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SOLUBLE SELENIDES AND TELLURIDES

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CONTENTS

ABBREVIATIONS

$AsPh_4$	tetraphenylarsonium (+1)
Bu	butyl
Cp	η^5-cyclopentadienyl

15-crown-5	1,4,7,10,13-pentaoxacyclopentadecane
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
2,2,2-crypt	4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane
DMF	*N*,*N*-dimethylformamide
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
en	1,2-diaminoethane
Et	ethyl
EtOH	ethanol
IR	infrared
Me	methyl
MeCN	acetonitrile
MeOH	methyl alcohol
MO	molecular orbital
NBu_4	tetra-*n*-butylammonium (+1)
NEt_4	tetraethylammonium (+1)
NMR	nuclear magnetic resonance
octyl	$n\text{-}C_8H_{17}$
PEt_3	triethylphosphine
Ph	phenyl
Por	tetraphenylporphyrin
PPh_3	triphenylphosphine
PPh_4	tetraphenylphosphonium (+1)
PPN	bis(triphenylphosphoranylidene)ammonium (+1)
ppp	bis(2-diphenylphosphinoethyl)phenylphosphane
Pr	propyl
Q	Se or Te or sometimes S
RT	room temperature
THF	tetrahydrofuran
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
UV–visible	ultraviolet–visible

A. INTRODUCTION

The beautiful chemistry of the heteropolymetallates has been developed and systematized over the past century [1,2]. However, the corresponding chemistry of the higher congeners of oxygen, namely the chalcogens sulfur, selenium and tellurium, is not as well developed. Owing to interest in the bioinorganic chemistry of Fe–Mo–S systems and to hydrodesulfurization processes, the chemistry of soluble metal sulfides has received considerable attention in the last two decades. Indeed, it has been reviewed extensively [3–10]. In contrast, until very recently the chemistry of soluble metal selenides and tellurides had received scant attention. In fact, most of the chemistry of metal selenides and tellurides had been limited to the solid state [11–14]. However, recent studies of the higher chalcogens has indicated that their metal chemistries differ from one another and from that of sulfur [15–22]. A review of this recent chemistry therefore seems propitious.

There are some semantic difficulties with the term "soluble metal chalcogenide". We will concern ourselves primarily with species that have been synthesized by solution techniques utilizing, in general, non-aqueous solvents, even though the ultimate characterization of such species entails the study of their salts in the solid state. But we will also discuss some species that result from solid state syntheses, especially if such species can be brought into solution.

B. PURE SELENIDE AND TELLURIDE IONS

(i) Anions

Uncoordinated polyselenide anions of different chain lengths have been synthesized by a variety of methods [23–33]. While it is difficult to stabilize the long-chain free polyselenides in solution, they can be isolated as salts through the use of long-chain quaternary ammonium or phosphonium cations [28] or alkali metal crown ethers [26,29]. Owing to the interconversion of these anions in solution, systematic spectroscopic data are lacking. However, each of the Se_n^{2-} ($n = 1$–6) anions shows an absorption at 285 cm^{-1} in the IR region; this absorption corresponds to an Se–Se stretching vibration [28]. A UV–visible study of Se^{2-} to Se_4^{2-} shows the following absorptions: Se^{2-}, 247 nm; Se_2^{2-}, 250 (sh), 432 nm; Se_3^{2-}, 252, 326, 370 (sh), 530 nm; Se_4^{2-}, 280, 375, 470 nm (aqueous KOH) [34]. For $[NBu_4]_2[Se_6]$, three absorptions occur at 385 (sh), 440 and 625 (br) (acetone) [32]. The results of a UV–visible spectrophotometric study on polysulfides in liquid ammonia suggest that S_6^{2-} is in equilibrium with the radical $S_3^{\cdot-}$ and that S_4^{2-} disproportionates to S_2^{2-} and $S_3^{\cdot-}$ [35]. Similar disproportionation and formation of the $Se_3^{\cdot-}$ radical in solution has been proposed [36].

For the unbranched polychalcogenide Q_n^{2-}, there are $2^{(n-3)}$ possible isomers [30]. The polyselenide ions Se_n^{2-} ($n = 2$–6) approximately represent part of a helical chain of polymeric selenium. The anion Se_4^{2-} in [Ba-2,2,2-crypt][Se_4] has a *trans* configuration [26], the terminal distance (2.325(5) Å) being shorter than the internal Se–Se distance (2.344(5) Å) (Table 1) [24–33,37–56]. This difference in terminal and internal bond distances, i.e. 2.312(3) Å and 2.397(4) Å [29], is more pronounced in $[PPN]_2[Se_4]$ where the anion is *cis* and planar. For Se_5^{2-} four isomers are possible (two enantiomeric *cis* and two enantiomeric *trans* forms; generally the two *cis*

TABLE 1

Q–Q distances in pure selenide and telluride ions

Material	Q–Q distance (Å)	Ref.
α-Se_8	2.34(2)	37
β-Se_8	2.337(19)	38
γ-Se_8	2.33(5)	39
Trigonal Se	2.373(5)	40
Se_2 (vapor)	2.19(3)	41
$Na_2[Se_2]$	2.38(5)	24
$K_2[Se_3]$	2.383(2)	25
$[Ba\text{-}2,2,2\text{-crypt}][Se_4]\cdot en$	2.325(5), 2.344(5), 2.325(5)	26
$[Ba(en)_4][Se_4]\cdot en$	2.329(3), 2.342(4), 2.329(3)	27
$[PPN]_2[Se_4]\cdot 4\ MeCN$	2.312(3), 2.397(4), 2.312(3)	29
$Rb_2[Se_5]$	2.31(2), 2.36(1), 2.37(2), 2.33(1)	30
$Cs_2[Se_5]$	2.33(1), 2.38(1), 2.34(1), 2.29(1)	31
$[Cs(18\text{-crown-}6)]_2[Se_5]$	2.316(3), 2.343(3), 2.343(3), 2.316(3)	29
$[NBu_4]_2[Se_6]$	2.295(2), 2.337(2), 2.362(3)	32
$[(CH_3)_3N(CH_2)_{13}CH_3]_2[Se_6]$	2.274(4), 2.268(5), 2.352(9)	28
$[PPh_4]_2[Se_{11}]$	2.659(2), 2.320(4), 2.319(4), 2.327(3), 2.332(4)	33
$[Se_4][HS_2O_7]_2$	2.286(4), 2.280(4)	42, 43
$[Se_8][AlCl_4]_2$	Within the ring 2.29–2.36, cross ring 2.84	44, 45
$[Se_{10}][SO_3F]_2$	2.246(5)–2.450(5)	46
Hexagonal Te	2.835(2)	47
Te_2 (gas)	2.864	41
$K_2[Te_2]$	2.86	48
$K_2[Te_3]$	2.802, 2.805	49, 50
$[K\text{-}2,2,2\text{-crypt}]_2[Te_3]\cdot en$	2.692(5), 2.720(4)	51
$[Ba(en)_3][Te_3]$	2.739, 2.785	52
$[Ba(en)_{4.5}][Te_3]$	2.721, 2.731	52
$[PPh_4]_2[Te_4]\cdot 2\ MeOH$	2.724(1), 2.762(1)	53
$[Na\text{-}2,2,2\text{-crypt}]_2[Te_4]$	2.702(3), 2.746(3), 2.702(3)	54
$[NBu_4]_2[Te_5]$	2.704(1), 2.746(1)	32
$[Te_4][AlCl_4]_2$	2.674(2), 2.663(2)	55
$[Te_4][Al_2Cl_7]_2$	2.659(2), 2.661(2)	55
$[Te_6][AsF_6]_4\cdot 2\ AsF_3$	2.675 (triangular face); 3.133 (between faces)	56

forms are identical (*meso* forms) [57]). In $Rb_2[Se_5]$ and $Cs_2[Se_5]$ the Se_5^{2-} species is *trans* (in $Rb_2[Se_5]$ a right-handed helix), whereas in $[Cs(18\text{-crown-}6)]_2[Se_5]$ the anion has the *cis* configuration [29]. In $[Cs(18\text{-crown-}6)]_2[Se_5]$ the terminal Se–Se bond (2.316(3) Å) is shorter than the internal bond (2.343(3) Å). For the Se_6^{2-} ion only a *trans* configuration has been reported [28,32] and again the terminal Se–Se bonds are the shortest (Table 1). The Se_{11}^{2-} anion (Fig. 1) consists of a central Se^{2+} cation coordinated in a square-planar manner to two Se_5^{2-} chelates [33]. Bonds to the central Se

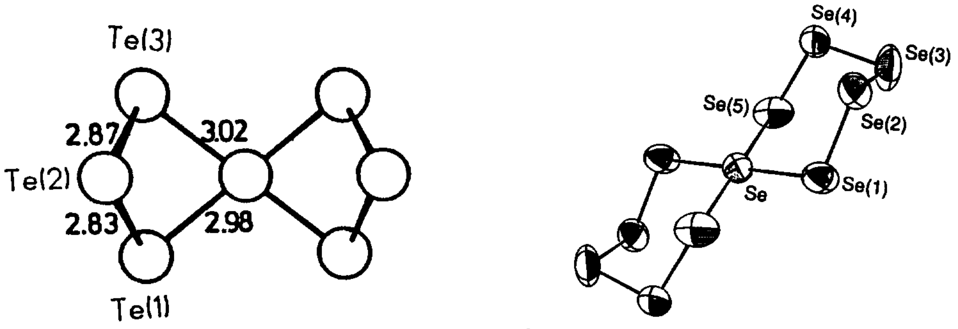


Fig. 1. The Te_7^{2-} anion in Re_2Te_5 [58] and the Se_{11}^{2-} anion in $[PPh_4]_2[Se_{11}]$ [33].

atom are the longest: compare the Se_{11}^{2-} ion with the Te_7^{2-} ion in Re_2Te_5 [58] (Fig. 1), where the central Te^{2+} ion is again square planar.

Polytellurides show structures different from the helical zigzag chain Q_n^{2-} ($Q = S$ or Se; $n = 4, 5, 6, \ldots$). Thus, in Rb_2Te_5 and Cs_2Te_5 there are infinite one-dimensional Te-atom chains [59,60]. The tellurides present a variety of structural possibilities because each Te atom, through the use of lone-pair electrons, can achieve a coordination number greater than two [14]. For example, Re_2Te_5 contains a square-planar $TeTe_4$ skeleton and Re_2Te_5 ($= Re_6Te_8^{2+}Te_7^{2-}$) features a butterfly-like Te_7^{2-} ion [58]. In $[K\text{-}2,2,2\text{-crypt}]_2[Te_3] \cdot en$ the Te_3^{2-} anion may be considered as a three-atom piece of the infinite helix that occurs in elemental tellurium, with external bond lengths reduced to complete the lone pair and furnish the charge [51]. Nevertheless, there exist the unbranched anions Te_n^{2-} ($n = 3$–5) completely analogous to those of the lower chalcogens (Table 1). One feature of these polytelluride anions is that both the terminal and the internal bond distances are generally shorter than that in elemental tellurium.

As is to be expected, the stereochemistry of these polyselenide and polytelluride anions changes significantly when they are bound to a metal center (see below).

(ii) Cations

The existence of the O_2^+ cation in the gas phase [61] as well as in the solid state is now well established [62–64]. Cations of the higher chalcogens (i.e. Se_n^{2+} and Te_n^{2+}) have been prepared through oxidation of the elements; for a review see ref. 65. The Se_4^{2+} cation has been isolated with a variety of anions [42,43,66]. The cation consists of a planar, square ring. This structure can be described by valence bond theory in terms of four resonating forms equivalent to Fig. 2(a) or by MO theory in terms of Fig. 2(b) where the circle denotes a closed-shell six-electron system [42,43,66]. The average Se–Se

Fig. 2. (a) Valence bond and (b) molecular orbital representations of the Se_4^{2+} cation [42,43,66].

bond distance in $[Se_4][HS_2O_7]_2$ (2.283(4) Å) is shorter than that of the Se_8 rings in α- and β-Se (2.34 Å) [37,38]. The Se_8^{2+} cation in $[Se_8][AlCl_4]_2$ consists of a folded ring in *endo,exo* conformation with C_s symmetry [44,45] (Fig. 3). The Se–Se distances vary from 2.29 to 2.36 Å and do not differ significantly from those found in the Se_8 rings of elemental selenium [37–39]. A striking structural difference between the Se_8^{2+} ion and the cyclic Se_8 ring is the *trans* annular closure to a distance of 2.84 Å in the anion (Fig. 3). The resultant structure has been described in valence bond terms (Fig. 3(a)).

The Se_{10}^{2+} cation in the solid state has a cage-like bicyclo[4.2.2]decane geometry as shown in Fig. 4. The Se–Se distances vary between 2.246(5) and 2.450(5) Å [46]. The ^{77}Se NMR spectra of these cations have been obtained and interpreted [46,67] (see below).

There is spectroscopic evidence for the existence of Te_x^{n+} cations (Te_2^+, Te_3^+, Te_4^{2+} and Te_6^{2+}) in solution [68]. In the crystal structures of $[Te_4][AlCl_4]_2$ and $[Te_4][Al_2Cl_7]_2$, the Te_4^{2+} ion lies on a center of symmetry and is almost square planar [55]. In $[Te_4][AlCl_4]_2$ the Te–Te distances of 2.674(2) and 2.663(2) Å are significantly shorter than that in elemental tellurium (2.864 Å) [47]. $[Te_6][AsF_6]_4 \cdot 2\,AsF_3$, and $[Te_6][AsF_6]_4 \cdot 2\,SO_3$ contain the trigonal prismatic Te_6^{4+} species with Te–Te distances (for example in $[Te_6][AsF_6]_4 \cdot 2\,AsF_3$) in the triangular faces ranging from 2.675 to 2.694 Å and those between the faces ranging from 3.121 to 3.148 Å [56] (Fig. 5).

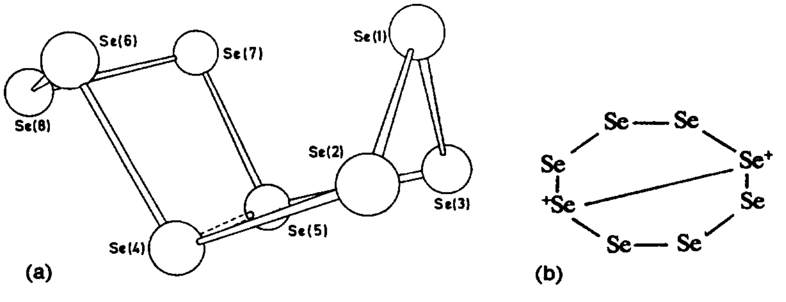


Fig. 3. (a) Structure of the Se_8^{2+} ion and (b) its valence bond representation [44,45].

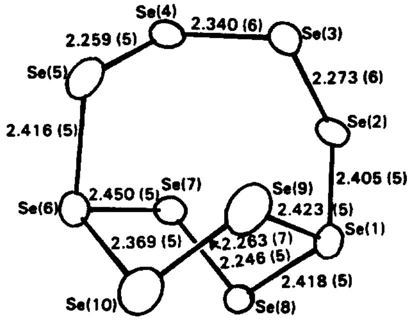


Fig. 4. A view of the Se_{10}^{2+} ion with principal bond lengths (Å) [46].

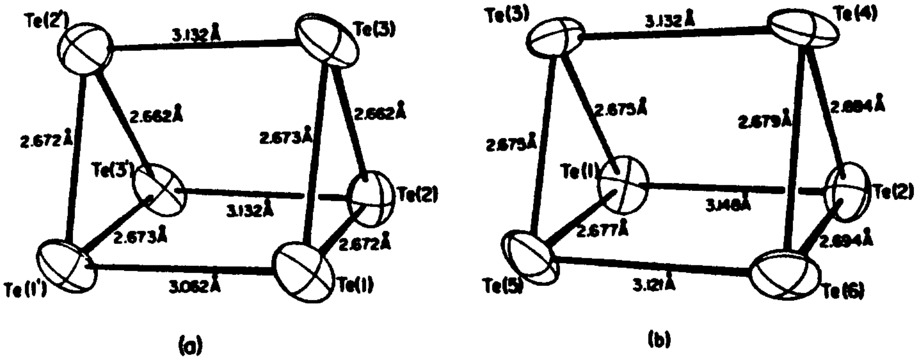


Fig. 5. Structure of the Te_6^{4+} cation in (a) $[Te_6][AsF_6]_4 \cdot 2AsF_3$ and (b) $[Te_6][AsF_6]_4 \cdot 2SO_2$ [56].

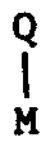
Some mixed-chalcogenide cationic species, e.g. $Te_2Se_6^{2+}$, $Te_2Se_4^{2+}$, $Te_3Se_3^{2+}$, $Te_2Se_8^{2+}$ and $Te_3S_3^{2+}$, have also been reported [69–73].

C. METAL SELENIDES AND TELLURIDES

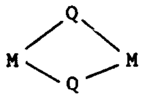
Compounds of selenium and tellurium (Q) with metals (M) show a variety of structural types; some of these are unknown in sulfur chemistry. Differences in redox potentials and in ionic radii probably account for these structural differences.

(i) Complexes containing no Q–Q bonds

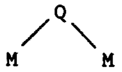
There are numerous examples where a bare chalcogen atom is bonded to one or more metals. The following structural types have been reported.



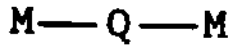
terminal
Ia



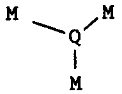
doubly bridging
Ib



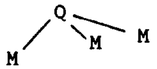
bridging bent
Ic



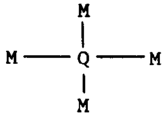
bridging linear
Id



trigonal planar
Ie



pyramidal
If



square pyramidal
Ig

Structural types **Ia** and **Ib** are very common and will be discussed only briefly. In such structural types the M–Q bond distances increase in the order M=Q < M–Q < M–Q–M. For example, consider W–Se distances. Typical W=Se distances are 2.258(2) and 2.242(2) Å in the $W_2Se_4(Se_2)(Se_3)^{2-}$ ion [20] (Fig. 6) and 2.253(2) and 2.248(2) Å in the $W_2Se_4(Se_2)(Se_4)^{2-}$ ion [20] (Fig. 7); typical W–Se terminal distances are 2.317(7) Å in WSe_4^{2-} [74] and 2.280(1) and 2.294(1) Å in $W_2Se_6^{2-}$ [75] (Fig. 8); typical W–Se–W bridging distances are 2.425(1) and 2.437(1) Å in $W_2Se_6^{2-}$ [75] and 2.384(7) Å in $W_2Cl_8Se(Se_2)^{2-}$ [76].

Examples of structural types **Ic** and **Id** are rare. An example of **Ic** is $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6(\mu\text{-}Te)$ (Fig. 9), which shows a very long Cr–Te dis-

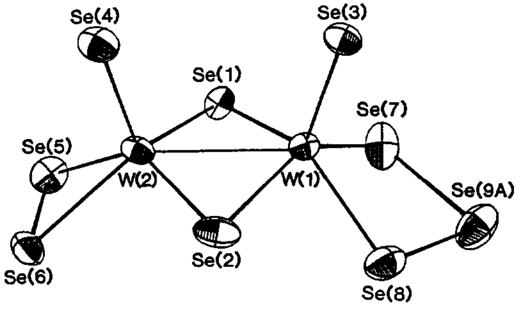


Fig. 6. The $W_2Se_4(Se_2)(Se_3)^{2-}$ ion [20].

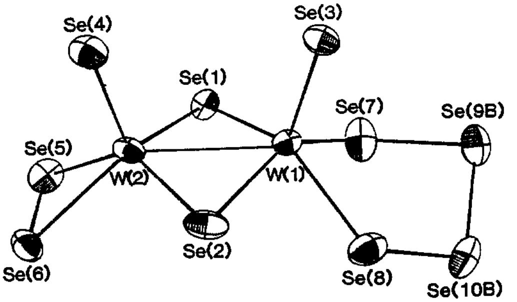


Fig. 7. The $W_2Se_4(Se_2)(Se_4)^{2-}$ ion [20].

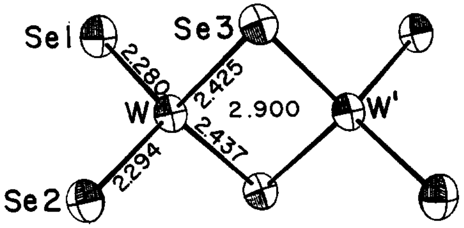


Fig. 8. The $W_2Se_6^{2-}$ ion [75].

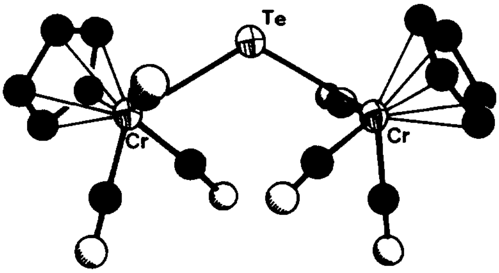


Fig. 9. Structure of the $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6(\mu\text{-}Te)$ molecule [77].

tance (2.80–2.81 Å; Cr–Te–Cr 117.2°) [77]. A similar manganese complex $(\eta^5\text{-}C_5Me_5)_2Mn_2(CO)_4(\mu\text{-}Te)$ exhibits an Mn–Te bond distance of 2.459(2) Å, which indicates the presence of a multiple bond because an Mn–Te single-bond distance is expected to be around 2.70 Å [78]. As examples of type **Id** the complexes with linear $[CrSeCr]^{2+}$, $[MoSeMo]^{2+}$ and $[VSeV]^{2+}$ units (Cr–Se 2.21 Å, Mo–Se 2.323(1) Å and V–Se 2.298(2) Å) are known [79–81]. However, the corresponding V–Te complex is not strictly linear (V–Te–V 165.9°, V–Te 2.518 Å) [81].

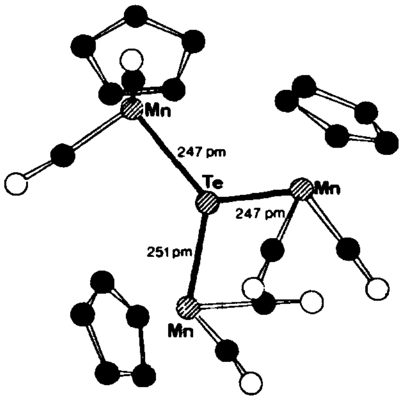


Fig. 10. Structure of the $(\eta^5\text{-}C_5H_5)_3Mn_3(CO)_6(\mu_3\text{-}Te)$ molecule [82].

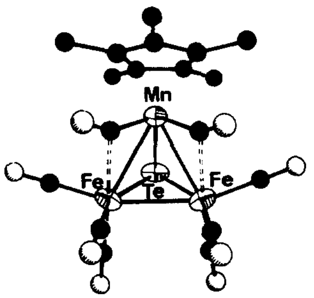


Fig. 11. The $(\eta^5\text{-}C_5Me_5)(CO)_2Mn(\mu_3\text{-}Te)Fe_2(CO)_6$ molecule [83].

An example of type **Ie** is the trigonal planar μ_3-Te complex $(\eta^5\text{-}C_5H_5)_3Mn_3(CO)_6(\mu_3\text{-}Te)$ [82] (Fig. 10) which has a short Mn–Te bond of length 2.485 Å. A remarkable example of type **If** is found in $(\eta^5\text{-}C_5Me_5)(CO)_2Mn(\mu_3\text{-}Te)Fe_2(CO)_6$ [83] (Fig. 11) where the M–Te distances range from 2.47 to 2.51 Å. Structural type **If** also occurs in the $KAu_9Te_7^{4-}$ ion [84] and in $(\eta^5\text{-}C_5H_5)_2Mo_2FeTe_2(CO)_7$ [85].

In $Nb_4Br_{10}Se_3(NCMe)_4$ [86] (Fig. 12) the Nb atoms are bridged by Se atoms in two different modes. Atoms Nb(1) and Nb(1′) are bridged by an Se_2^{2-} unit and, in addition, atom Se(3) is bonded to all four Nb atoms, presenting an example of structural type **Ig**. Another example of this type is found in $Fe_2(CO)_6(\mu_4\text{-}Te)(\mu_3\text{-}Te)Ru_3(CO)_{11}$ [87].

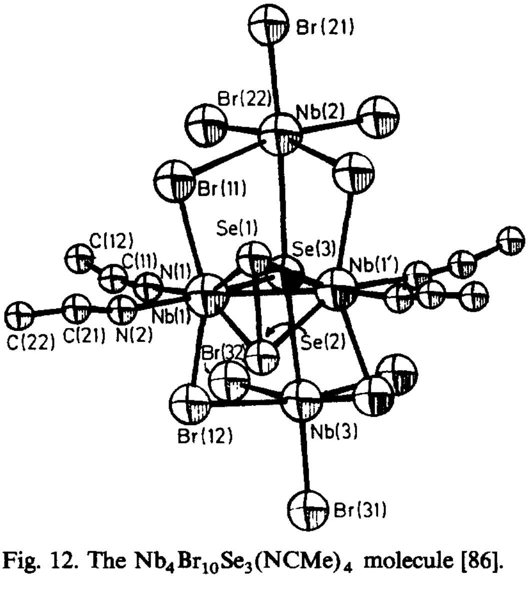
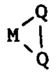


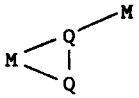
Fig. 12. The $Nb_4Br_{10}Se_3(NCMe)_4$ molecule [86].

(ii) Complexes containing Q_2^{2-}

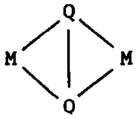
Complexes containing Se_2^{2-} are relatively common. As a function of the metal and its other ligands the Q_2^{2-} unit may exhibit a variety of modes of coordination, as shown below:



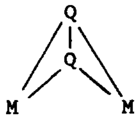
IIa



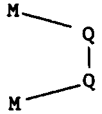
IIb



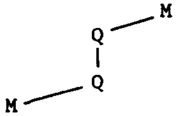
IIc



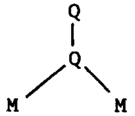
IId



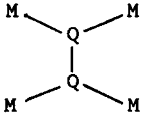
IIe



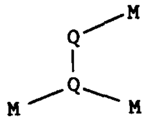
IIf



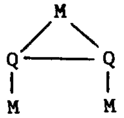
IIg



IIh



IIi



IIj

Compounds in which Q_2^{2-} is bonded to a metal in a side-on fashion (type **IIa**) are listed in Table 2 [19,20,76,79,86,88–107]. The resultant three-membered ring, which is similar to those in peroxy and persulfido complexes, can be thought of either as analogous to a cyclopropane (M–Q σ bonding) or as analogous to a metal–olefin complex (π bonding and back donation). However, the angle at the metal is smaller in the peroxo and persulfido complexes. For example, the Se–Ir–Se angle in the $[Ir(Se_2)(dppe)_2]^+$ cation is 54.28(7)° [90], while the S–Ir–S angle in the $[Ir(S_2)(dppe)_2]^+$ cation is 50.8(2)° [108]. The Se–Se distance in these complexes varies from 2.255(8) to 2.348(4) Å (Table 2). The exceptionally short Se–Se bond in $(\eta^5\text{-}C_5H_5)Mn(CO)_2Se_2$ has been attributed to multiple Se–Se bonding [91]; perhaps the subtle effect of thermal motion is a more likely explanation.

An interesting variation may be found in $[W_2(CO)_{10}Se_4][AsF_6]_2$ [109] and $[W_2(CO)_{10}Se_4][SbF_6]_2$ [110]. The cation in these compounds can be thought of as two side-on bonded $W(CO)_5Se_2^+$ fragments (Se–Se = 2.208(1) Å) interacting through a long Se–Se bond (3.017(1) Å) to yield a W_2Se_4 core with a chair conformation (Fig. 13). The planar Se_4 group makes an angle of 102.3° with the WSe_2 plane. Alternatively, the cation may be considered as one in which a rectangular Se_4 ring bridges two metal centers.

TABLE 2

Q–Q distances in complexes containing Q_2^{2-} ligands

Compound	Type	Q–Q distance (Å)	Ref.
$[NEt_4]_2[V_2(Se_2)_4(Se_5)]$	**IIa**	2.336(3)	19
		2.331(3)	
	IId	2.305(3)	
$[PPh_4]_2[W_2Se_4(Se_2)(Se_4)]$	**IIa**	2.348(4)	20
$[PPh_4]_2[W_2Se_4(Se_2)(Se_3)]$	**IIa**	2.340(4)	20
$[PPh_4]_2[Ni(Se_2)(WSe_4)]$	**IIa**	2.328(1)	88
$Os(Se_2)(CO)_2(PPh_3)_2$	**IIa**	2.321(1)	89
$[Ir(Se_2)(dppe)_2]Cl$	**IIa**	2.312(3)	90
$(\eta^5\text{-}C_5Me_5)Mn(CO)_2(Se_2)$	**IIa**	2.263(8)	91
$(triphos)Ni(Te_2)$	**IIa**	2.668(1)	92
$(ppp)Ni(Te_2)$	**IIa**	2.665(2)	92
$[(triphos)Rh(\mu\text{-}Se_2)_2Rh(triphos)][BPh_4]_2$	**IIb**	2.298(1)	93
$(\eta^5\text{-}C_5H_5)Fe(CO)_2(Se_2)Cr(CO)_2(\eta^5\text{-}C_5H_5)$	**IIb**	2.297(1)	94
$(\eta^5\text{-}C_5Me_5)(CO)_2Re(\mu\text{-}Te_2)Re(CO)_2(\eta^5\text{-}C_5Me_5)$	**IIb**	2.703(1)	95
$[(triphos)Ni]_2(\mu\text{-}\eta^2\text{-}Te_2)$	**IIc**	2.802(1)	96
$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4Se_2$	**IIc**	2.277	79
$Fe_2(\mu\text{-}Se_2)(CO)_6$	**IId**	2.293(2)	97
$[FeW(CO)_8(Se_2)][SbF_6]_2$	**IId**	2.281(3)	98, 99
$Nb_4Br_{10}(Se_2)Se(NCMe)_4$	**IId**	2.289(3)	86
$(\eta^5\text{-}C_5H_4Me)_2V_2Se_5$	**IId**	2.295(2)	100
	IIe	2.290(2)	
$Nb_2Cl_4(Se_2)_2(SMe_2)_4$	**IId**	2.289(3)	101
$Nb_2Cl_4(Se_2)_2(C_4H_8S)_4$	**IId**	2.260(5)	102
$[AsPh_4]_2[W_2Cl_8Se(Se_2)]$	**IId**	2.255(8)	76
$[(\eta^5\text{-}C_5H_4Me)_2Ti]_2Se_4$	**IIf**	2.343(1)	103
$[K\text{-}2,2,2\text{-}crypt]_2[Mo_4Te_{16}(en)_4]$	**IIg**	2.841(2)	104
	IIh	—	
$[NBu_4]_4[Hg_4Te_{12}]$	**IIh**	—	105
$[\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_3(Se_2)][BF_4]$	**IIi**	2.378(2)	106
$(CO)_5W(\mu\text{-}Te_2)[W(CO)_5]_2$	**IIj**	2.686(4)	107
$(\eta^5\text{-}C_5Me_5)(CO)_2Re(\mu\text{-}Te_2)Mn_2(\eta^5\text{-}C_5H_5)_2(CO)_4$	**IIj**	2.732(1)	95

The ligating behavior of MS_4^{2-} towards transition metals (M′) to form $M'(MS_4)_2^{2-}$ (M = Mo or W; M′ = Fe, Co, Ni, Pd, Pt, Zn, Cd or Hg) has been studied in detail [3]. Similar chemistry affords the expected $Ni(WSe_4)_2^{2-}$ anion, but also the $Ni(Se_2)(WSe_4)^{2-}$ anion [88]. The $Ni(Se_2)(WSe_4)^{2-}$ anion (Fig. 14), which has no known sulfur analogue, features a square-planar Ni center ligated to a slightly distorted tetrahedral WSe_4 group and a side-on bound Se_2 ligand (type **IIa**). The Se–Se distance of 2.328(1) Å is normal (Table 2) while there are no differences in the terminal W–Se distances in $Ni(Se_2)(WSe_4)^{2-}$ (2.281(1) and 2.288(1) Å) and $Ni(WSe_4)_2^{2-}$ (2.277(1),

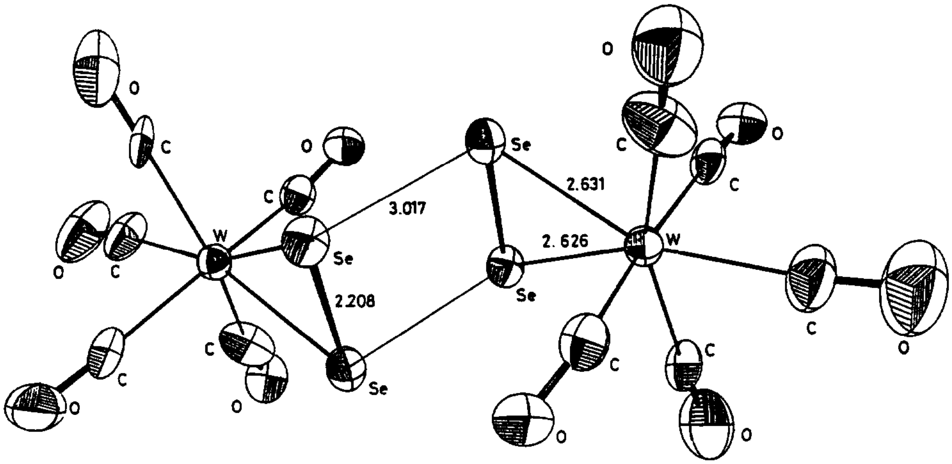


Fig. 13. The $W_2(CO)_{10}Se_4^{2+}$ ion [110].

2.285(1) Å). The Ni–Se bridge distances in $Ni(Se_2)(WSe_4)^{2-}$ are much shorter (2.285(1) and 2.295(1) Å vs. 2.347(1) and 2.353(1) Å), presumably because there is no longer an Se atom directly *trans* to these Ni–Se bridges.

Complexes containing Te_2^{2-} units are unstable and therefore extremely rare. The few examples that are known (Table 2) have been stabilized by bulky chelating ligands. As expected, the Q–Q bond lengths vary in the order Te–Te > Se–Se > S–S. In (triphos)Ni(Te_2) [92] (Fig. 15) and (ppp)Ni(Te_2) [92], the Te–Te distances (2.665(2) and 2.668(1) Å) are much shorter than that in $K_2[Te_2]$ (2.86 Å) [48].

Another structural type of importance is **IIb**, where one Q atom is bridged η^1 and the other η^2 to the M centers. In $(\eta^5\text{-}C_5H_5)Fe(CO)_2(Se_2)Cr(CO)_2(\eta^5\text{-}C_5H_5)$ [94] (Fig. 16), the Se–Se distance is 2.297(1) Å. In (triphos)Rh(μ-

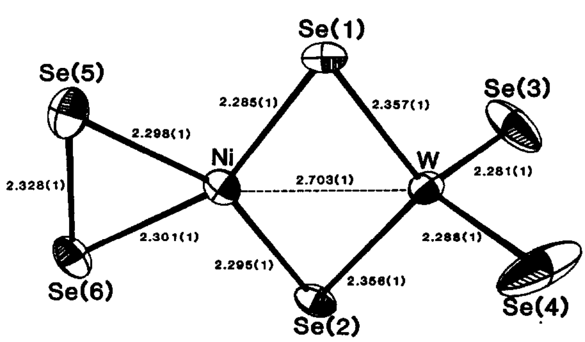


Fig. 14. The $Ni(Se_2)(WSe_4)^{2-}$ anion [88].

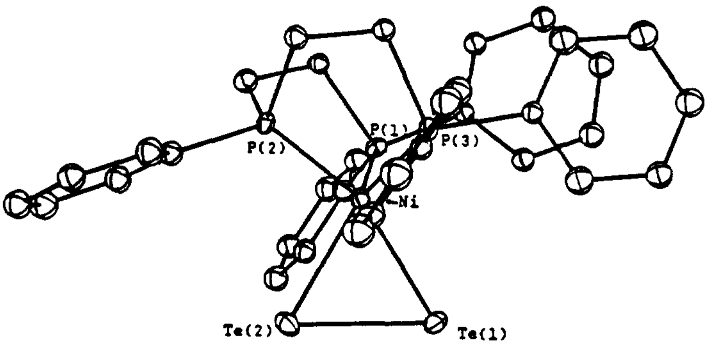


Fig. 15. Molecular structure of (triphos)Ni(Te_2) [92].

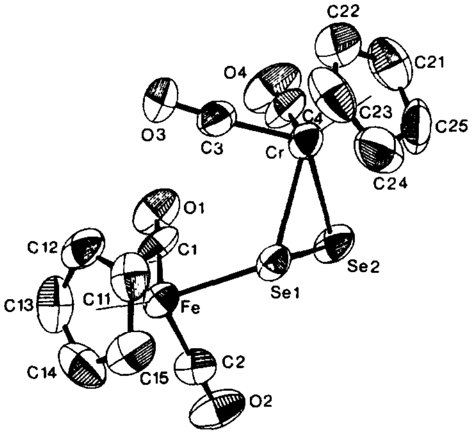


Fig. 16. The (η^5-C_5H_5)$(CO)_2$Fe(Se_2)Cr$(CO)_2$(η^5-C_5H_5) molecule [94].

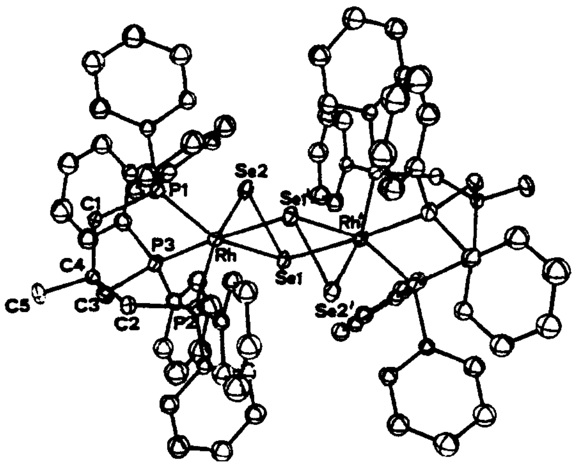


Fig. 17. The (triphos)Rh(μ-Se_2)$_2$Rh(triphos)$^{2+}$ cation [93].

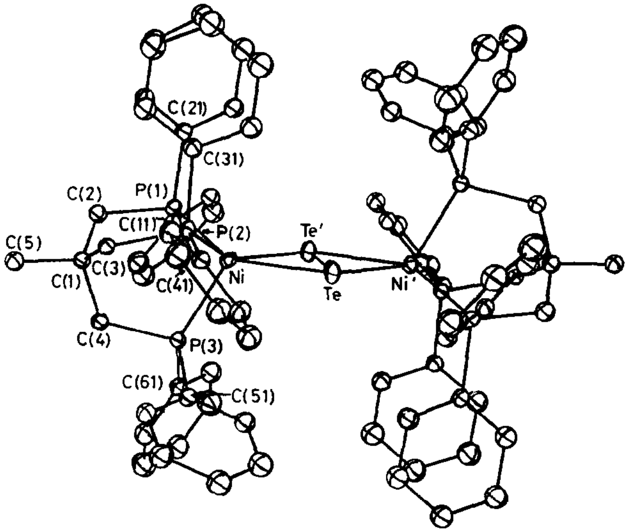


Fig. 18. Structure of the $[(\text{triphos})\text{Ni}]_2(\mu\text{-}\eta^2\text{-Te}_2)$ molecule [96].

$\text{Se}_2)_2\text{Rh}(\text{triphos})^{2+}$ [93] (Fig. 17), there are two such bridges (Se–Se = 2.298(1) Å). The Se–Se distances in these complexes, since they are very close to those in type **IIa** complexes, are apparently unaffected by the formation of additional Se–M bonds. Similarly, the Q–Q bonds (Table 2) in type **IIc** and type **IId** complexes are similar to those in type **IIa** complexes. In type **IIc** complexes the M_2Q_2 unit is planar, whereas in type **IId** complexes the M_2Q_2 unit is folded along the Q–Q bond. Figure 18 shows $[(\text{triphos})\text{Ni}]_2(\mu\text{-}\eta^2\text{-Te}_2)$ [96] as an example of a type **IIc** arrangement, while Fig. 19 shows the $\text{W}_2\text{Cl}_8\text{Se}(\text{Se}_2)^{2-}$ ion [76] as an example of a type **IId** arrangement.

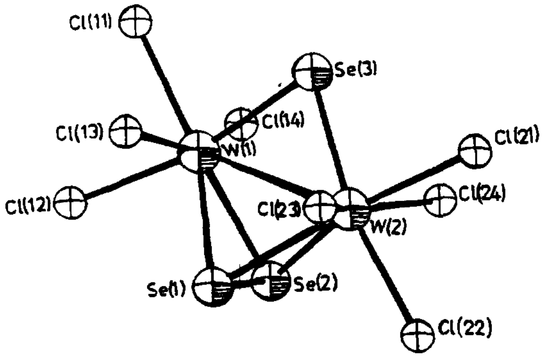


Fig. 19. Structure of the $\text{W}_2\text{Cl}_8\text{Se}(\text{Se}_2)^{2-}$ ion [76].

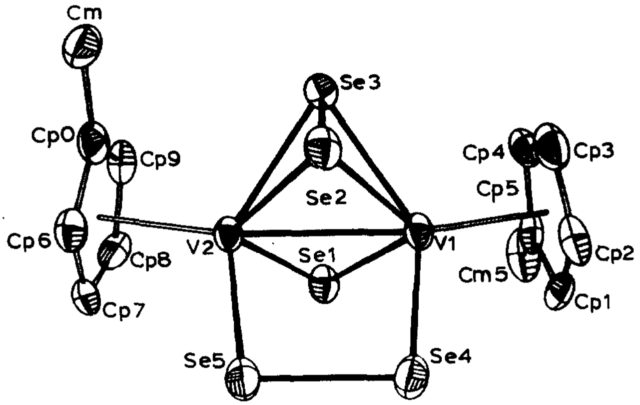


Fig. 20. Structure of the $(\eta^5\text{-}C_5H_4Me)_2V_2Se_5$ molecule [100].

In type **IIe** complexes a Q_2^{2-} unit is bridged symmetrically between two M centers in a *cis* M–Q–Q–M arrangement while in type **IIf** complexes the arrangement is *trans*. In the structure of $(\eta^5\text{-}C_5H_4Me)_2V_2Se_5$ [100] (Fig. 20) a V–V bond, 2.779(4) Å in length, is bridged by two different types of Se_2^{2-} ligands $\mu\text{-}\eta\text{-}Se_2$ (Se–Se = 2.295(2) Å, type **IId**) and *syn*-μ-Se_2 (Se–Se = 2.290(2) Å, type **IIe**). The structure may be compared with those of $(Me_3PtBr)_2(Me_2Se_2)$ (Se–Se = 2.359(10) Å [111] and $Re_2Br_2(CO)_6(Se_2Ph_2)$ (Se–Se = 2.411(23) Å) [112], where the RSe–SeR group is bridged between two metal atoms. The one-dimensional polymer $[(PPh_4)_2(Hg_2Te_5)]_n$ displays both the **IIe** and **IIf** arrangements [105].

In $[(\eta^5\text{-}C_5H_4Me)_2Ti]_2Se_4$ [103] (Fig. 21) the two Ti atoms are bridged by two Se_2^{2-} ligands in a type **IIf** arrangement (Se–Se distance 2.343(1) Å). The

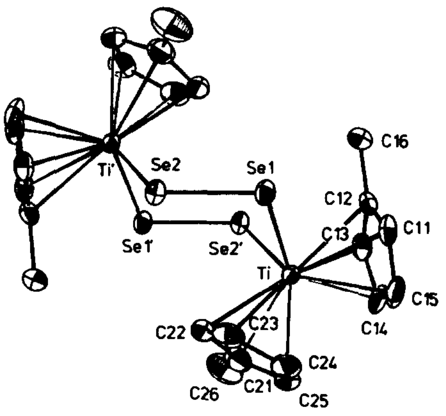


Fig. 21. Structure of the $[(\eta^5\text{-}C_5H_4Me)_2Ti]_2Se_4$ molecule [103].

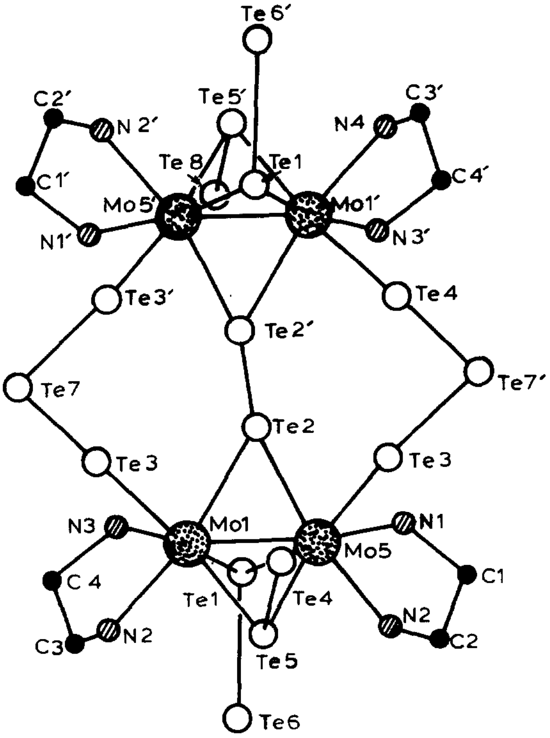


Fig. 22. Structure of the $Mo_4Te_{16}(en)_4^{2-}$ ion [104].

Ti_2Se_4 core adopts a chair conformation and is similar to the W_2Se_4 core in $[W_2(CO)_{10}Se_4][AsF_6]_2$ (Fig. 13).

In the $Mo_4Te_{16}(en)_4^{2-}$ ion [104] (Fig. 22) both type **IIg** and type **IIh** arrangements (Te–Te = 2.841(2) Å) occur. All the Te–Te distances in this complex structure are in the range of the Te–Te single bond value (2.74–2.84 Å).

We have discussed above the ability of Q_2^{2-} units to enter into trimetallic organometallic clusters. An example is the $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_3(Se_2)^+$ cation, in which the Se_2 unit is unsymmetrically bonded to three Fe atoms in a type **IIi** arrangement [106] (Fig. 23). Here the Se–Se bond distance (2.378(2) Å) is much longer than those found in type **IIa–IId** complexes (Table 2). Closely related to this type **IIi** arrangement is one in which one of the metals is replaced by a non-metal, e.g. a halogen. In $(\eta^5\text{-}C_5H_5)Mo(Te_2Br)Fe(CO)_5$ [113] there is a tetrahedral $MoFeTe_2$ core with a Br atom bonded to one Te atom. In $(\eta^5\text{-}C_5H_4Me)(CO)_2MoFe(Te_2SC(S)NEt_2)(CO)_5$ [113] there is a similar arrangement, but the Te–Te bond distances in the two complexes are significantly different (2.807(1) vs. 2.954(1) Å).

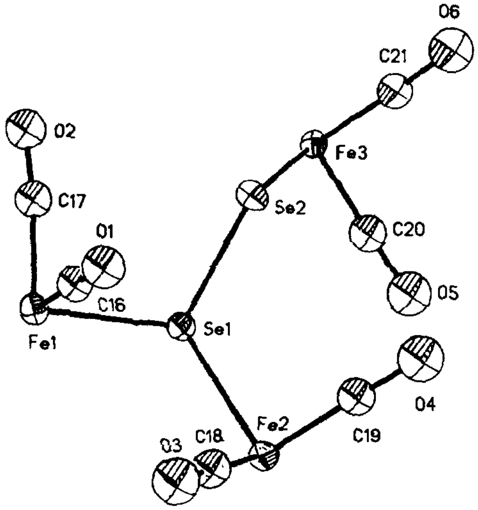


Fig. 23. Structure of the $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_3(Se_2)^+$ cation with C_5H_5 units omitted for clarity [106].

While $(\eta^5\text{-}C_5Me_5)(CO)_2Re(\mu\text{-}Te_2)Re(CO)_2(\eta^5\text{-}C_5Me_5)$ [95] is similar in structure to $(triphos)Rh(\mu\text{-}Se_2)_2Rh(triphos)^{2+}$ [93] (Fig. 17), $(\eta^5\text{-}C_5Me_5)(CO)_2Re(\mu\text{-}Te_2)Mn_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ [95] (Fig. 24) and $(CO)_5W(\mu\text{-}Te_2)[W(CO)_5]_2$ [107] interestingly display the type **IIj** arrangement not known in selenium chemistry. In spite of the additional bonds on the tellurium atoms, the complexes are stable and the Te–Te distances (2.732(1) Å and 2.686(4) Å, respectively) are normal (Table 2).

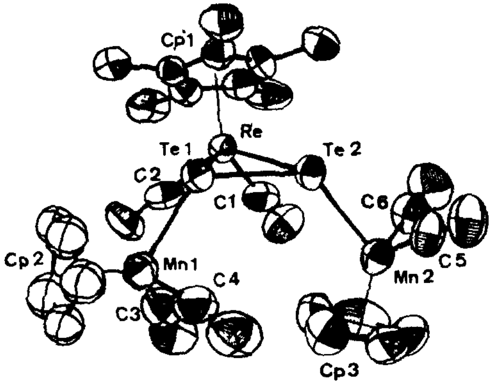
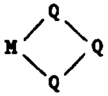


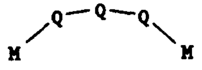
Fig. 24. Structure of the $(\eta^5\text{-}C_5Me_5)(CO)_2Re(\mu\text{-}Te_2)Mn_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ molecule [95].

(iii) Complexes containing Q_3^{2-}

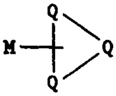
While S_3^{2-} as a ligand is rare in sulfur chemistry [6–9], it appears from recent work that the Se_3^{2-} ligand may be relatively common (Table 3) [19,20,33,36,74,114–122]. The modes of coordination of the Q_3^{2-} ligand are shown below.



IIIa



IIIb



IIIc

Coordination type **IIIa** occurs in the $W_2Se_4(Se_3)_2^{2-}$ [20] (Fig. 25) and the $W_2Se_4(Se_2)(Se_3)^{2-}$ ions [20] (Fig. 6). The Se–Se distance (Table 3) varies from 2.372(9) to 2.64(1) Å. Because of cocrystallization of various similar anions and the resultant disorder of the crystal structures, these distances may not be representative. The puckering of the WSe_3 rings resembles that in cyclobutane. The ring-puckering angles in the W–Se ions are smaller than that in the known S_3^{2-} complex: $W_2Se_4(Se_2)(Se_3)^{2-}$ 23°; $W_2Se_4(Se_3)_2^{2-}$ 25°; $(\eta^5\text{-}C_5Me_5)_2Ti(S_3)$ 49° [123].

A slight variation of type **IIIa** is observed in the $NbTe_{10}^{3-}$ ion [22] (Fig. 26) where the rings interact through a long Te–Te distance (3.132(2)–3.161(2) Å). The intraring Te–Te distances range from 2.825(2) to 2.906(2) Å and can be compared with those found in Te_3^{2-} ions (Table 1).

The structure of $[NBu_4]_4[Hg_4Te_{12}]$ reveals that four coplanar Hg atoms are coordinated in a distorted tetrahedral fashion to μ-Te^{2-}, μ-Te_2^{2-}, and η^3-Te_3^{2-} ligands [105] (Fig. 27). The Te_3^{2-} Hg–Te (two coordinate) distances (range 2.706–2.776, average 2.737 Å) and Hg–Te (three coordinate) distances can be compared with those found in $[K\text{-}2,2,2\text{-crypt}]_2[HgTe_2]$ (2.589 Å) [124] and HgTe (2.79 Å) [125]. In the structure of [K-2,2,2-

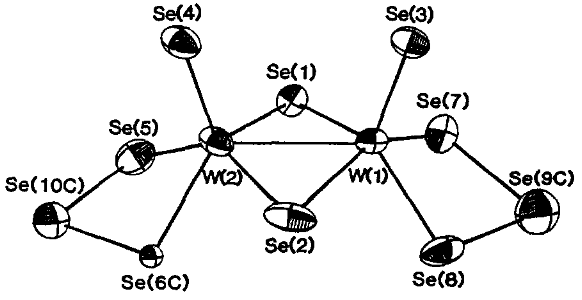
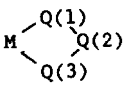
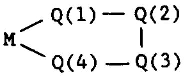


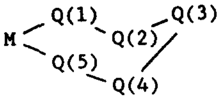
Fig. 25. The $W_2Se_4(Se_3)_2^{2-}$ ion [20].

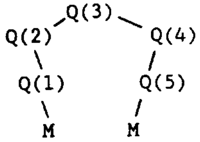
TABLE 3

Q–Q distances in complexes with M–Q_n ($n = 3$–5) rings









Complex	Distance (Å)				Ref.
	Q(1)–Q(2)	Q(2)–(3)	Q(3)–Q(4)	Q(4)–Q(5)	
$[PPh_4]_2[W_2Se_4(Se_3)_2]$	2.57(1)	2.64(1)			20
	2.44(1)	2.372(9)			
$[PPh_4]_2[W_2Se_4(Se_2)(Se_3)]$	2.431(6)	2.402(6)			20
$[IrSe_4(Me_2PCH_2CH_2PMe_2)_2]Cl$	2.340(3)	2.301(5)	2.340(3)		114
	2.305(4)	2.251(7)	2.305(4)		
$[PPh_4]_2[W_2Se_4(Se_2)(Se_4)]$	2.314(7)	2.282(7)	2.327(7)		20
$[NEt_4]_2[Mo(O)(Se_4)_2]$	2.390(1)	2.303(2)	2.446(2)		115
	2.399(2)	2.304(2)	2.425(1)		116
$[PPh_4]_2[Mo(O)(Te_4)_2]$	2.763(2)	2.686(2)	2.838(3)		
$[AsPh_4]_2[W(S)(Se_4)_2]$	2.416(2)	2.300(2)	2.514(2)		115
	2.419(2)	2.301(2)	2.458(2)		
$[PPh_4]_2[W(O)(Te_4)_2]$	2.778(2)	2.682(2)	2.858(2)		116
$[PPh_4]_2[(CO)_4Cr(Te_4)]$	2.751	2.716	2.705		117
$[PPh_4]_2[(CO)_4W(Te_4)]$	2.764(2)	2.719(1)	2.703(1)		117
$[PPh_4]_2[Mo(Se)(Se_4)_2]$	2.384(5)	2.291(3)	2.461(5)		74
	2.395(5)	2.307(5)	2.446(5)		
$[PPN]_2[Au_2Se_2(Se_4)_2]$	2.357(3)	2.304(3)	2.332(3)		33
$[PPh_4]_2[Zn(Se_4)_2]$	2.328(5)	2.341(5)	2.335(5)		118
	2.327(6)	2.424(7)	2.401(7)		
	2.322(5)	2.332(5)	2.330(5)		
	2.325(5)	2.364(5)	2.347(5)		
$[Na(15\text{-crown-}5)]_2[Zn(Se_4)_2]$	2.338(3)	2.321(4)	2.338(3)		119
	2.323(3)	2.334(5)	2.323(3)		
$[Na(15\text{-crown-}5)]_2[Cd(Se_4)_2]$	2.344(4)	2.321(6)	2.344(4)		119
	2.332(4)	2.340(8)	2.322(4)		
$[Na(15\text{-crown-}5)]_2[Hg(Se_4)_2]$	2.331(3)	2.324(4)	2.331(3)		119
	2.313(4)	2.341(5)	2.313(4)		
$[PPh_4]_4[Pd(Te_4)_2]$	Average 2.74(4)				120
$[PPh_4]_4[In_2(Se_4)_4(Se_5)]$ Se_4 ring	2.330(7)	2.334(5)	2.349(6)		36
	2.311(8)	2.289(7)	2.337(5)		
Se_5 chain	2.383(9)	2.322(9)	2.171(9)		
$(\eta^5\text{-}C_5H_5)_2Ti(Se_5)$	2.343(1)	2.337(2)	2.338(2)	2.354(2)	121
$[PPh_4]_2[Fe_2Se_2(Se_5)_2]$	2.345(2)	2.318(2)	2.337(2)	2.347(2)	122
$[NEt_4]_2[V_2(Se_2)_4(Se_5)]$	2.425(3)	2.360(3)	2.339(3)	2.431(3)	19

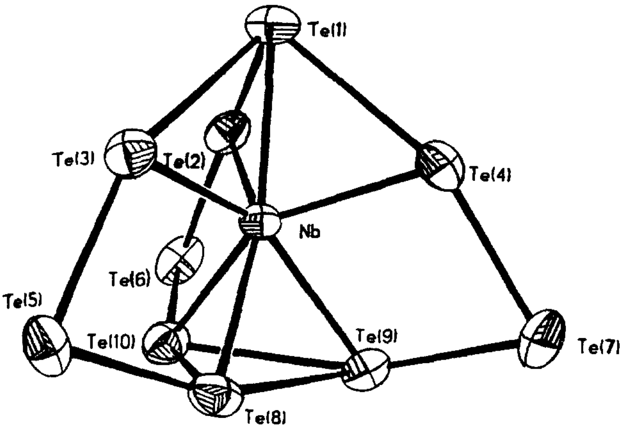


Fig. 26. Structure of the $NbTe_{10}^{3-}$ ion [22].

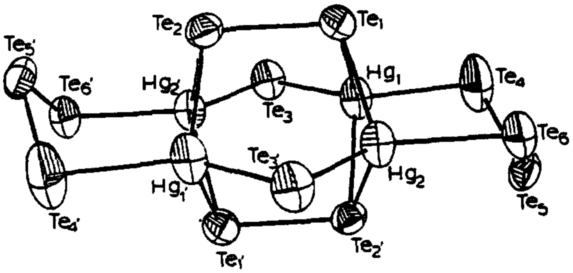


Fig. 27. Structure of the $Hg_4Te_{12}^{4-}$ anion [105].

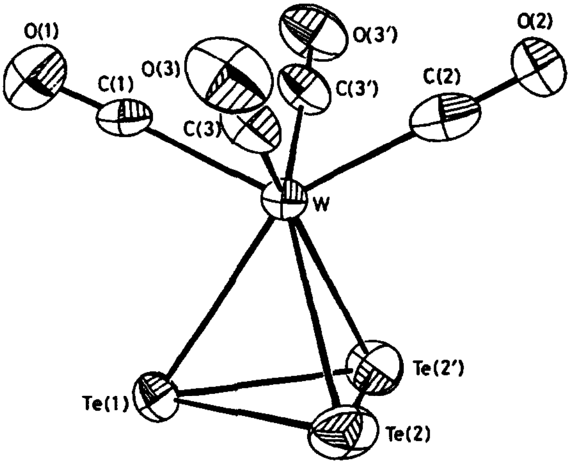


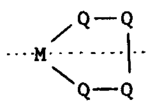
Fig. 28. The $W(CO)_4(Te_3)^{2+}$ cation [126].

crypt)]$_2$[Mo$_4$Te$_{16}$(en)$_4$] [104] (Fig. 22) another example of a type **IIIb** Te_3^{2-} ligand occurs.

While there are apparently no known examples of type **IIIc** Q_3^{2-} ligands, the Te_3^{2+} ligand is known to bond to metals in a type **IIIc** manner, that is in the η^3 fashion reminiscent of the cyclopropenium ion. In [Mo(CO)$_4$(Te$_3$)]-[SbF$_6$]$_2$ [99] and the corresponding tungsten complex [126] this type **IIIc** Te_3^{2+} ligand occurs. In the tungsten complex (Fig. 28), for example, the WTe$_3$ moiety is very symmetric with W–Te bond lengths of 2.802(1). 2.802(1) and 2.817(1) Å, and Te–Te bond lengths of 2.718(1) and 2.736(1) Å. The structure can be compared with compounds containing C$_3$ rings (e.g. (η^5-C$_5$H$_5$)W[η^3-C$_3$(CMe$_3$)$_2$Me](PMe$_3$)Cl$_2$ [127]) or As$_3$ [128] rings bound to a metal center.

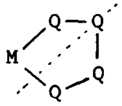
(iv) Complexes containing Q_4^{2-}

Q_4^{2-} ligands are fairly common and bond to metals in the following ways:



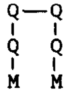
half-chair

IVa



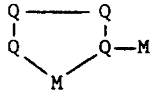
envelope

IVb



symmetrically bridged

IVc



unsymmetrically bridged

IVd

Simple M–Q_4^{2-} complexes have either the "half-chair" (**IVa**) or "envelope" (**IVb**) conformation of the M–Q$_4$ five-membered ring (analogous to the conformations of cyclopentane). In (Ir(Se$_4$)(dmpe)$_2$]Cl [114] the IrSe$_4$ ring has a "half-chair" conformation (**IVa**). The mean Se–Se (2.307 Å) and Ir–Se distances (2.545 Å) are close to those found in the [Ir(Se$_2$)(dppe)]$^+$ cation: Se–Se = 2.312(3) Å and Ir–Se = 2.534(2) Å [90]. The alternation of Se–Se bond distances (Se(external)–Se(internal) = 2.340(3) Å; Se(internal)–Se(internal) = 2.301(5) Å) is similar to that found in other M–Se_4^{2-} complexes (Table 3) but is opposite to that observed in [PPN]$_2$[Se$_4$] (Se(external)–Se(internal) = 2.312(3) Å; Se(internal)–Se(internal) = 2.397(4) Å) [29]. In the Pd(Te$_4$)$_2^{2-}$ anion [120] (Fig. 29), which has an Ni–S analogue [129], the Pd–Te$_4$ ring has the **IVa** conformation. The Pd–Te distances (average 2.59(2) Å and Te–Te distances within the Te$_4$ ring (average 2.74(4) Å) are normal.

A series of polyselenido complexes with the general formula [Na(15-crown-5)]$_2$[M(Se$_4$)$_2$], (M = Zn, Cd or Hg) has been synthesized [119]. In these complexes the metal atom is approximately tetrahedrally coordinated to two Se_4^{2-} ligands (type **IVb**). The angle between the MSe$_2$ planes is 73°,

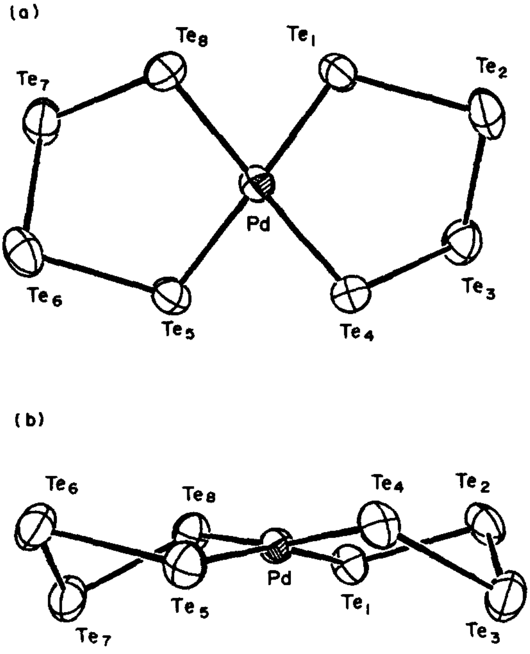


Fig. 29. Two views of the $Pd(Te_4)^{2-}$ anion [120].

rather than the expected 90° for a tetrahedron. These anions are very similar to a sulfur analogue (M = Zn) [130].

The binuclear complex $[PPN]_2[Au_2Se_2(Se_4)_2]$ [33] (Fig. 30) consists of two non-bonding Au atoms (3.660(1) Å apart) bridged by two Se^{2-} and liganded by Se_4^{2-} groups to afford type **IVb** coordination. The Au^{3+} centers show the expected square-planar geometry. The variation between the Se(external)-Se(internal) and Se(internal)-Se(internal) bonds is more pronounced than in the Se_4 complexes of the zinc group (Table 3). Type **IVb** rings are also known for the Te_4^{2-} ligand in $[PPh_4]_2[(CO)_4Cr(Te_4)]$ (Fig. 31) and $[PPh_4]_2[(CO)_4W(Te_4)]$ [117].

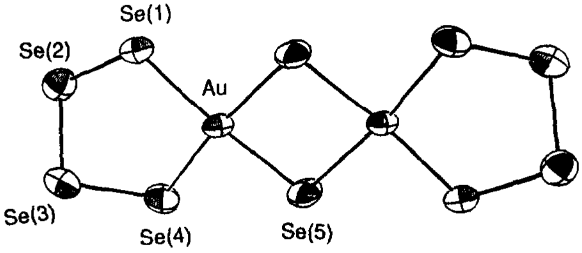


Fig. 30. The $Au_2Se_2(Se_4)_2^{2-}$ anion [33].

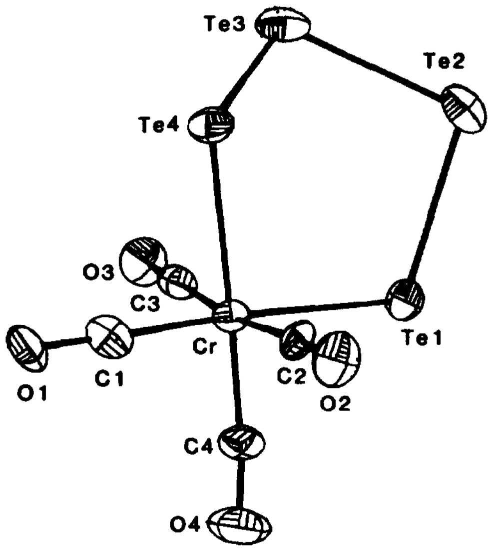


Fig. 31. Structure of the $(CO)_4Cr(Te_4)^{2-}$ anion [117].

The complete series $MQ(Se_4)_2^{2-}$ (M = Mo or W; Q = O, S or Se) has been synthesized and $[NEt_4]_2[MoO(Se_4)_2]$ [115], $[PPh_4]_2[MoSe(Se_4)_2]$ [74], and $[AsPh_4]_2[WS(Se_4)_2]$ [115] (Fig. 32) have been characterized structurally. Analogous W–S complexes are not known. The metal atoms are displaced from the basal planes toward the apical O or S atoms by 0.760 and 0.754 Å in $MoO(Se_4)_2^{2-}$ and $WS(Se_4)_2^{2-}$ respectively [115]. The $M–Se_4$ rings are puckered (type **IVb**) and show alternation in Se–Se bond distances (Table 3) as observed in analogous sulfur complexes [131]. In the sulfur systems, π bonding between the sulfur and the metal atom has been proposed to explain this alternation [132]. The $MoO(Te_4)_2^{2-}$ and $WO(Te_4)_2^{2-}$ ions [116] are essentially isostructural to their $MQ(Se_4)_2^{2-}$ analogues [74,115]. The

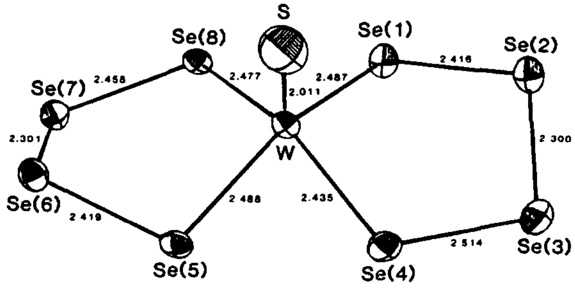


Fig. 32. The $WS(Se_4)_2^{2-}$ anion [115].

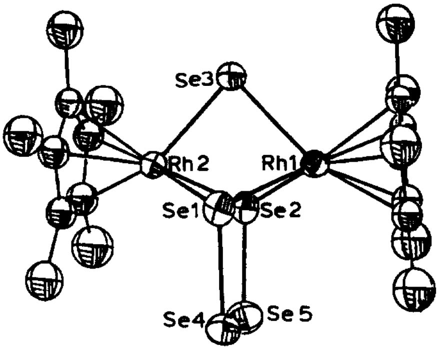


Fig. 33. The $(\eta^5\text{-}C_5Me_5)_2Rh_2Se_5$ molecule [133].

Mo–Te distances (average 2.697 Å) are slightly longer than the W–Te distances (average 2.685 Å). The differences in length between the Te(external)–Te(internal) and Te(internal)–Te(internal) distances are much larger than for the selenium analogues (Table 3).

There are examples where a Q_4^{2-} ligand is bonded to a second metal atom either symmetrically (type **IVe**) or unsymmetrically (type **IVd**). Examples of type **IVc** are the complexes $(\eta^5\text{-}C_5Me_5)_2M_2Se_5$ (M = Co or Rh) [133]. The molecule $(\eta^5\text{-}C_5Me_5)_2Rh_2Se_5$ (Fig. 33) consists of two Rh atoms bridged by two types of selenide ligands, an Se^{2-} and a nearly planar Se_4^{2-} ligand. The Se(1)–Se(2) distance is 3.115(2) Å.

Type **IVd** coordination occurs in the one-dimensional polymer $[(PPh_4)AgSe_4]_n$ [134] (Fig. 34). This polymeric anion consists of trigonal planar Ag atoms with two different intraring Ag–Se bonds (2.672(2) and 2.553(2) Å) and a much shorter interring Ag–Se bond (2.545(2) Å). The Se–Se distances within the Se_4^{2-} ligand (2.360(3), 2.339(3) and 2.358(4) Å) are similar to those found in $[PPN]_2[Se_4]\cdot 4$ MeCN (Table 1). A similar bridging mode of M–Q_4–M coordination has been observed in the

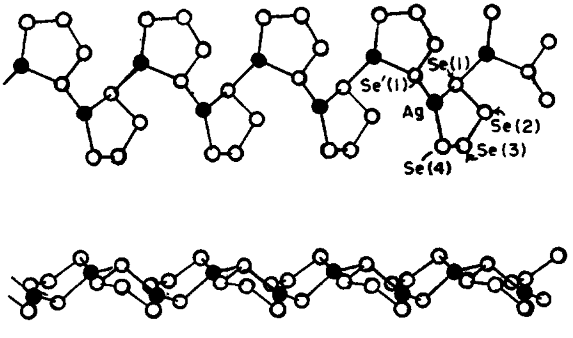


Fig. 34. Two views of the $[Ag(Se_4)]_n^{n-}$ chain [134].

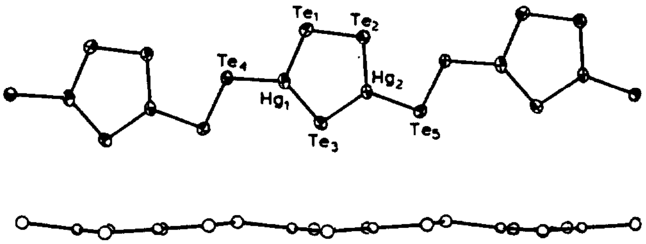


Fig. 35. Two views of the ${}^{1}_{\infty}[Hg_2Te_5]^{2-}$ chain [105].

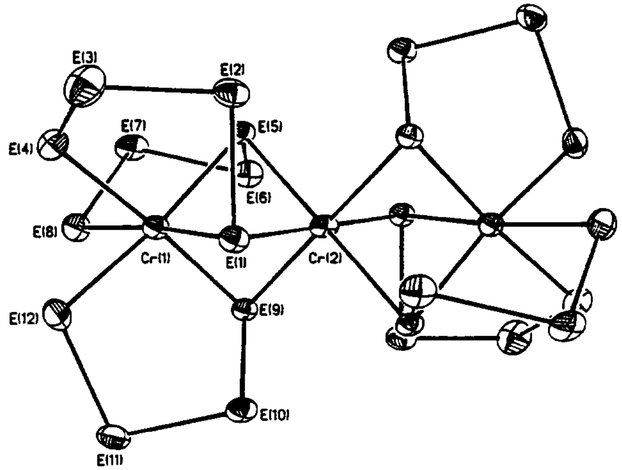


Fig. 36. View of the $Cr_3Q_{24}^{3-}$ ion (Q = Se or Te) [21].

$Mn_2(CO)_6(Se_4)_2^{2-}$ ion [135] and in the polysulfide complex $[Cu(S_4)]_3^{3-}$ [136]. The Ag–Se polymer may be compared with the one-dimensional Hg–Te polymer, $[(PPh_4)_2Hg_2Te_5]_n$ [105] (Fig. 35).

Type **IVd** coordination is also encountered in $[PPh_4]_2[Cr_3Se_{24}]$ [21] and $[PPh_4]_3[Cr_3Te_{24}]$ [21] (Fig. 36). The anions consist of three octahedrally coordinated Cr atoms linked by six bidentate Q_4^{2-} units. In the selenide, typical Se–Se distances (for example, in one ring 2.378(13), 2.317(13) and 2.368(15) Å) can be compared with the similarly coordinated type **IVd** Se_4^{2-} ligand in $[(PPh_4)AgSe_4]_n$ (2.360(3), 2.339(3) and 2.358(4) Å) [134]. In the $Cr_3Te_{24}^{3-}$ anion the Cr–Te and Te–Te distances (average 2.767 and 2.719 Å) resemble those in the solid state layer compound $CrTe_3$ (2.82 Å) [137].

(v) Complexes containing Q_5^{2-}

The four compounds known that contain the Q_5^{2-} ligand are all selenides; the coordination modes are shown below:

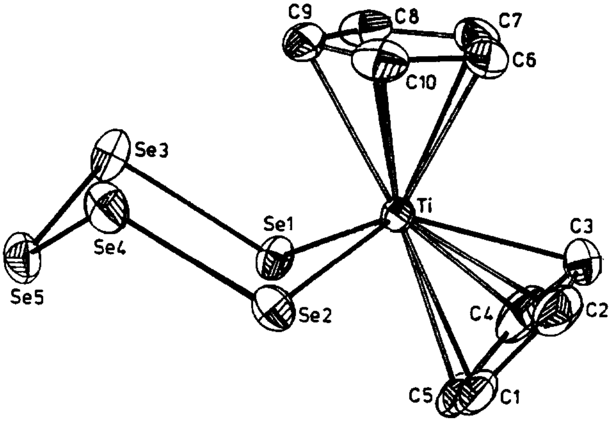
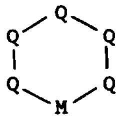
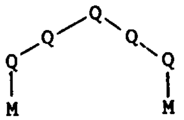


Fig. 37. Structure of the $(\eta^5\text{-}C_5H_5)_2Ti(Se_5)$ molecule [121].



Va



Vb

In $(\eta^5\text{-}C_5H_5)_2Ti(Se_5)$ [121] (Fig. 37), for which there is a sulfur analogue [138], type **Va** coordination occurs. The $TiSe_5$ ring is in the chair conformation with an average dihedral angle of 72.3°. As opposed to trends noted earlier in smaller rings, the Se–Se distances are essentially constant (2.337(2)–2.354(2) Å). The Se–Ti–Se bite angle (95.4(1)°) is smaller than that observed for the $FeSe_5$ rings of the $Fe_2Se_2(Se_5)_2^{2-}$ anion (108.61(7)°) [122] (Fig. 38). These rings are also of type **Va**. The Se–Se distances are again equal and are typical of those in Se_8 rings.

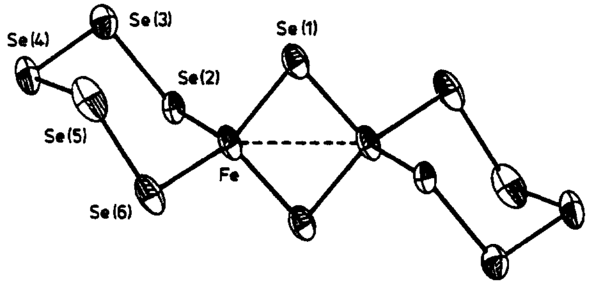


Fig. 38. Structure of the $Fe_2Se_2(Se_5)_2^{2-}$ ion [122].

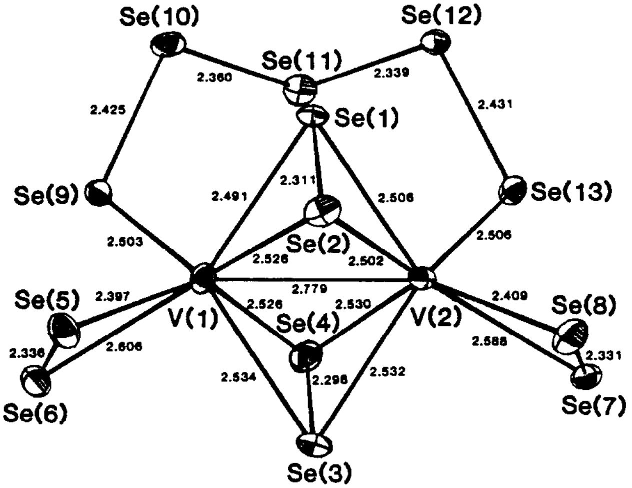


Fig. 39. Structure of the $V_2(Se_2)_4(Se_5)^{2-}$ anion [19].

$[NH_4]_3[VSe_4]$ [3] and $[NEt_4]_2[V_2(Se_2)_4(Se_5)]$ [19] are the only known purely inorganic soluble vanadium selenides. The $V_2(Se_2)_4(Se_5)^{2-}$ ion (Fig. 39) features two heptacoordinated V atoms (2.779(5) Å apart) bridged by two Se_2^{2-} units and a type **Vb** Se_5^{2-} chelate. Each V atom is also coordinated to an η^2-Se_2^{2-} ligand, thereby generating a $[V_2(\mu\text{-}\eta^2\text{-}Se_2)_2(\eta^2\text{-}Se_2)_2]$ core that has also been observed in the pseudo-one-dimensional polymer $[V_2Se_9]_x$ [139]. Type **Vb** Q_5^{2-} ligation occurs also in sulfur chemistry, e.g. in the anions $Mo_2(NO)_2(S_2)_3(S_5)(OH)^{3-}$ [140] and $Nb_2(O)(OMe)_2(S_2)_3(S_5)^{2-}$ [141]. The anion $V_2(Se_2)_4(Se_5)^{2-}$ can also be compared with the $In_2(Se_4)_4(Se_5)^{4-}$ ion [36] (Fig. 40), where the Se_5^{2-} ligand is again of type **Vb**. In both these examples of type **Vb** coordination the external Se–Se distances are greater than the internal ones.

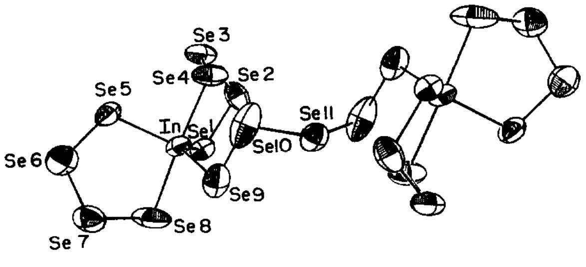
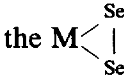


Fig. 40. The $In_2(Se_4)_4(Se_5)^{4-}$ anion [36].

D. SPECTROSCOPY

Unlike the identification of metal sulfides, identification of selenides on the basis of the ν(M–Se$_{\text{ring}}$) and ν(Se–Se) modes is not an easy task as these modes fall in the same low frequency IR region (200–340 cm^{-1}). Where only the  $\mathrm{M}\langle{}^{\mathrm{Se}}_{\mathrm{Se}}|$ group is present along with other ligands, the absorbance in the range 320–340 cm^{-1} has been unambiguously assigned to ν(Se–Se) [90]. From this information it has been possible, in some cases, to interpret the IR spectra of metal selenide monomers and oligomers. For example, the $W_2Se_{10}^{2-}$/$W_2Se_9^{2-}$ anion mixture exhibits absorptions at 330 and 280 cm^{-1}; these have been assigned to ν(Se–Se) and ν(W–Se) respectively [20]. Raman spectroscopy should prove to be very helpful in identifying the different modes of vibration.

The tetraselenometallates MSe_4^{n-} ($n = 2$ or 3; M = Mo, W, V, Nb or Ta) show intense bands in their UV–visible absorption spectra. The band positions and their origins have been discussed previously [3]. Some heterometallic clusters show very intense bands in their UV–visible spectra: $Ni(Se_2)(WSe_4)^{2-}$ 510, 472, 364 and 336 nm; $Ni(WSe_4)_2^{2-}$ 512, 394 and 332 nm; $Pd(WSe_4)_2^{2-}$ 470, 388, 364 and 326 nm; $Pt(WSe_4)_2^{2-}$ 488, 355 and 335 nm) [88]. These absorptions can be compared with those of WSe_4^{2-} (463, 316, 242 nm) [3]. The selenium-rich monomers $MQSe_8^{2-}$ (Q = O, S or Se) and oligomers $W_3QSe_8^{2-}$ (Q = O or Se), $W_2Se_9^{2-}$ and $W_2Se_{10}^{2-}$ show no characteristic bands in their UV–visible spectra [20]. Transition metal tellurides are also usually UV–visible silent [116,117].

Fortunately, selenium and tellurium both have NMR-active nuclei (^{77}Se: spin 1/2; natural abundance = 7.6%; receptivity/^{13}C = 2.98. ^{125}Te (^{123}Te): spin 1/2 in both the cases; natural abundance, 7% (0.89%); receptivity, 12.5 (0.89)) [142]. The use of NMR spectroscopy has proved extremely valuable in the study of selenium- and tellurium-containing species in solution; no comparable structural tool exists for metal sulfides.

The ^{77}Se NMR technique has been applied successfully in the characterization of organic polyselenides [143], Zintl anions [144], selenocations [70–72] and, recently, homometallic and heterometallic selenides [20,75,88,115]. The selenium chemical shifts of a large number of organic [145,146] and organometallic compounds [103,133,147–156] and a few purely inorganic monomers and oligomers have been reported in the literature [20,75,88,115]. The chemical shifts (referenced to Me_2Se and Me_2Te) and coupling constants (wherever available) for representative compounds are listed in Table 4 [20,67,69,75,88,95,103,115,116,118,133,144,148,153,155,157,159–164]. It is evident from the data in Table 4 that the range of chemical shifts is very wide (ca. 3000 ppm) and the chemical-shift pattern is complex. However, an

TABLE 4

Chemical shifts and coupling constants for selenium- and tellurium-containing compounds

Compound	Solvent	δ ^{a} (ppm)	J (Hz)	Ref.
Me_2Se	Liquid	0	–	157
$K(Se_2CN\text{-}{}^iBu_2)$	D_2O	582	–	148
$Ni(Se_2CNEt_2)_2$	$CDCl_3$	386	–	148
$Pd(Se_2CNEt_2)_2$	$CDCl_3$	265	–	148
$Pd(Se_2CN\text{-}{}^iBu_2)_2$	$CDCl_3$	378	–	148
$Ni(Se_2CN\text{-}{}^iBu_2)_2$	$CDCl_3$	401	–	148
$Pt(Se_2CN\text{-}{}^iBu_2)_2$	$CDCl_3$	415	Pt–Se, 111.7	148
$Zn(Se_2CN\text{-}{}^iBu_2)_2$	$CDCl_3$	668	–	148
$Zn(Se_2CNEt_2)_2$	$CDCl_3$	648	–	148
$Cd(Se_2CN\text{-}{}^nBu_2)_2$	$CDCl_3$	717	–	148
CSe_2	CH_2Cl_2	299	–	148
KSeCN	EtOH	–322	–	148
$[NEt_4]_2[MoSe_4]$	DMF	1643	–	115
$[NH_4]_2[WSe_4]$	DMF	1235	W–Se, 52	20
$[NEt_4]_2[MoSe(Se_4)_2]$	DMF	t, 2357	–	115
		m, 1163	–	
		r, 403	–	
$[AsPh_4]_2[WSe(Se_4)_2]$	DMF	t, 1787	–	115
		m, 1034	W–Se, 108	
		r, 324		
$[NEt_4]_2[MoS(Se_4)_2]$	DMF	m, 1122	–	115
		r, 396	–	
$[AsPh_4]_2[WS(Se_4)_2]$	DMF	m, 993	W–Se, 106	115
		r, 313		
$[NEt_4]_2[MoO(Se_4)_2]$	DMF	m, 946		115
		r, 380	–	
$[AsPh_4]_2[WO(Se_4)_2]$	DMF	m, 828	W–Se, 98	115
		r, 280	–	
$[PPh_4]_2[Ni(Se_2)(WSe_4)]$	DMF	t, 1399	–	88
		b, 855	W–Se, 109	
		r, 608	Se–Se, 138	
$[PPh_4]_2[Ni(WSe_4)_2]$	DMF	t, 1628	–	88
		b, 994	W–Se, 112	
$[PPh_4]_2[Pd(WSe_4)_2]$	DMF	t, 1673	–	88
		b, 1135	W–Se, 119	
$[PPh_4]_2[Pt(WSe_4)_2]$	DMF	t, 1627	–	158
		b, 949	Pt–Se, 470	
$[PPh_4]_2[W_2Se_6]$	DMF	t, 1559	–	75
		b, 591	W–Se, 575	
$[PPh_4]_2[Zn(Se_4)_2]$	DMF	m, 598	–	118
		r, 127		

TABLE 4 (continued)

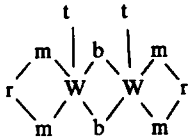
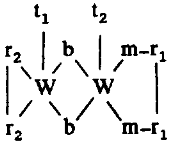
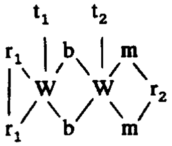
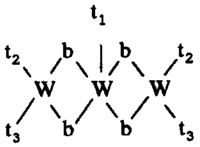
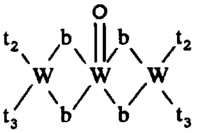
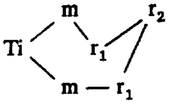
Compound	Solvent	δ ^a (ppm)	J (Hz)	Ref.
$[PPh_4]_2[W_2Se_4(Se_3)_2]$	DMF	t, 1897	–	20
or		b, 864	W–Se, 92	
		m, 605	W–Se, 48	
		r, 190	–	
$[PPh_4]_2[W_2Se_4(Se_2)(Se_4)]$	DMF	t_1, 1940	–	20
or		t_2, 2086	–	
		b, 858	W–Se, 83	
		m, 799	W–Se, 89	
		r_1, 554	–	
		r_2, 131	W–Se, 69	
$[PPh_4]_2[W_2Se_4(Se_2)(Se_3)]$	DMF	t_1, 1926	–	20
or		t_2, 1787	–	
		b, 859	W–Se, 85	
		m, 625	W–Se, 47	
		r_1, 132	W–Se, 70	
		r_2, 152	–	
$[PPh_4]_2[W_3Se_9]$	DMF	t_1, 2262	–	20
or		t_2, 1739	–	
		t_3, 1618	–	
		b, 889	W–Se, 112, 90	
$[PPh_4]_2[W_3OSe_8]$	DMF	t_2, 1653	–	20
or		t_3, 1540	–	
		b, 731	W–Se, 113, 66	
$(\eta^5\text{-}C_5H_4\text{-}{}^iPr)_2Ti(Se_5)$	CH_2Cl_2	m, 1147		103
or		r_1, 688		
		r_2, 610		
$[(\eta^5\text{-}C_5H_4\text{-}{}^iPr)_2Ti]_2Se_4$	CH_2Cl_2	1412		103
$Ti(Se_2C_2(COOMe)_2(\eta^5\text{-}C_5H_5)_2$	$CDCl_3$	1001		159

TABLE 4 (continued)

Compound	Solvent	δ [a] (ppm)	*J* (Hz)	Ref.
$[AsPh_4]_2[W(Se_2C_2(COOMe)_2)_3]$	DMF	839	W–Se, 34	160
$[PPh_4]_2[W_2Se_2(Se_2C_2(COOMe_2)_4]$	DMF	Bridging, 1360	W–Se, 38	160
		Ligand, 874	–	
$(\eta^5\text{-}C_5Me_5)_2Co_2Se_5$	$CDCl_3$	618.6		133
		779.1		
$(\eta^5\text{-}C_5Me_5)_2Rh_2Se_5$	$CDCl_3$	485.2		133
		783.1		
$(\eta^5\text{-}C_5H_5)_2Ti(SePh)_2$	$CDCl_3$	549.9		155
$(\eta^5\text{-}C_5H_5)_2Zr(SePh)_2$	$CDCl_3$	672.9		155
$(\eta^5\text{-}C_5H_5)_2Hf(SePh)_2$	$CDCl_3$	847.1		155
$(\eta^5\text{-}C_5H_4\text{-}{}^tBu)_4Zr_2(\mu\text{-}Se)_2$	$CDCl_3$	802.6		155
$HgSe_2^{2-}$	en	−142.3	Hg–Se, 2258	144
$HgSeTe^{2-}$	en	Se, −30.5	Hg–Se, 2270	144
		Te, −1495	Hg–Te, 6470	
$HgTe_2^{2-}$	en	−726	Hg–Te, 6500	144
$CdTe_2^{2-}$	en	−1159	Cd–Te, 2148	144
$Zn(SePh)_4^{2-}$	MeOH	15.7	–	153
$Pb_2Se_3^{2-}$	en	−99.4	Pb–Se, 149	161
$Pb_2Te_3^{2-}$	en	−927.1	Pb–Te, 1070	161
Se_4^{2+}	30% oleum	1958		69
Se_8^{2+}	30% oleum	−106.1	64, 41	67
		219.3	152, 65, 35	
		668.0	248, 153, 84	
		−231	247, 86, 37	
		−256.3	All < 40	
Me_2Te	Liquid	0		162
Te_6^{2+}	30% oleum	152		69
Te_4^{2+}	30% oleum	2811		69
$Te_2Se_2^{2+}$	30% oleum	Se, 1638		69
		Te, 3102		
$[PPh_4]_2[MoO(Te_4)_2]$ [b]	DMF	717		116
		89		
$[PPh_4]_2[WO(Te_4)_2]$ [b]	DMF	−120		116
		−903		
$[PPh_4]_2[MoO(Te_2C_2(COOMe)_2)_2]$ [b]	DMF	71		116
$(\eta^5\text{-}C_5Me_5)Re(CO)_2H(TeH)$	Toluene-d_8	−901.3	^1H, 151	95
			^1H, 16	
$\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}_2(\eta^2\text{-}Te_2)$	Toluene-d_8	−200.3	–	95
		434.4	–	
$\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}_2(\mu\text{-}Te)$	Toluene-d_8	613.7	–	95

TABLE 4 (continued)

Compound	Solvent	δ ^a^ (ppm)	J (Hz)	Ref.
$\{(\eta^5\text{-}C_5Me_5)Re(CO)_2\}_2(\mu\text{-}Te)_2$	Toluene-d_8	−510	-	95
$\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2(Te_2)(\eta^5\text{-}C_5Me_5)Re(CO)_2$	Toluene-d_8	848		95
$Fe_2(Te_2)(CO)_6$		−733		163
$[(\eta^5\text{-}C_5H_5)MoFeTe_2(CO)_5][SbF_6]$	$CDCl_3$	−839		164
$(\eta^5\text{-}C_5H_5)Mo_2FeTe_2(CO)_7$	$CDCl_3$	−1092		164
$Fe_3Te_2(CO)_9(PPh_3)$	$CDCl_3$	−887, −938	-	164
$Fe_3Te_2(CO)_7(PPh_3)_2$	$CDCl_3$	1123		164
$Cp_2Mo_2FeTe_2(CO)_3(C_2H_2)$	$CDCl_3$	931		164

[a] t, Terminal; b, bridging; m, metal bound; r, ring. [b] Chemical shifts referenced to $Te(OH)_6$ in H_2O.

approximate scale for soluble tungsten and molybdenum selenides has been deduced: terminal Se $\delta > 1000$ ppm; bridging Se $1100 \leqslant \delta \leqslant 600$ ppm; metal-bound Se (in an MSe_n ring) $1100 \leqslant \delta \leqslant 500$ ppm; and ring Se (in an MSe_n ring), $\delta \leqslant 400$ ppm [88,115]. If the selenium atom is bound to an NMR-active nucleus, J–J coupling may be observed. This scale has proved to be very useful. For example, the correct structure (as confirmed by an X-ray study) was deduced for the $Ni(Se_2)(WSe_4)^{2-}$ anion from ^{77}Se NMR chemical-shift data [88]. The chemical shifts for metal-bound and ring selenium nuclei in molybdenum compounds are downfield relative to the analogous tungsten compounds (Table 4). There is probably greater orbital overlap between selenium and molybdenum which leads to increased deshielding. In both molybdenum and tungsten complexes, the substitution of selenium by sulfur or oxygen results in upfield shifts of the remaining selenium resonances, i.e. δ $MSe(Se_4)_2^{2-} > MS(Se_4)_2^{2-} > MO(Se_4)_2^{2-}$. The availability of low lying vacant d orbitals on selenium and sulfur atoms favors greater overlap with the metal atom.

The $MQ(Se_4)_2^{2-}$ series of compounds have puckered MSe_4 rings. The solution (DMF) NMR spectrum shows only one resonance for each type of site for each compound; the puckered rings are fluxional at room temperature in solution. Cooling of the solution to −60 °C did not affect the spectrum. However, the attempt to resolve the axial and equatorial selenium resonances for the $W_2Se_2(Se_2C_2(COOMe)_2)_4^{2-}$ anion (distorted octahedral) was successful [160]. This anion displays a two-line ^{77}Se NMR spectrum at room temperature. The resonance at 874 ppm is assigned to diselenene by analogy with $W(Se_2C_2(COOMe)_2)_3^{2-}$ ($\delta = 839$ ppm) and the resonance at

1360 ppm is then assigned to bridging selenium atoms. However, the variable-temperature ^{77}Se NMR spectrum shows that this resonance at 874 ppm collapses by $-40\,°C$ and then reappears on further cooling ($-90\,°C$) as two broad resonances of equal intensity at 754 and 967 ppm. The low temperature spectrum is consistent with the solid state structure.

^{77}Se NMR spectroscopy has also been useful in monitoring reactions in solution. For example, the anion $Ni(WSe_4)_2^{2-}$ ($\delta = 1628$, 994 ppm) was found to decompose slowly in solution (DMF) to give three additional lines corresponding to $Ni(Se_2)(WSe_4)^{2-}$ ($\delta = 1399$, 855, 608 ppm) [88].

The chemical shifts and coupling constants of representative tellurium-containing species are given in Table 4. Although the chemical-shift range for ^{125}Te (and ^{123}Te) nuclei is very wide (ca. 4000 ppm), NMR spectroscopy has been used successfully to determine the structures of cationic tellurides, Se–Te mixed cations [74], a large number of organometallic compounds [145,164,165] and, very recently, a few soluble metal tellurides [116]. For example, the oxytelluride anions $MO(Te_4)_2^{2-}$ display two resonances of equal intensity (Table 4). The resonances at 717 ppm (M = Mo) and -120 ppm (M = W) are far downfield of the other resonance (i.e. 89 and -903 ppm). From previous assignments to analogous selenium anions [115], these low field signals have been assigned to metal-bound tellurium; the remaining peak in each case is assigned to the ring tellurium which is not bound to metal.

E. SYNTHESES

We summarize some of the more general routes to the synthesis of soluble metal selenides and tellurides. As the field expands, undoubtedly new and more efficient routes will be developed.

(i) Reaction of metal salts or metal carbonyls with M_2Q_n (M = Li, Na, K, Rb or Cs; Q = Se or Te; n = 1–5)

This is the most common method. Many selenides and tellurides have been synthesized by reacting metal salts or carbonyls with M_2Q_n in polar non-aqueous solvents [21,121], e.g.

$$Cr^{3+} + 2\,Q_4^{2-} \xrightarrow[RT]{DMF} 1/3[Cr_3Q_{24}]^{3-} \qquad (1)$$

$$Cp_2TiCl_2 + Na_2Se_5 \xrightarrow[RT]{EtOH} Cp_2TiSe_5 + 2\,NaCl \qquad (2)$$

In some cases the polyselenide is generated in situ and then reacted with the appropriate metal salt [122], e.g.

$$2\,FeCl_2 + 12\,Se + 6\,Na \xrightarrow[70\,°C]{DMF} Na_2[Fe_2Se_2(Se_5)_2] + 4\,NaCl \qquad (3)$$

(ii) Reaction of metal complexes with Se or SeS_2

Abstraction of sulfur or selenium by many complexes to afford chalcogen-rich compounds is well known [89,79].

$$Os(CO)_2(PPh_3)_2 + 2\ Se \xrightarrow[RT]{benzene} Os(Se_2)(CO)_2(PPh_3)_2 \tag{4}$$

$$2\ CpCr(CO)_3 + 2\ Se \xrightarrow[RT]{THF} Cp_2Cr_2(CO)_4(Se_2) \tag{5}$$

Analogous to sulfur chemistry, terminal selenium ligands react with Se_8 to afford MQ_x rings [20,115]:

$$2\ WSe_4^{2-} + 2\ Se \xrightarrow[reflux]{CH_3CN} W_2Se_{10}^{2-} \tag{6}$$

$$WSe_4^{2-} + 5\ Se \xrightarrow[RT]{DMF} WSe(Se_4)_2^{2-} \tag{7}$$

Under similar conditions, the use of SeS_2 gives $WS(Se_4)_2^{2-}$.

(iii) Reaction of oxymetallates with H_2Se

$MoSe_4^{2-}$ and WSe_4^{2-} were first synthesized by saturating an alkaline solution of MO_4^{2-} with H_2Se [3]. H_2Se has also been used in the synthesis of other selenides, e.g. $(\eta^5\text{-}C_5H_5)_2V_2Se_5$ [100].

(iv) Reaction of oxymetallates with $(R'R_2Si)_2Q$ ($R = CH_3$; $R' = CH_3$ or C_8H_{17}; $Q = Se$ or Te)

An improved method of preparing MSe_4^{2-} ($M = Mo$ or W) is to react MO_4^{2-} with $(Me_2(octyl)Si)_2Se$ [115]. Use of this reagent with $(NH_4)_3VO_4$ affords the $V_2(Se_4)_2(Se_5)^{2-}$ ion [19]. A number of metal-rich chalcogen clusters have been prepared with the use of $(Me_3Si)_2Q$ [17].

(v) Reaction of metal complexes with COSe, CSe_2, Se_2Cl_2, or SeO_3^{2-}

There are a few examples where these reagents have been used. Reaction of $CpMn(CO)_2(OC_4H_8)$ with COSe leads preferentially to the binuclear complex $Cp_2Mn_2(CO)_4Se_2$ [166]. (triphos)RhCl reacts with CSe_2 to give (triphos)RhCl(η^2-CSe_2) which on treatment with PEt_3 and oxidation in air gives the dimer $(triphos)_2Rh_2(\mu\text{-}Se_2)_2^{2+}$ [93]. The $Cp_2Cr(CO)_3^-$ ion reacts with Se_2Cl_2 and SeO_3^{2-} to give $Cp_2Cr_2(CO)_4(Se_2)$ and $Cp_2Cr_2(CO)_4Se$ respectively [167].

(vi) Reaction of metal carbonyls with chalcogen cations

When $M(CO)_6$ ($M = Mo$ or W) is allowed to react with Q_4^{2+}, different types of compounds are formed depending on the nature of Q [99]:

$$2M(CO)_6 + Se_4^{2+} \xrightarrow[RT]{SO_2} M_2(Se_4)(CO)_{10}^{2+} + 2\ CO \qquad (8)$$

$$M(CO)_6 + Te_4^{2+} \xrightarrow[RT]{SO_2} M(Te_3)(CO)_4^{2+} + 2\ CO + Te \qquad (9)$$

The $FeW(Se_2)(CO)_8^{2+}$ cation was obtained by treating a mixture of $W(CO)_6$ and $Fe_2(CO)_9$ in SO_2 with $[Se_4][SbF_6]_2$ [99].

(vii) Transfer of selenium from metal selenides

Examples [86,168] of the transfer of selenium from metal selenides include

$$4NbBr_4(NCMe)_2 + Sb_2Se_3 \xrightarrow[50\,^\circ C,\ 7\ days]{MeCN} Nb_4Br_{10}Se_3(NCMe)_4 + 2SbBr_3 \qquad (10)$$

$$(Por)TiF_2 + Cp_2TiSe_5 \xrightarrow[reflux]{toluene} (Por)TiSe_2 + byproducts \qquad (11)$$

As observed for sulfides [6,9], the size of the resultant selenide or telluride ring does not depend on the starting metal chalcogenide; it is the metal that chooses the appropriate component of the polychalcogenide mixture [21,22].

Some interesting metal chalcogenides have been isolated by the extraction of solid state compounds in polar organic solvents. $[PPN]_2[Au_2Te_4]$ was obtained by layering [PPN]Cl in en over an en extract of compounds of nominal composition $KAuTe_2$ or $K_2AuAsTe_3$ or $K_3AuGeTe_3$ [169]. The dissolution of K_3AuTe_2 in H_2O–MeOH–DMF and the addition of PPh_4Cl to the solution gives $[PPh_4]_4[KAu_9Te_7]$ and $[PPh_4]_2[K_3Au_4Te_4] \cdot 2DMF \cdot 2CH_3OH$ [84]. Use of en gives $[PPh_4]_2[K_3Au_4Te_4(en)_4]$ [84]. Similarly, $K_2Hg_2Te_3$ dissolves in en to give $[NBu_4]_4[Hg_4Te_{12}]$ or the one-dimensional polymer $[PPh_4]_2[Hg_2Te_5]$, depending upon the cation used [105].

F. REACTIVITY

As opposed to metal sulfides, the reaction chemistry of soluble metal selenides and tellurides is not well developed. We and others have carried out a few reactions; these are summarized below.

(i) Reaction of soluble metal chalcogenides with activated acetylenes

$Cp_2Ti(Se_5)$, $WSe(Se_4)_2^{2-}$, $W_2Se_{10}^{2-}$ and $MoO(Te_4)_2^{2-}$ react with $RC{\equiv}CR$ ($R = COOMe$) rapidly for selenides and slowly for the telluride to give diselenene and ditellurene complexes respectively [116,159,160]. For example

$$WSe(Se_4)_2^{2-} + RC\equiv CR \xrightarrow[RT]{DMF} W(SeRC{=}CRSe)_3^{2-} \tag{12}$$

The mechanism of these reactions is not understood.

(ii) Reaction of soluble metal chalcogenides with BH_4^- and CN^-

$[PPh_4]_2[W_2Se_{10}]$ reacts with $NaBH_4$ or KCN in DMF to give $[PPh_4]_2[W_2Se_6]$ [75]

$$W_2Se_{10}^{2-} + BH_4^-(\text{excess}) \xrightarrow[24\ h,\ RT]{DMF} W_2Se_6^{2-} + \text{byproducts} \tag{13}$$

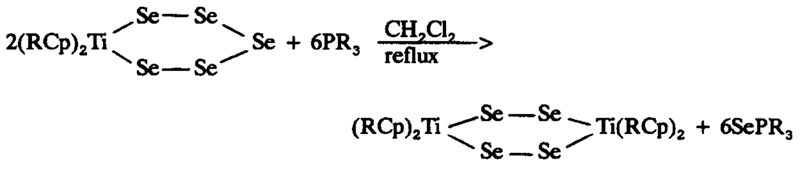
This one-step reaction can be compared with the reaction of $Mo_2Se_{10}^{2-}$ with $NaBH_4$ to give $Mo_2S_7^{2-}$, which in turn reacts with PPh_3 to yield the $Mo_2S_6^{2-}$ anion [170].

(iii) Reaction of soluble metal chalcogenides with phosphines

Triphenylphosphine is known to abstract chalcogen atoms from polychalcogenide complexes [171,172]. When treated with PPh_3, $Cp_2Mn_2(CO)_4(Se_2)$ is transformed to a monobridged complex [166]:

$$Cp_2Mn(CO)_4(Se_2) + PPh_3 \xrightarrow[-40\,^\circ C]{THF} Cp_2Mn_2(CO)_4Se + SePPh_3 \tag{14}$$

Treatment of $(RCp)_2Ti(Se_5)$ (R = H, Me or ^iPr) with triphenylphosphine or tributylphosphine in CH_2Cl_2 gives the binuclear compound $[(RCp)_2Ti]_2[\mu\text{-}Se_2]_2$ in good yield [103]:



(15)

This reaction can be compared with that between the analogous sulfur compound and phosphine where $[Cp_2Ti]_2S_6$ is obtained [173].

G. CONCLUSION

This review of soluble metal selenides and tellurides reveals an exciting incipient chemistry that promises to differ significantly from the chemistry of soluble metal sulfides.

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NOTE ADDED IN PROOF

New developments are summarized here:

The $CpMo(Se_4)_2^-$ anion contains a square-pyramidal Mo center, with a cyclopentadienyl ring in the apical position and two Se_4^{2-} ligands in the basal sites [174]. The $CpMo(CO)_2(Se_2)^-$ anion (Se–Se distance 2.310(2) Å) is also known [175]. The $[PPh_4]_2[Mn(Se_4)_2]$ [135], $[PPh_4]_2[Pd(Se_4)_2]$ [176] and $[PPh_4]_2[Hg(Se_4)_2]$ salts [176] are essentially isostructural with their Zn analogue $[PPh_4]_2[Zn(Se_4)_2]$ [118]. In $[PPh_4]_2[Ni(Se_4)_2]$ [176] and $[PEtPh_3]_2[Ni(Se_4)_2]$ [118] the Ni center has square-planar coordination; the $NiSe_4$ rings are in the distorted envelope configuration (type **IVa**). In $[PEtPh_3]_2[Ni(Se_4)_2]$, the Se(int)–Se(int) distance (2.321(1) Å) is shorter than the Se(int)–Se(ext) distances (2.398(1) and 2.344(1) Å). In the $Pb(Se_4)_2^{2-}$ anion, three Pb–Se distances are 0.3–0.4 Å shorter than the fourth one. The geometry around Pb can be described as a trigonal bipyramid with a vacant equatorial position [176].

The $Pt(Se_4)_3^{2-}$ anion consists of a Pt^{IV} center in pseudo-octahedral geometry chelated to three Se_4^{2-} ligands [177]. Each $PtSe_4$ ring is in the envelope conformation (type **IVb**): Se–Se distances vary from 2.315(5) Å to 2.343(5) Å and do not show a significant alternation. The $Sn(Se_4)_3^{2-}$ anion [174] has a structure similar to that of the $Pt(Se_4)_3^{2-}$ anion [177].

The tetranuclear complexes $M_4(Se_4)_x(Se_5)_{3-x}^{2-}$ (M = Cu, Ag; $x = 2, 3$) can be regarded as derived from $M_3(Se_n)_3^{3-}$ (Fig. 41) by folding up the terminal donor atoms Se′ to coordinate another M^+ atom [178]. Synthesis of the ordered $Ag_4(Se_4)_3^{2-}$ [179] and $Cu_4(Se_4)_3^{2-}$ ions [180] has also been achieved.

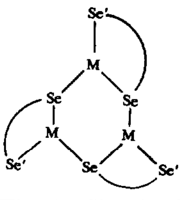

Fig. 41. Sketch of the structure of the $M_3(Se_n)_3^{3-}$ ion [178].

The $[Ag(Se_4)]_4^{4-}$ ion features two different kinds of Ag coordination. Two of the Ag atoms are tetrahedrally coordinated while the other two possess trigonal planar coordination [179].

The polymer $[Ag(Se_5)]_n^{n-}$ [179] differs from the previously reported $[Ag(Se_4)]_n^{n-}$ polymer (Fig. 34) [134] in two ways: Se_5^{2-} ligands instead of Se_4^{2-} ligands are present with a distinct mode of coordination and the Ag atoms assume tetrahedral geometry compared to trigonal planar in $[Ag(Se_4)]_n^{n-}$.

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