sulfides, using MoS_4^{2-} as a precursor to an enormous number of compounds (ref. 23,25).

These routes are not suitable for the preparation of heavier metal chalcogenides due to the stench, toxicity and cost of H_2Se and the complete instability of H_2Te. Though both of these reagents have been used to prepare metal chalcogenides (ref. 26,27), they are far from the ideal starting materials.

Recently however, several methods have been developed to improve access to complexes of the heavier chalcogenides. The first successful method involved preparation of ternary Zintl type phases of the type $A_xM_yE_z$, where A in an alkali metal and M is a d- or p-block metal and E is a chalcogen (ref. 28). These either form crystalline phases directly from the molten state (ref. 29), or can be extracted with a basic amine solvent in the presence of 2,2,2-crypt. (refs. 30-32). For example see equation 3.

$$K_2Hg_2Te_3 + en \text{ ------> } Hg_4Te_{12}^{4-} \quad (3)$$

en = ethylenediamine

Another development has been the introduction of bis silyl chalcogenides such $R_3Si\text{-}E\text{-}SiR_3$ (where E = S, Se, Te and R = alkyl or aryl) (ref. 13). These compounds can be easily made (ref. 33), and are stable analogs of the parent hydrides. They have the advantage that varying R can change the properties and reactivity of the reagent. They react with metal halides and oxyanions by exploiting the high oxophilicity and halophilicity of silicon.

$$VO_3^- + R_3Si\text{-}Se\text{-}SiR_3 \text{ ---> } V_2Se_{13}^{2-} \quad \text{(ref. 18)} \quad (4)$$

$$Nb(OEt)5 + R_3Si\text{-}S\text{-}SiR_3 \text{ ----> } Nb_6S_{17}^{4-} \quad \text{(ref. 34)} \quad (5)$$

$$NiCl_2(PPh_3)_2 + R_3Si\text{-}Se\text{-}SiR_3 \text{ -----> } [Ni_{34}Se_{22}(PPh_3)_{10}] \quad (6)$$

(ref. 35)

These reagents have led to several stunning compounds as shown in eqs. 4-6, and will see much greater development in coming years.

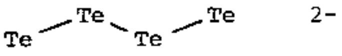
The reagents which have received the most attention are the alkali metal polychalcogenides. These have the general formula A_2E_y (where A is an alkali metal, E = S, Se, Te, and y = 1-6) (ref. 36), and can be easily prepared by several methods. The most common techniques involve melting the elements together in a quartz tube, or by dissolving the alkali metal in liquid NH_3, reducing the chalacogen, and removing the ammonia.

$$2Na + 3Se \xrightarrow{250°C} Na_2Se_3 \quad (7)$$

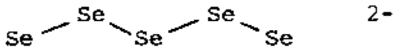
$$2K + 4Te \xrightarrow{NH_3} K_2Te_4 \quad (8)$$

Similar products are obtained in either case, and the resulting powders are reasonably stable for long periods, if protected from air, and are versatile reagents for further chemistry.

These polychalcogen anions form readily with most of the alkali metals, and their nuclearity is determined simply by the ratio of the starting elements. The alkali metal cations can also be readily metathesized with large organic counterions, such as quaternary phosphonium or ammonium ions, forming salts like $[(C_6H_5)_4P]_2[Te_4]$ and $[(C_4H_9)_4N]_2[Se_5]$ (refs. 37,38). The organic salts are often highly crystalline products which can be easily characterized structurally. Most of the anions have similar structures, which consist of bent chains of the chalcogen having little or no interaction with the countercation.



Te_4^{2-}



Se_5^{2-}

However, the tellurides can display some very unusual structural properties in the solid state (ref. 39)

These salts are quite soluble in water or amines, but of greater importance to us, are also soluble in polar organic solvents such as DMF (ref. 38). However, the nature of the polychalcogenide solutions is not well understood. They appear to be complex equilibria of varying nuclearity (refs. 40,41). There are some examples where the nature of the products is affected by the composition of starting material. However, in many cases, the composition of a final crystalline product is determined by the reaction conditions and the counterion present, and the nuclearity of the starting material has no obvious effect. In any event, the nature of neither reactants nor products in solution has been well investigated.

The polychalcogenide anions are most generally reacted with metal halides in polar solvents like DMF. This strategy is directly analogous to the synthesis of polysulfides, but the products are usually quite different. Some examples are listed below.

$$NbCl_5 + Te_x^{2-} \text{ ----> } NbTe_{10}^{3-} \quad \text{(ref. 16)} \qquad (9)$$

$$CrCl_3 + Te_x^{2-} \text{ ----> } Cr_3Te_{24}^{3-} \quad \text{(ref. 17)} \qquad (10)$$

$MnCl_2 + Se_x^{2-} \text{ -----> } Mn(Se_4)_2^{2-}$ (ref. 42) (11)

$AgNO_3 + Se_x^{2-} \text{ -----> } [AgSe_4]_n^{n-}$ (ref. 43) (12)

These reactions are driven by the nucleophilicity of the polychalcogen anion. Most often the resulting product is an anion and large organic counterions are used to isolate crystalline products. These are best characterized by X-ray diffraction.

We have developed a useful variation of the above theme. Workers in our lab have uncovered an enormously varied coordination chemistry involving soluble polychalcogen anions and simple transition metal carbonyls. This area has been surprisingly neglected even for such classical reagents as polysulfides. We attribute this neglect to the traditional practice of using polysulfides in aqueous solutions, and the complete incompatability of metal carbonyls with that solvent. However, the use of polar organic solvents has allowed for the rapid development of this area.

In this review, we summarize our results to date involving polychalcogenides and metal carbonyls, with particular focus on the oxidative decarbonylation reaction. The review is current, but our work is by no means complete, and many of the results have not been thoroughly explained. Though the review will primarily discuss work from our labs, other workers' results will be mentioned where pertinent.

The paper will be generally divided into reactions involving polysulfides and selenides and reactions of polytellurides. This is because in our hands, the reactions of sulfur and selenium are often related, as opposed to those of tellurium, which does not induce oxidation of low valent metal centers as readily.

REACTION OF POLYSULFIDES AND POLYSELENIDES WITH GROUP SIX CARBONYLS

Our initial entry to this field came when we were attempting to prepare simple substitution complexes involving $M(CO)_6$ and polyselenide anions as shown in eq. 13.

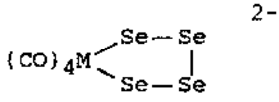
$$M((CO)_6\ (M = Mo,W)\ +\ Se_n2-\ \longrightarrow\ (CO)_4M(Se_4)^{2-} \tag{13}$$

Instead, gentle heating of a mixture of polyselenide and molybdenum or tungsten carbonyl, followed by addition of a large organic counterion, results in isolation of the tetraselenometalates in nearly quantitative yield (eq. 14)(ref. 44). These are not new compounds, having been prepared previously by reaction of H_2Se with the tetraoxometalates (ref. 23). However, our method is simpler and cleaner, and represents a much more convenient entry to these compounds.

$$M(CO)_6\ +\ Se_n^{2-}\ \longrightarrow\ MSe_4^{2-} \tag{14}$$
$$M = Mo,\ W$$

Even though the tetratellurometalates are known compounds, the synthetic reaction is quite unusual. It involves a six electron oxidation of the metal center by a polyselenide dianion, which is an unlikely oxidant at best. Formally the polyselenide oxidizes the metal center, with formation of Se^{2-} as the depository for the electrons.

Though we have been hitherto unsuccessful in isolating any other species in this reaction, we have spectroscopic evidence for an intermediate (ref. 45). An IR spectrum of the carbonyl region shortly after addition of the polyselenide is almost superimposable with that of the well characterized $[(CO)_4M(Te_4)]^{2-}$ (vida infra) (ref. 46). This suggests very stongly that a key intermediate has the following structure.



Formation of this molecule in solution is presumably followed by transfer of three pairs of electrons from the metal center. This reduces the three Se-Se linkages, resulting in transfer of the Se^{2-} ions to the metal center and loss of the CO groups. This mechanism is highly speculative, but other experiments hint that the presence of E-E groups are crucial to the oxidative decarbonylation. Indeed, it would be hard to imagine another destination for the electrons.

We were readily able to show that the oxidative decarbonylation reaction could be extended to include polysulfides, as in eq 15.

$$M(CO)_6 \quad + \quad S_x^{2-} \quad \text{----->} \quad MS_4^{2-} \qquad (15)$$
$$M \; = \; \text{Mo, W}$$

As with the polyselenides, the reaction was performed in DMF with gentle heating (90° C) . However, thermolysis seems only to serve to speed up the reaction (30 min.), since prolonged stirring at room temperature (1 week) leads to the same products.

Although this type of reaction has not been previously reported for any other metal polychacogenides, it is well known that internal electron transfer bewteen metal and ligand is often a dominant reaction of metal chalcogen clusters (ref. 4). It is also known that these reactions often take place in a counterintuitive fashion. Indeed, this propensity for unusual electron transfer is believed to be the basis for much of the activity of sulfide catalysts and molybdenum sulfur electron transfer enzymes. The large degree of electron transfer described by us had not been previously encountered only because polychalcogenides have traditionally been coordinated to higher valent metal centers, such as Mo(IV) and Fe(III) (refs. 1,2).

It was of particular interest to investigate the reaction of $Cr(CO)_6$ with polychalcogenides, since molecules like CrS_4^{2-} have not been reported, due to the high oxidizing power of Cr(VI). Accordingly, the reaction of chromium carbonyl with polysulfides goes by an an entirely different pathway (ref. 45). The novel trisdithiocarbonate can be isolated in good yield.

$$Cr(CO)_6 \; + \; S_x^{2-} \quad \text{----->} \quad [Cr(S_2CO)_3]^{3-} \qquad (16)$$

In this reaction, solution IR data reveals that preliminary coordination of polysulfide to the metal center occurs as with the heavier metals. However, oxidation of the metal center does not proceed beyond the 3+ state, since Cr(VI) requires very electronegative ligands for stability. In this case, three coordinated carbon monoxide ligands are oxidized by the polysulfides to form dithiocarbonate ligands which are stabilized by coordination to the Cr(III) center. The coordination environment is a severely distorted octahedron (Fig 1).

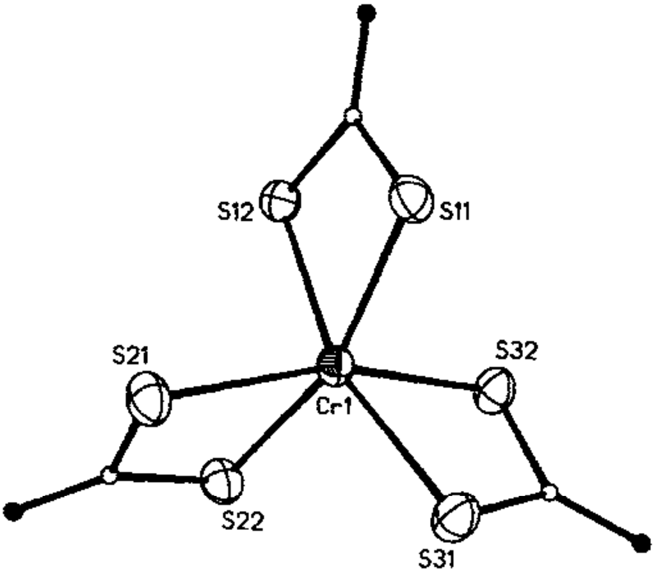
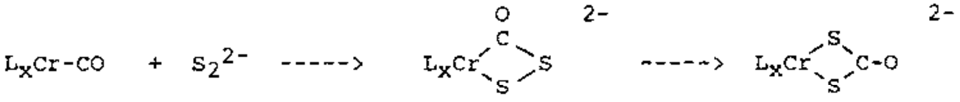


Figure 1. View of chromium trisdithiocarbonate $[Cr(S_2CO)_3]^{3-}$ showing the distorted octahedral coordination environment

The mechanism of this reaction is not known, but could involve the formation of a four membered ring followed by rearrangement.



(17)

This pathway is analogous to that proposed for the oxidation of coordinated carbonyls by O_2 to form carbonate (ref. 47).

Transition metal dithiocarbonates are somewhat unusual species. Alkali metal dithiocarbonates are unstable with respect to redistribution to carbonate and trithiocarbonate, so simple starting materials are not usually available for exploration of their coordination chemistry. However, some work has been done on the chemistry of coordinated dithiocarbonates, and most reactions appear to involve decomposition of the ligand by CO extrusion with formation of a metal disulfide (ref. 48). We are currently exploring those possibilites with this compound.

Reaction of $Cr(CO)_6$ with polyselenides seems to result in complete oxidative decarbonylation and formation of multinuclear polyselenides. However, we have been unable to purify or crystallize any of these species, nor have we been able to see any spectroscopic evidence for diselenocarbonate formation to date. Work on these complex systems is being carried out by our group.

REACTIONS OF POLYSULFIDES AND POLYSELENIDES WITH OTHER METAL CARBONYLS

The oxidative decarbonylation reaction now provides an entry to metal sulfides and selenides starting with metal carbonyls, which are readily available and easily manipulated. Thus we have begun extending the oxidative carbonylation reaction to other organometallic compounds.

The group 7 metals attracted our attention since their molecular chalcogen chemistry is so underdeveloped. There has been some recent work in the area (refs. 49-51), but in general the chalcogenide chemistry of manganese and rhenium is surprisingly neglected compared to that of molybdenum, tungsten and iron. In fact, there has still only been one binary manganese sulfide cluster reported (ref. 52).

We have found that reaction of polyselenides with $Mn_2(CO)_{10}$ generates an interesting series of compounds (ref. 53). Use of excess metal carbonyl with soluble polyselenide results in formation of a manganese dimer which contains two side bonded Se_2 groups. This compound has undergone partial oxidative decarbonylation as it contains formal Mn(I) metal centers with no Mn-Mn bond (Fig. 2). Use of excess polyselenide or addition of red selenium to the above compound leads to buildup of the selenide rings to Se_4 as in eqs. 19 and 20 (Fig.3).

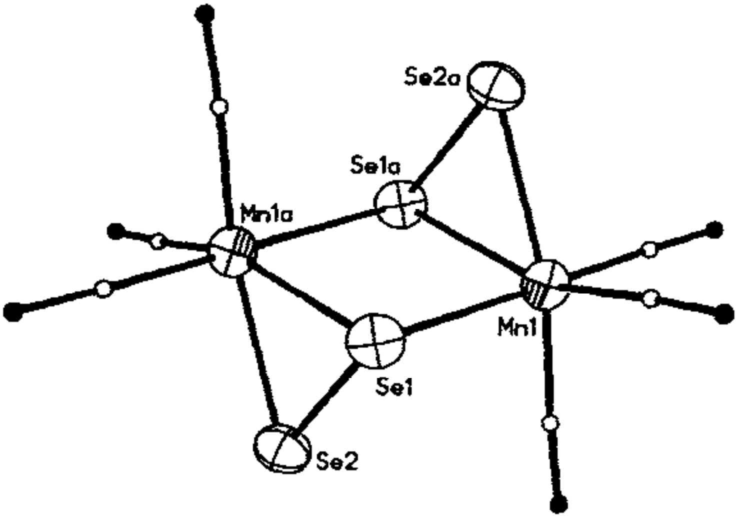


Figure 2. View of $[Mn_2(CO)_6(Se_2)_2]^{2-}$ showing the bridging Se_2^{2-} groups.

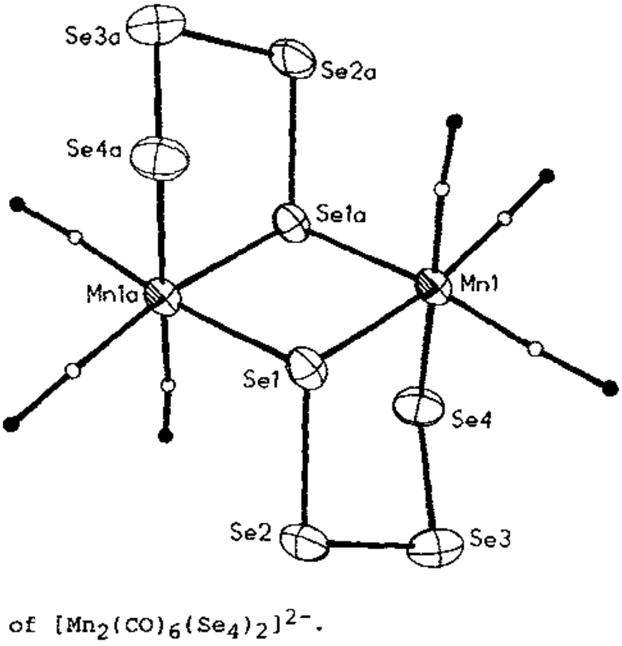


Figure 3. View of $[Mn_2(CO)_6(Se_4)_2]^{2-}$.

$$\text{xs } Mn_2(CO)_{10} + Se_x^{2-} \text{ -----> } [Mn_2(CO)_6(Se_2)_2]^{2-} \quad (18)$$

$$[Mn_2(CO)_6(Se_2)_2]^{2-} + Se_8 \text{ -----> } [Mn_2(CO)_6(Se_4)_2]^{2-} \quad (19)$$

$$Mn_2(CO)_{10} + \text{xs } Se_x^{2-} \text{ -----> } [Mn_2(CO)_6(Se_4)_2]^{2-} \quad (20)$$

Finally, thermolysis of $[Mn_2(CO)_6(Se_4)_2]^{2-}$ leads to loss of all CO ligands and formation of the binary metal selenide anion $[Mn(Se_4)_2]^{2-}$ (Fig 4).

$$[Mn_2(CO)_6(Se_4)_2]^{2-} \xrightarrow{90°} Mn(Se_4)_2^{2-} \quad (21)$$

In this case, the polyselenide rings remain intact, but the manganese center has been oxidized to Mn(II), and all of the Co ligands have been removed.

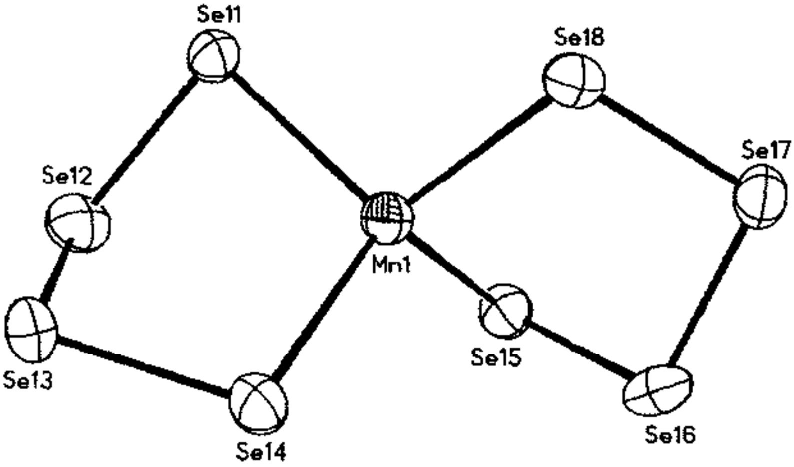


Figure 4. View of $[Mn(Se_4)_2]^{2-}$ showing tetrahedral coordination of the polyselenides around the Mn(II) center.

It is unlikely that polychalcogenides will be able to oxidize this first row element beyond the 2+ oxidation state. This compound is the first molecular binary manganese selenide reported. It has also been recently prepared by the more conventional reactions discussed in the introduction (ref. 42).

We have been able to prepare the rhenium analog of $[Mn_2(CO)_6(Se_4)_2]^{2-}$ using similar chemistry (ref. 54), but have thus far been unsuccessful in attempts to convert it to a binary rhenium selenide, observing only decomposition.

$$Re_2(CO)_{10} + xsSe_x{}^{2-} \text{------>} [Re_2(CO)_6(Se_4)_2]^{2-} \quad (22)$$

$$Mn_2(CO)_{10} + xsS_x{}^{2-} \text{------>} [Mn_2(CO)_6(S_4)_2]^{2-} \quad (23)$$

Similarly, attempts to prepare manganese sulfide analogs lead to ready formation of $[Mn_2(CO)_6(S_4)_2]^{2-}$ (eq. 23), but conversion to binary manganese sulfides has not yet been successful.

Reaction of other simple metal carbonyls with polychalcogenides is under active investigation in other laboratories as well. One group of metal carbonyls which has only received modest attention is the group 8 carbonyls. These have a high affinity for sulfur and probably for the heavier chalcogenides as well. This class is extremely promising as recent results with iron tellurides (refs. 55,56) and ruthenium selenides (ref. 57) suggest (eqs. 24,25).

$$Fe(CO)3(C_4H_6) + Te_x{}^{2-} \text{---->} [Fe_2(CO)_6Te_3]^{2-} \quad (24)$$

$$Ru_3(CO)_{12} + Se_5{}^{2-} \text{----->} [Ru(CO)_2(Se_4)_2]^{2-} \quad (25)$$

In addition to simple metal carbonyls, we are interested in extending the oxidative decarbonylation reaction to other classes of organometallic compounds. The chemistry of cyclopentadienyl sulfides is quite extensive, but it predominantly involves neutral species (ref. 58). We have found that reaction of cyclopentadienyl metal carbonyls with polysulfides and selenides can generate new types of compounds. Both polysulfides and polyselenides react with $[(C_5H_5)_2Mo_2(CO)_6]$ to form side bonded E_2 compounds (refs. 59,60).

$$[(C_5H_5)_2Mo_2(CO)_6] + E_x{}^{2-} \text{----->} [(C_5H_5)Mo(CO)_2(E_2)]^- \quad (26)$$

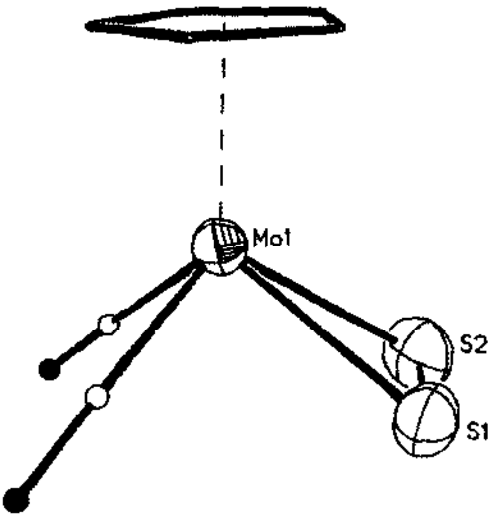


Figure 5. View of [CpMo(CO)$_2$(S$_2$)]$^-$.

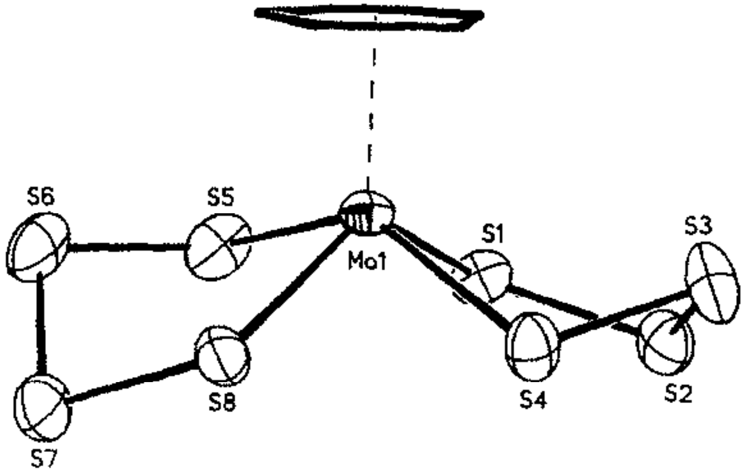
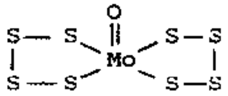


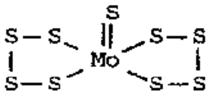
Figure 6. View of [CpMo(S$_4$)$_2$]$^-$ with pseudo square pyramidal coordination environment.

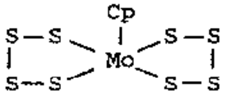
The metal center is formally Mo(II) so the oxidative decarbonylation process has begun by oxidizing the metal metal bond (Fig 5). Reaction of this species with elemental sulfur or selenium leads to the completely decarbonylated product (Fig. 6), with the metal in the 4+ state (refs. 59,61).

$$[(C_5H_5)Mo(CO)_2(E_2)]^- \;+\; E_8 \;\text{------->}\; [(C_5H_5)Mo(E_4)_2]^- \qquad (27)$$

This complex is an interesting addition to the series of molybdenum complexes $Y{=}Mo(E_4)_2$, where Y = O, S (ref. 62), and now Cp^- .







Extension of this reaction to those involving the pentamethyl molybdenum analog is complicated by the relative instability of the starting material. Instead the alkyl monomer $[C_5(CH_3)_5]Mo(CO)_3(CH_3)$, was found to be a suitable substitute, reacting cleanly to form the side bonded disulfide in solution. This converts to another bright red intermediate which can be isolated and characterized (Fig. 7). Surprisingly, it proves to be another dithiocarbonate (eq. 29) (ref. 63).

$$[C_5(CH_3)_5]Mo(CO)_3(CH_3) \;+\; S_x^{2-} \;\text{--->}\; [(C_5(CH_3)_5)Mo(CO)_2(S_2)]^- \qquad (28)$$

$$[(C_5(CH_3)_5)Mo(CO)_2(S_2)]^- \;+\; S_x^{2-} \;\text{--->}\; [(C_5(CH_3)_5)Mo(S_4)(S_2CO)]^- \qquad (29)$$

$$[(C_5(CH_3)_5)Mo(S_4)(S_2CO)]^- \;+\; S_8 \;\text{---->}\; [(C_5(CH_3)_5)Mo(S_4)_2]^- \qquad (30)$$

The dithiocarbonate intermediate reacts with elemental sulfur to generate the permethylated Mo(IV) complex with two of the ubiquitous chelating S_4 chains (eq. 30). The sporadic appearance of the dithiocarbonate ligands is not understood at this time, nor is it known whether these are intermediates in the oxidative decarbonylation reaction, or merely interesting side products.

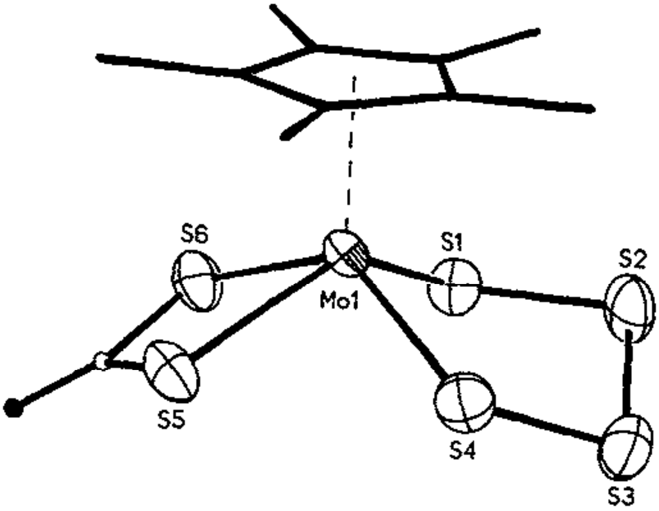


Figure 7. View [$(Me_5C_5)Mo(S_4)(S_2CO)]^-$, showing the novel dithiocarbonate ligand,

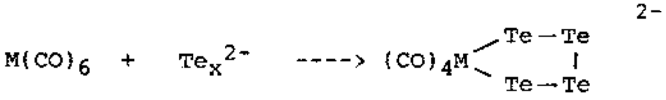
REACTION OF METAL CARBONYLS WITH POLYTELLURIDES

While the reactions of metal carbonyls with polysulfides is sometimes different from that with polyselenides, they generally demonstrate the same kinds of reactivity patterns. However, the reactions with polytellurides are dramatically different from the lighter chalcogenides and hence are treated as a separate topic.

One important reason for the obvious change in reactivity of polytellurides is the increased reducing ability of polytellurides versus the lighter polychalcogenides. There have been few quantitative studies on this subject, but our qualitative observation is that polytellurides can reduce functional groups like metal-metal bonds to form metal carbonyl anions. Thus reactions such as those shown below often occur (ref. 64).

$$Cp_2Mo_2(CO)_6 + Te_x^{2-} \text{ ------> } 2[CpMo(CO)_3]^- + Te \qquad (31)$$

Substitution does occur in several cases, leading to a variety of novel products. With the simple group six hexacarbonyls, an excess of polytellurides leads to simple substitution with formation of a chelated tetratelluride (Fig. 8), which can be isolated in good yield (ref. 46).



$$M(CO)_6 \quad + \quad Te_x{}^{2-} \quad \text{---->} \quad (CO)_4M\begin{array}{l} \diagup Te - Te \\ \qquad\quad\ | \\ \diagdown Te - Te \end{array}{}^{2-} \qquad (32)$$

M = Cr, Mo, W

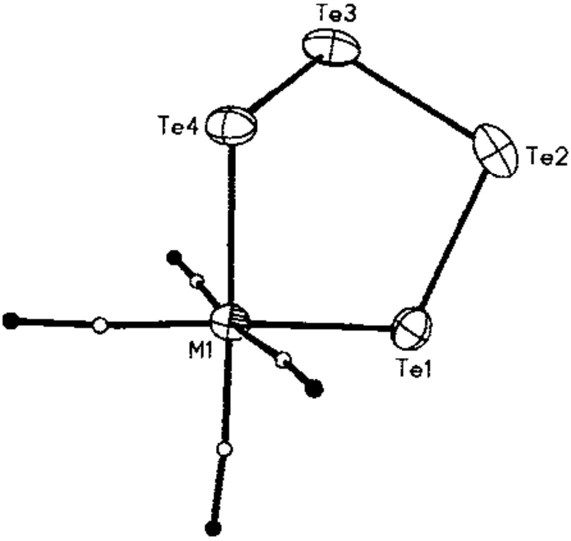


Figure 8. View of $[(CO)_4M(Te_4)]^{2-}$ where M = Cr, Mo, W.

We attempted to convert these to the tetratellurometalates $MTe_4{}^{2-}$, since these have not been previously prepared by any method, to our knowledge. Despite the similarity to the apparent intermediate in the oxidative decarbonylation of lighter polychalcogenides, we have been unable to induce oxidation in this case. Extensive thermolysis or photolysis does not produce any observable oxidative decarbonylation. The reluctance to undergo oxidative decarbonylation could be due to a variety of factors. In particular, the products $MTe_4{}^{2-}$ may be inherently unstable due to the large size of the tellurides or the poor pi overlap with metal orbitals. More likely, the tellurides do not induce oxidation because of the lower electron affinity of tellurium and the

the large size of the tellurides or the poor pi overlap with metal orbitals. More likely, the tellurides do not induce oxidation because of the lower electron affinity of tellurium and the resulting increased reduction potential to Te^{2-}. In any case, $(CO)_4WTe_4{}^{2-}$ was the first metal polytelluride prepared in our labs, and it showed such remarkable stability as to cause discouragement.

However, subsequent careful work with the group hexacarbonyls has shown that changes in reactant stoichiometry lead to dramatic differences in reactivity. This observation has led us to an extraordinarily rich area of chemistry. By simply increasing the ratio of metal carbonyl to polytelluride, a number of new products could be isolated. Furthermore, in this system we note for the first time, a clear influence of the nature of the starting polytelluride on product formation. Previously, the inital nuclearity of the polychalcogenide dianion was irrelevent to product formation. However, in the system, $3M(CO)_6 + K_2Te_x$ (where M = Cr, Mo, W, and x = 1-4), the value of x has a substantial impact on the final products.

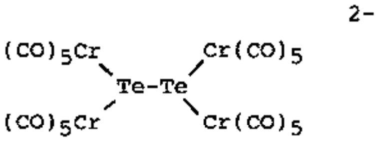
In the case of chromium, lower nuclearity polytellurides, such as K_2Te_2, generates the new dinuclear cluster (ref. 65) in eq. 33.

$$3Cr(CO)_6 + K_2Te_2 \text{ ------> } [Cr_4(CO)_{18}Te_2]^{2-} \qquad (33)$$

This reaction involves some oxidation, as two of the chromium atoms are formally Cr(I) and are bonded to each other (Fig. 9). (The Cr-Cr distance is long at 3.04Å, but this is typical for Cr-Cr singly bonded systems. For example the Cr-Cr distance in the prototype $Cp_2Cr_2(CO)_6$ is 3.28Å (ref. 66).) Presumably a $Te_2{}^{2-}$ group has undergone an oxidative addition across a metal center, causing dimerization. The $Cr(CO)_5$ groups act as Lewis acids, forming adducts with a lone pair on each telluride.

If increased amounts of ditelluride are used, an entirely different reaction occurs.

$3Cr(CO)_6 + 2K_2Te_2$ --->



(34)

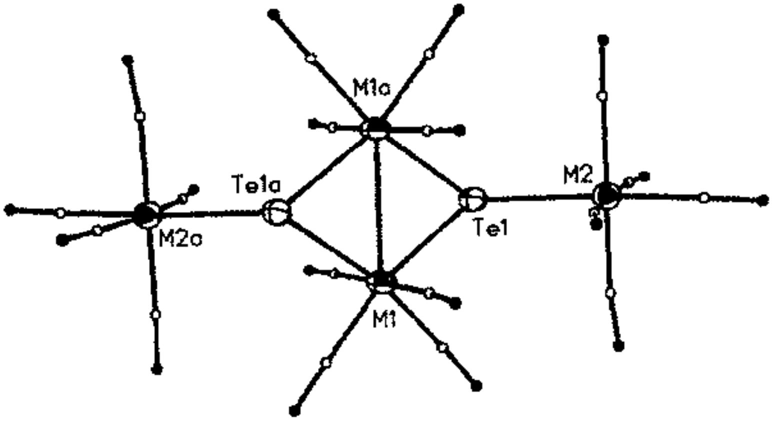


Figure 9. View of $[M_4(CO)_{18}Te_2]^{2-}$ where M = Cr and W.

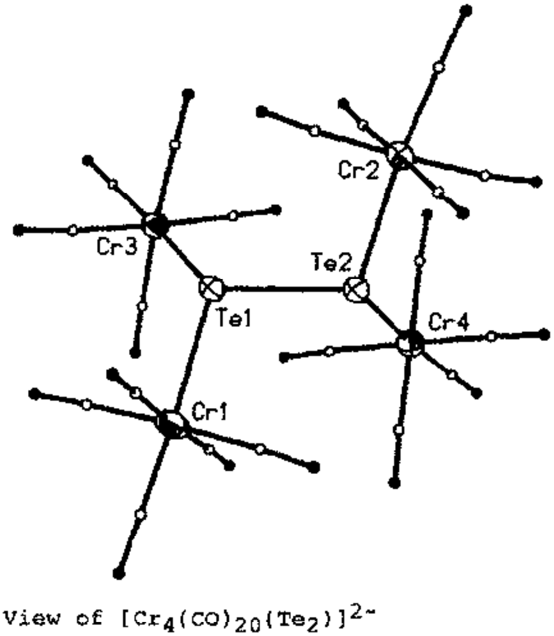
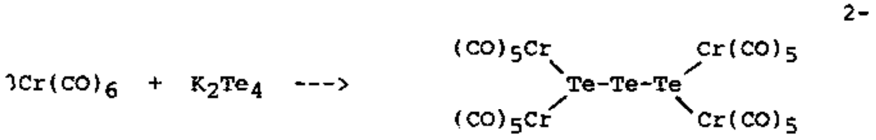


Figure 10. View of $[Cr_4(CO)_{20}(Te_2)]^{2-}$

There have been several examples of metal fragments bound to Te_2 groups (refs. 19,67), but the presence of the four metal pentacarbonyls makes this a very sterically hindered molecule, and it probably owes its existence to the large size of the tellurium atoms.

Use of any higher nuclearity polytellurides such as K_2Te_3, K_2Te_4, $[(C_6H_5)_4P]_2[Te_4]$ or $[(t\text{-}Bu)_4N]_2[Te_5]$ leads to formation of the extremely stable $\{[Cr(CO)_5]_4Te_3\}^{2-}$ in good yield (Fig. 11).



(35)

Surprisingly, this molecule appears to be the thermodynamic sink in this system. It can be isolated analytically pure in high yield, and shows no tendency to extrude elemental tellurium. It is stable to air in solution, and can be heated for days with no apparent decomposition. Coordinated three membered tellurium chains are somewhat rare. There is an example of a Te_3 chain capped by alkyl silyl groups (ref. 68), and several chelated Te_3 groups. Interestingly, all the chromium compounds can ultimately be converted into $[Cr_4(CO)_{20}Te_3]^{2-}$ using a mild oxidant such as CH_2Cl_2. Clearly this system is quite complex and more work is needed to clarify all the reaction pathways.

When excess $W(CO)_6$ is reacted with polytellurides an entirely different scheme is observed. Use of K_2Te or K_2Te_2 generates a tungsten compound having the formula $[W_4(CO)_{18}Te_2]^{2-}$, in excellent yield (eq. 36). The structure is virtually identical to the corresponding chromium compound, but the tungsten compound is quite stable and unreactive.

$$3W(CO)_6 \; + \; K_2Te_2 \; \longrightarrow \; [W_4(CO)_{18}Te_2]^{2-} \qquad (36)$$

However, when a higher nuclearity polytelluride is used as a starting material, such as $[(C_6H_5)_4P]_2[Te_4]$, a new three dimensional cluster can be crystallized (ref. 69).

$$W(CO)_6 \;+\; [(C_6H_5)_4P]_2[Te_4] \text{ -----> } [(W(CO)_3)_6(Te_2)_4]^{2-} \qquad (37)$$

This beautiful cluster contains a pinwheel with a Te_2^{2-} dimer as the axis and three W-W bonds acting as paddles, with all tungsten atoms in a formal W(I) oxidation state. Each face of the cluster is bridged by another Te_2^{2-} group (Fig. 12). Presumably, the oxidation of the metal centers is caused by the reduction of Te_4^{2-} to $2Te_2^{2-}$. In addition, the striking pinwheel geometry can be attibuted to the fortuitous similarity in Te-Te and W-W bond lengths.

This molecule is one of the very few 14 vertex clusters which have been reported, and the first with this unusual geometry. It is valence precise in the sense that it contains an equal number of bonds as valence electron pairs. However, each tellurium atom of the central ditelluride unit is bound to three tungsten atoms in a severely distorted sp^3 fashion. The three tungsten atoms are essentially planar with respect to the central tellurium atoms. This unusual bonding is in keeping with the ability of tellurium to adopt unconventional geometries (ref. 37).

SUMMARY

We report here a preliminary review of reactions of polychalcogenide anions with transition metal carbonyl compounds. The reactions clearly are quite varied and generally undergo complex redox reactions. The polysulfides and polyselenides seem to show similar reactivity in many cases, whereas the polytellurides behave quite differently. In addition, the first row metal carbonyls react differently from their heavier cogeners, since the heavier elements have a much greater tendency to assume higher oxidation states.

The logical extensions of the reactions described above are currently under investigation in our labs. In general, it appears that the primary ingredients for oxidative decarbonylation are a polychalcogenide chain chelated to a low valent metal center. The chalcogen-chalcogen bonds act as a receptical for electrons from the metal center, causing loss of CO, cleavage of the polychalcogen chain and formation of a higher valent metal. We make no pretense of understanding the factors which control the reactivity of even

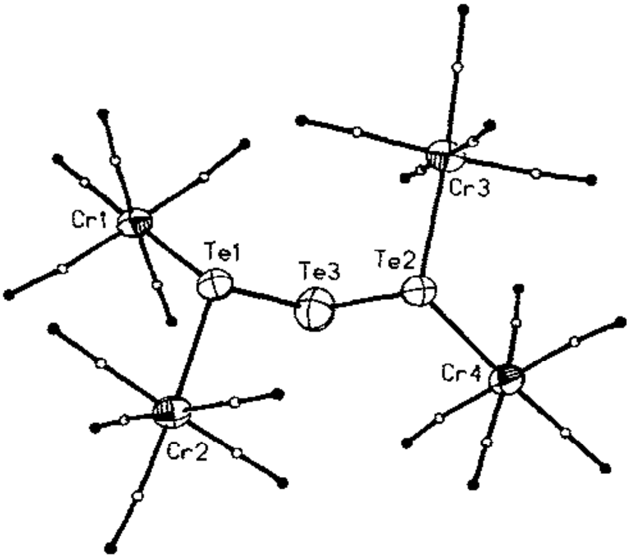


Figure 11. Side view of $[Cr_4(CO)_{20}(Te_3)]^{2-}$.

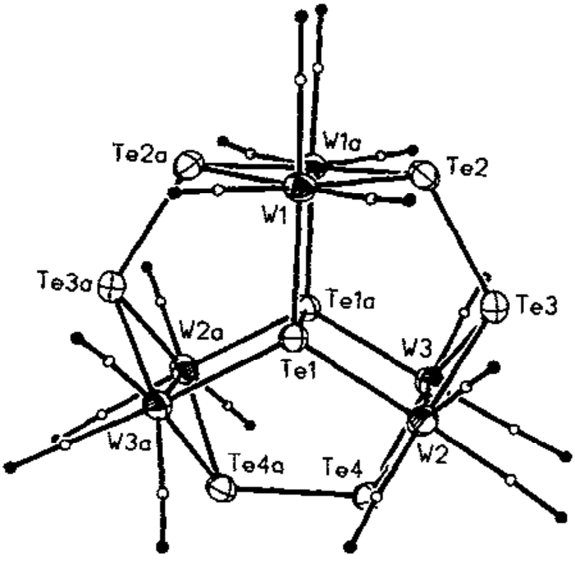


Figure 12. View of $[(W(CO)_3)_6(Te_2)_4]^{2-}$ showing pinwheel structure of the cluster.

the simplest systems. However, as we continue our survey of reactions, it becomes obvious that there is a wide range of reactivity, and a variety of compounds can be prepared using these reagents.

It is appropriate in closing to mention a preliminary result involving another related class of ligands, which illustrates the breadth of reactivity in this area. The introduction of one or more trivalent elements to a polychalcogen cluster greatly increases the structural possibilities, since it can lead to cage formation. Reduction of arsenic selenide glass generates the mixed 15/16 anion $As_4Se_6^{2-}$. This also induces oxidative decarbonylation when reacted $W(CO)_6$, forming the molecule shown in equation 38 (Fig. 13).

$$W(CO)_6 + xs\ As_4Se_6^{2-} \text{ -----> } [W(As_3Se_3)_2(CO)_2]^{2-} \tag{38}$$

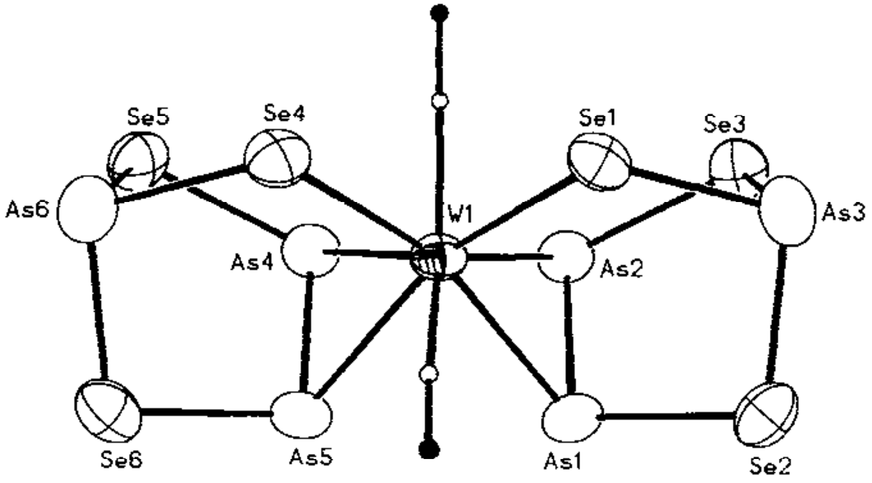


Figure 13. View of $[W(As_3Se_3)_2(CO)_2]^{2-}$ containing an eight coordinate W(IV) center.

This molecule contains a W(IV) center which is in the basal plane of two birdcages, formally replacing an arsenic atom from a conventional As_4Se_3 birdcage type structure (ref 70). The metal center is eight coordinate since it still has two CO ligands attached. This compound is quite stable and can be prepared in good yield (ref. 71). It is presumably the forerunner to an even greater number of novel coordination complexes.

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