# Coordination Complexes and Applications of Transition Metal Sulfide and Selenide Halides

Victoria K. Greenacre, William Levason*, Gillian Reid and Danielle E. Smith
School of Chemistry, University of Southampton, Southampton SO17 1BJ. U.K. (* Email: wxl@soton.ac.uk)

## Abstract

Metal chalcogenide halides are less studied analogues of metal oxide halides, where the oxido-group is replaced by heavier Group 16 elements, specifically sulfur, selenium or tellurium. This article reviews the chemistry of neutral ligand complexes of *molecular* chalcogenide halides of the d-block metals. The majority of these complexes contain the higher oxidation states of niobium, tantalum and tungsten, with more limited examples of titanium, molybdenum and vanadium compounds. The synthesis, structures and properties are described, and areas in need of further study identified. The recent application of several examples as low pressure chemical vapour deposition reagents for the production of thin films of semiconducting metal dichalcogenide materials is also discussed.

## Abbreviations:

E = S, Se; X = F, Cl, Br; bipy = 2,2'-bipyridyl, Cp = cyclopentadienide, dmso = dimethylsulfoxide; dmpe = 1,2-bis(dimethylphosphino)ethane, phen = 1,10-phenanthroline, thf = tetrahydrofuran, thiox = 1,4-thioxane, tht = tetrahydrothiophene, 15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane, dppmO$_2$ = bis(diphenylphosphinyl)methane, dppeO$_2$ = 1,2-bis(diphenylphosphinyl)ethane, ppO$_2$ = 1,2-bis(diphenylphosphinyl)benzene, py = pyridine, LPCVD = low pressure chemical vapour deposition.

**Keywords:** chalcogenide halides; sulfide chloride; selenide chloride; sulfide bromide; selenide bromide; sulfide fluoride.

**Contents**

## 1. Introduction

Oxide-chlorides and -bromides are well known for many of the d-block metals and have played a significant role in the development of the coordination and organometallic chemistry of the elements [1,2,3]. In contrast, few metal oxide iodides have been described, and they are usually of limited stability and have very limited Lewis acidity. While metal oxide fluorides are more numerous, apart from the derived fluoroanions, their coordination chemistry, which is often quite different to that with the heavier halogens, has only been explored in recent years [4,5]. Analogues with the heavier Group 16 elements (S, Se, Te) replacing oxygen, the metal chalcogenide halides, were first studied in any detail in the 1960s, although a much more limited number of examples was described [6,7,8]. The chalcogenide halides have not been reviewed for nearly 40 years, and their complexes only very briefly mentioned, if at all, in larger compilations [1,2].

## 2. Chalcogenide Halides

In general, chalcogenide halides are of two main types, those in lower oxidation states of the metals are typically polymeric with structures (where known) based upon lattices of halide and chalcogenide $[E]^{2-}$ or dichalcogenide $[E_2]^{2-}$ ions with metal ions distributed throughout the lattice [6,7,8]. The second type, found with higher oxidation state d-block metals, are molecular, much more reactive, and have significant Lewis acidity. This latter type is the focus of this review, which describes the coordination chemistry of molecular metal chalcogenide halides with neutral ligands containing N, P, As, O, S and Se donor atoms. In practice, these are mostly compounds bearing chloride or bromide co-ligands. Several metal chalcogenide fluorides are known, but their chemistry is only beginning to be explored, which in part reflects the limited number of laboratories able to access and handle the hazardous binary fluorides and the anhydrous HF used to make them.

The original syntheses of metal chalcogenide halides typically involved heating the metal halide with the elemental chalcogen or a chalcogen source, such as $S_2Cl_2$, $SCl_2$, $Sb_2S_3$, $Sb_2Se_3$ or $B_2S_3$, usually in a sealed tube, but sometimes reactions were conducted in an organic solvent, like $CS_2$ or benzene. These syntheses produced mixtures, from which the desired product was isolated by distilling off the by-products or washing them out with organic solvents. Sometimes the chalcogenide halide was separated by sublimation *in vacuo* [6,7]. More recently, more gentle methods using silyl chalcogenides, $E(SiMe_3)_2$ (E = S, Se), have been developed. For example, $WSCl_4$, $WS_2Cl_2$ and $MoSCl_3$ can be made in high yield from $WCl_6$, $WSCl_4$ and $MoCl_5$, respectively, with $S(SiMe_3)_2$ in $CH_2Cl_2$ at ambient temperatures or below [9,10].

This review does not discuss in detail the synthesis and structures of the ternary metal chalcogenide halides themselves, but instead focuses on the synthesis, structures and chemistry of their complexes with neutral ligands containing Group 15 and 16 donor atoms, and with the corresponding halide ions (F, Cl, Br). No examples of complexes of *molecular* chalcogenide halides containing tellurium or iodine appear to be known. Similarly, chalcogenide halide complexes with neutral antimony or tellurium donor ligands have not been reported.

In passing, we note that theoretical studies (including Huckel, *ab initio,* X-alpha or DFT methods) of metal oxide halides, which sometimes extended to sulfide or selenide analogues, were popular in the late twentieth century, and typically concluded that although the compounds containing the heavier chalcogens were predicted to be less stable than the oxide halides, many compounds of these types appeared viable and were expected to exist [e.g. 11,12,13,14]. As is usually the case, such studies modelled the gas phase monomers and linked experimentally to electron diffraction or gas phase spectroscopy, whereas the experimental data obtained from solid compounds are significantly different, with the solids having higher coordination numbers for the metal. It is also fair to point out that a quarter of a century after these studies, many of the compounds deemed viable, remain unknown experimentally.

## 3. Complexes

### 3.1 Titanium and Vanadium

No molecular sulfide halides of zirconium or hafnium have been reported, and little is known about titanium compounds. A black $TiSCl_2$ of unknown structure is formed from $TiCl_4$ and $S(SiMe_3)_2$ or $Na_2S_4$ in $CH_2Cl_2$ solution under a dinitrogen atmosphere [15,16,17]. In the presence of $[Et_4N]Cl$ or $[Ph_4P]Cl$ the corresponding olive-green $[Et_4N]_2[TiSCl_4]$ or $[Ph_4P]_2[TiSCl_4]$ are formed, which contain the square pyramidal $[TiSCl_4]^{2-}$ dianion with apical sulfide (Ti-S = 2.111(2) Å, Ti-Cl = 2.371(2) Å) (Fig. 1). In the presence of dioxygen, or when using dmso as solvent, the reaction yields small oxido-titanium clusters containing disulfide links, such as $[Ph_4P]_2[Ti_3(\mu^3\text{-}O)(S_2)_3Cl_6]$. The $TiSCl_2$ dissolves in dry MeCN or thf to form $[TiSCl_2(L)_3]$ (L = thf, MeCN), characterised by microanalysis and IR spectroscopy [18]. The reaction of $[TiCl_4(MeCN)_2]$ with $S(SiMe_3)_2$ in benzene gives $[TiSCl_2(MeCN)_2]$, suggested to be dimeric [18].

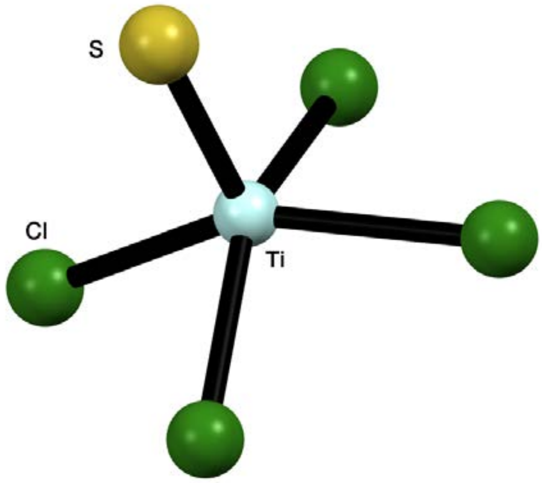


*Fig. 1: Structure of the anion* $[TiSCl_4]^{2-}$ *redrawn from Ref. [17]*

Very surprisingly, given the key role of vanadium oxide halides in vanadium chemistry, little is known about vanadium chalcogenide halides. An impure brown-black $VSCl_2$ is reported to be formed from $VCl_4$ and $S(SiMe_3)_2$ in $CH_2Cl_2$, but reaction of this with $[Ph_4P]Cl$ in $CH_2Cl_2$, gave $[Ph_4P]_3[V_2Cl_9]$, whilst in the presence of dioxygen the product was $[Ph_4P][VOCl_4]$ [19]. The formation and stability of vanadium chalcogenide halides would seem to merit a more detailed investigation both experimentally and by DFT methods.

### 3.2 Niobium

Although $NbOF_3$ is known [20] and a series of six-coordinate complexes with phosphine oxides, diimines, diamines and dmso have been described [21], no reports of either $NbSF_3$ or derived complexes were found. In marked contrast to the paucity of vanadium compounds, the four niobium chalcogenide halides $NbSCl_3$, $NbSBr_3$, $NbSeCl_3$ and $NbSeBr_3$ are among the most studied in the Periodic Table, and a considerable range of complexes has been described (Scheme 1 and Table 1).

The $NbEX_3$ (E = S, Se; X = Cl, Br) were made from $NbX_5$ and the appropriate $Sb_2E_3$, with reaction in $CS_2$ or $CH_2Cl_2$ giving a purer product than heating in sealed tubes [6,22,23]. More recently, reaction of $NbX_5$ with $E(SiMe_3)_2$ has become favoured [24,25]. Spectroscopically identical products often exhibit a range of colours in different batches, for example, $NbSCl_3$ has been variously described as golden yellow through to dark green. It has been suggested that the pure product is golden yellow, while the darker solids may also contain differing amounts of $Nb_2S_3Cl_4$ impurity [26]. The structures of the solid niobium sulfide halides are unknown, but they vaporise on heating as pseudo-tetrahedral monomers, confirmed by both electron diffraction and matrix IR spectroscopy

[26]. The structures of both $NbSeX_3$ are known and contain seven-coordinate niobium ($X_5Se_2$) in chains with alternating long and short Nb-Nb distances and $[Se_2]^{2-}$ units between alternate niobium pairs (Fig. 2), leading to the conclusion that the solids should be formulated as Nb(IV) compounds $Nb_2^{8+}$, $Se_2^{2-}$, $6X^-$ [27,28,29]. The red crystals used in these determinations were grown at high temperatures (720 K) and it is not clear if there are low temperature forms which contain Nb(V). Certainly, there is clear evidence for Nb(V) in the sulfide halide complexes from the X-ray structures as described below, although a structure of a complex containing an $NbSeX_3$ unit is lacking.

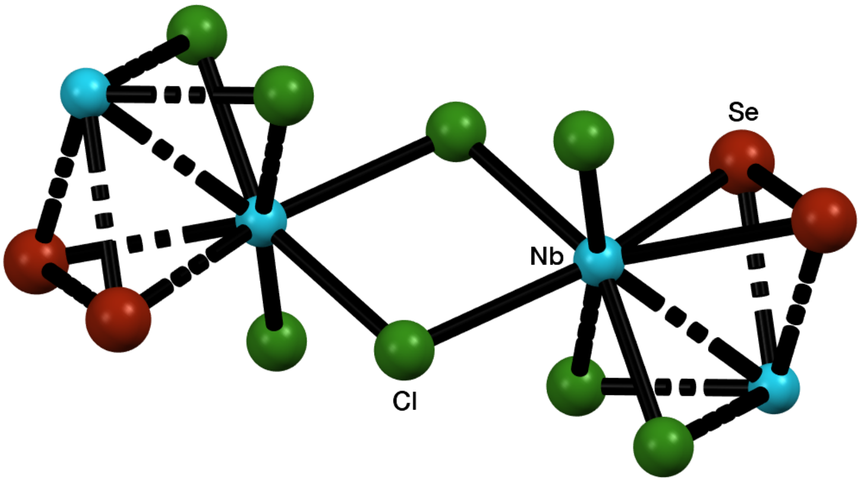
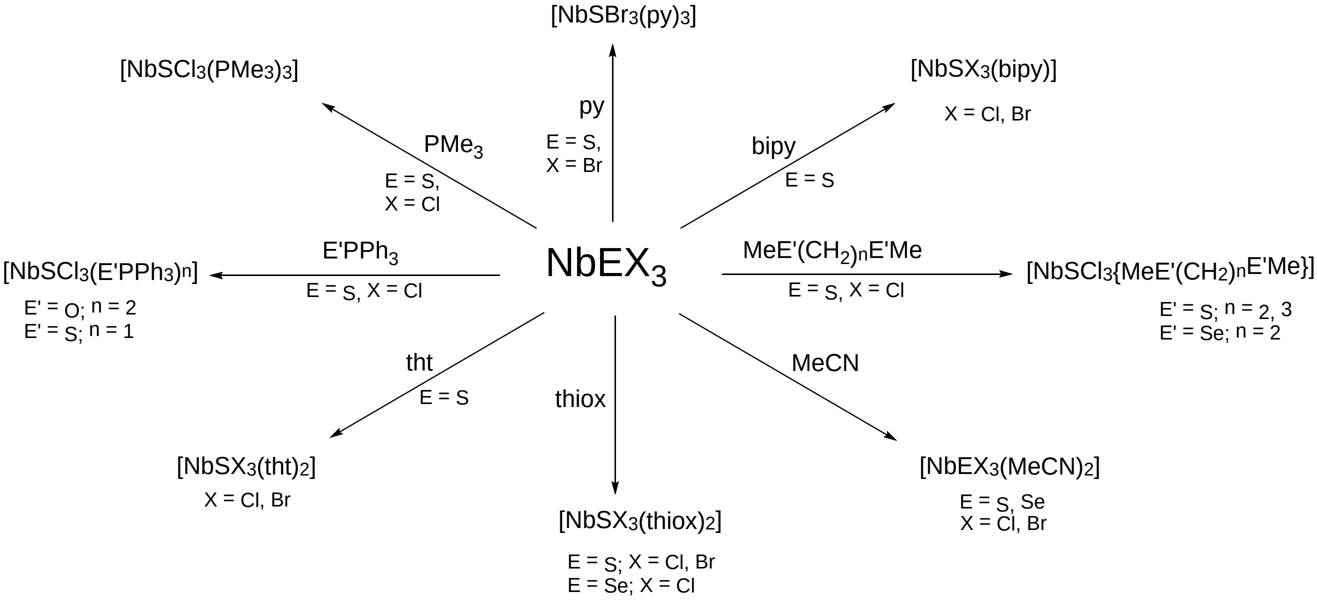


*Fig. 2: Part of the chain structure of $NbSeCl_3$ redrawn from Ref. [29].*



*Scheme 1: Selected complexes of $NbEX_3$.*

The square pyramidal $[NbSCl_4]^-$ is made by reaction of $NbSCl_3$ with the $[Ph_4P]Cl$ in $CH_2Cl_2$ [30], and this anion was also formed by photochemical irradiation of the reaction mixture of $NbCl_5$ and tetramethylthiourea [31]. The $[PPh_4][NbSBr_4]$ is formed from reaction of $[PPh_4][NbBr_6]$ and $S(SiMe_3)_2$ [24], but the same reaction with $[PPh_4][NbCl_6]$ produced the six-coordinate dianion in $[PPh_4]_2[NbSCl_5]$ [24]. The latter anion was also identified in the complex $[Nb(S_2CNEt_2)_4]_2[NbSCl_5]$, formed by decomposition of $[NbCl_2(S_2CNEt_2)_3]$ in $CH_2Cl_2$ solution [32].

Table 1 Neutral ligand complexes of $NbEX_3$, $Nb_2X_4S_3$ and $Nb_2X_4S_2$

| Complex | Notes | Reference |
|---|---|---|
| $[NbSCl_3(MeCN)_2]$ | | 9,25, 33,34 |
| $[NbSBr_3(MeCN)_2]$ | | 38 |
| $[NbSeCl_3(MeCN)_2]$ | | 25, 34 |
| $[NbSeBr_3(MeCN)_2]$ | | 38 |
| $[NbSX_3(bipy)]$ | X = Cl, Br | 34,38 |
| $[NbSX_3(phen)]$ | X = Cl, Br | 34,38 |
| $[NbSBr_3(tht)_2]$ | X-ray structure | 35,38 |
| $[NbSCl_3(tht)_2]$ | | 34,35 |
| $[NbSX_3(thiox)_2]$ | X = Cl, Br | 34, 38 |
| $[NbSeCl_3(thiox)_2]$ | | 34 |
| $[NbSCl_3(OPPh_3)_2]$ | | 33 |
| $[NbSCl_3(SPPh_3)]$ | Monomer and dimer forms confirmed by X-ray structures | 36 |
| $[NbSBr_3(py)_3]$ | Unlikely to be 7-coordinate? | 38 |
| $[Nb_2Cl_4S_2(\mu\text{-}Cl)_2(SMe_2)_2]$ | X-ray structure, also $^nBu_2S$ complex | 25 |
| $[NbSCl_3(SEt_2)]$ | Possibly a dimer? | 33 |
| $[NbSCl_3\{RS(CH_2)_nSR\}]$ | R = Me, $^i$Pr, n = 2; R = Me, $^n$Bu n= 3. X-ray Structures | 25 |
| $[NbSCl_3\{MeSe(CH_2)_3SeMe\}]$ | X-ray structure | 25 |
| $[NbSCl_3(Se^nBu_2)]$ | Possibly a dimer? | 25 |
| $[NbSCl_3(PMe_3)_3]$ | Orange and green forms (see text); X-ray structures | 37 |
| | | |
| $[Nb_2X_4S_3L_4]$ | X = Cl, Br, L = $SMe_2$, tht | 35,44,47 |

|  |  |  |
|---|---|---|
| $[Nb_2X_4S_3\{PhS(CH_2)_2SPh\}_2]$ | X = Cl, Br | 47 |
| $[Nb_2Cl_4S_2(tht)_4]$ |  | 47 |
| $[Nb_2X_4S_2(MeCN)_4]$ | X = Cl, Br | 48 |
| $[Nb_2Cl_4S_2(thf)_4]$ |  | 51 |
| $[Nb_2Cl_4(Se_2)_2(SMe_2)_4]$ | X-ray structure | 41 |
| $[Nb_2Cl_4(Se_2)_2(tht)_4]$ | X-ray structure | 49 |
|  |  |  |
| $[Nb_4Br_{10}Se_3(MeCN)_4]$ |  | 50 |

The reactions of neutral N- or O-donor ligands with $NbSX_3$ or $[NbSX_3(MeCN)_2]$ typically give six-coordinate complexes, $[NbSX_3(L)_2]$ or $[NbSX_3(L\text{-}L)]$ (Table 1). The presence of terminal Nb=S links is shown by a strong band ~ 550–520 $cm^{-1}$ in the IR spectra [25, 33,34,36,38]. The $^{93}$Nb NMR spectra are also characteristic of the presence of the Nb=S unit, with chemical shifts substantially to high frequency of those in the analogous pentachloride complexes; a further shift to higher frequency is found in complexes of $NbSeCl_3$ [25,39, 40]. The reactions of $NbSX_3$ or $[NbSX_3(MeCN)_2]$ with sulfur donor ligands are more complicated and need careful control of the reaction conditions. The green $[NbSCl_3\{RS(CH_2)_2SR\}]$ (R = Me, $^i$Pr) and $[NbSCl_3\{RS(CH_2)_3SR\}]$ (R = Me, $^n$Bu) were obtained in high yield from reaction of $[NbSCl_3(MeCN)_2]$ with the dithioethers in 1:1 molar ratio in $CH_2Cl_2$ solution [25]. X-ray crystal structures of $[NbSCl_3\{RS(CH_2)_2SR\}]$ (R = Me, $^i$Pr) showed the dithioether *trans* to S/Cl and appeared largely free from S/Cl disorder (Fig. 3), which is a commonly observed problem in this type of complex.

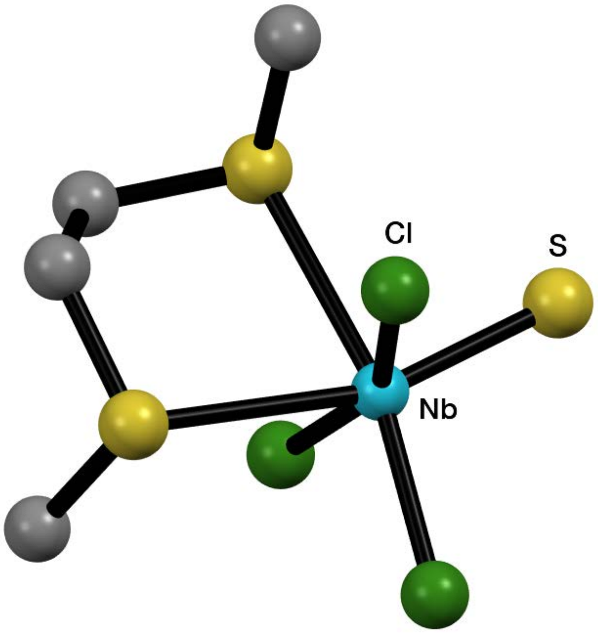


*Fig. 3: Structure of [$NbSCl_3\{MeS(CH_2)_2SMe\}$] redrawn from Ref. [25].*

Yellow-brown [$NbSCl_3\{MeSe(CH_2)_3SeMe\}$] was obtained similarly using $MeSe(CH_2)_3SeMe$, and has an analogous structure, but with disordered S/Cl *trans* to the neutral ligand [25]. The yellow-green [$NbSCl_3(SMe_2)$], formed by reaction of $NbCl_5$, $SMe_2$ and $S(SiMe_3)_2$ in $CH_2Cl_2$ at 0°C [25], was shown by an X-ray structure to be a chloride-bridged dimer, [$Nb_2Cl_4S_2(\mu\text{-}Cl)_2(SMe_2)_2$], rather unusually containing *syn* $SMe_2$ ligands (Fig. 4).

The reactions of $NbSX_3$ (X = Cl, Br) with excess $SMe_2$ or tht (L) in the absence of a solvent, gave complicated redox chemistry, with the [$NbSX_3(L)_2$] initially formed converting into green Nb(IV) compounds, [$Nb_2X_4S_3(L)_4$] (see below), which contain both $S^{2-}$ and $[S_2]^{2-}$ groups [35]. Orange crystals of [$NbSBr_3(tht)_2$] were isolated from the same reaction mixture and identified by their crystal structure [35]. A third (red) product remains unidentified.

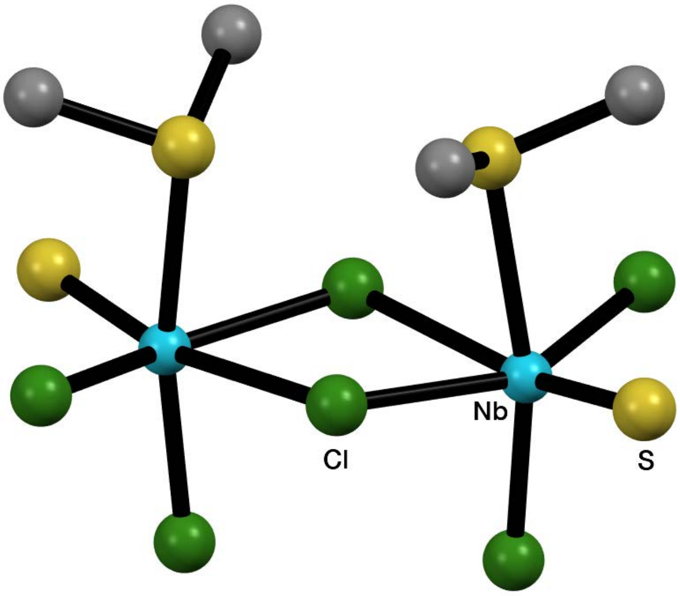


*Fig. 4: Structure of* $[Nb_2Cl_4S_2(\mu\text{-}Cl)_2(SMe_2)_2]$ *redrawn from Ref. [25].*

Redox chemistry is evident in the selenide halides. Although brown $[NbSeX_3(MeCN)_2]$ were isolated [25,34,38], attempts to prepare thioether or selenoether complexes were found to involve redox chemistry [25,41]. The reactions with a large excess of $SMe_2$ or tht and prolonged stirring (several weeks) gave mixtures, partially characterised as containing $[NbSeX_3(L)_2]$ and $[Nb_2Cl_4(Se_2)_2(L)_2]$ [44] (see below). Reaction of $NbCl_5$, $Se(SiMe_3)_2$ and $Se^nBu_2$ in $CH_2Cl_2$ gave a black solid, possibly $[NbSe_2Cl_3(Se^nBu_2)]$ containing diselenide, $[Se_2]^{2-}$, ions [25].

In contrast to most of the reactions described above, the reaction of $SPPh_3$ and $NbSCl_3$ in $CS_2$ solution produced a 1:1 complex [36]. Most unusually, the unit cell of the orange crystals grown from this complex showed two five-coordinate $[NbSCl_3(SPPh_3)]$ molecules and a dimer unit $[(Ph_3PS)Cl_2SNb(\mu\text{-}Cl)_2NbSCl_2(SPPh_3)]$ (Fig. 5). The monomer is a square pyramid with the Nb=S apical (2.114(4) Å), whilst in the dimer the Nb=S units are *trans* to the chloride bridges (2.129(4) Å).

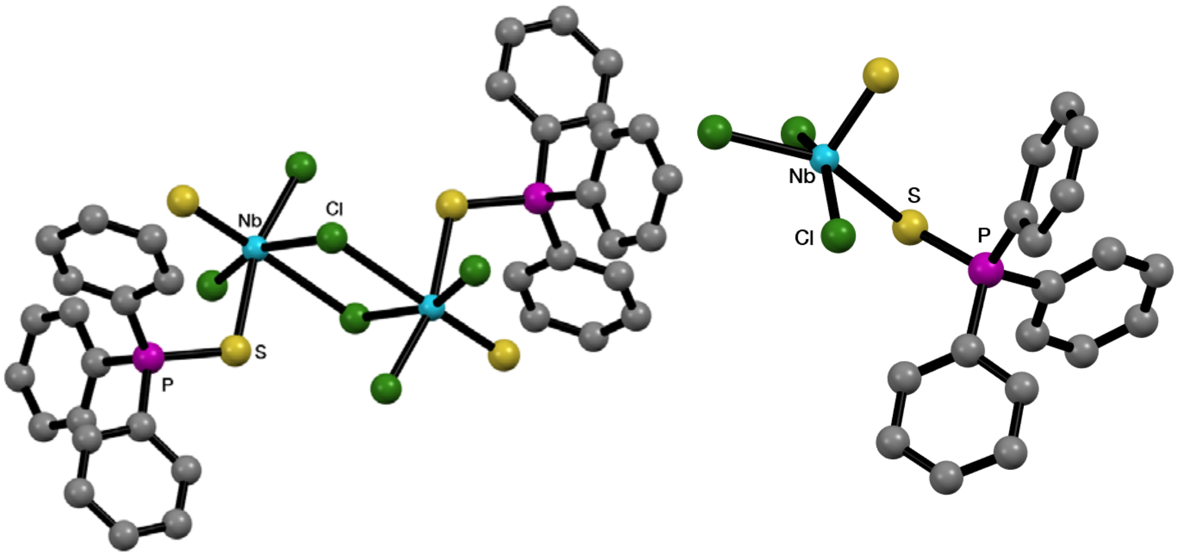


*Fig. 5: Structures of co-crystallised [(Ph$_3$PS)Cl$_2$SNb(μ-Cl)$_2$NbSCl$_2$(SPPh$_3$)]] and [NbSCl$_3$(SPPh$_3$)] redrawn from Ref. [36].*

The only phosphine complex reported, the seven-coordinate [NbSCl$_3$(PMe$_3$)$_3$], was isolated as both orange and green crystals, which differed in their spectroscopic properties. The structures of both were determined and show the same geometric arrangement of ligands. These were originally suggested to be examples of *distortional isomerism* [37], a concept now viewed as erroneous [42]. Their nature remains unclear despite further work [43].

The use of the thioether complexes to deposit NbS$_2$ films by LPCVD is discussed in Section 4.

The reactions of NbSX$_3$ (X = Cl or Br) with tetrahydrothiophene result in redox chemistry, in addition to the formation of the simple adduct, [NbSX$_3$(tht)$_2$], as outlined above. Single crystals of green [Nb$_2$X$_4$S$_3$(tht)$_4$] were separated from the reaction mixture and the structures of both the chloride and bromide complexes were determined [35,44]; that of the bromide is shown in Fig. 6. The structures show each niobium coordinated to two terminal tht ligands and two terminal halides, with bridging S$^{2-}$ and [S$_2$]$^{2-}$ anions disordered across the Nb-Nb bond in the chloride; the bromide appears to be free from disorder. The Nb-Nb distances of 2.844(2) (Cl) and 2.830(5) Å (Br) are shorter than in NbX$_4$ (3.029(2) X = Cl; 3.113(1) Å X = Br) [45,46] and are consistent with single σ-bonds.

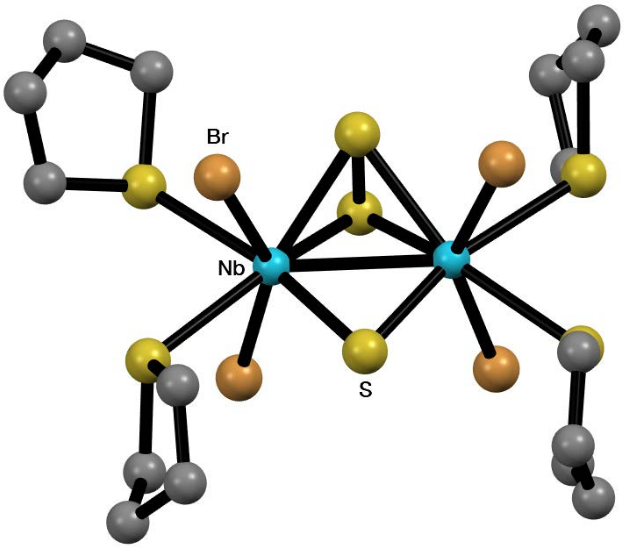


*Fig. 6: Structure of [$Nb_2Br_4$(μ-$S_2$)(μ-S)$(tht)_4$] redrawn from Ref. [35].*

The parent diamagnetic Nb(IV) chalcogenide halides $Nb_2X_4S_3$ (X = Cl, Br) were made in the absence of added ligand from $NbX_5$ with $Sb_2S_3$ in $CS_2$ solution, and subsequent reaction with the appropriate ligands gave [$Nb_2X_4S_3(L)_4$] (L = MeCN, $SMe_2$, tht) or [$Nb_2X_4S_3\{PhS(CH_2)_2SPh\}_2$] [47]. Treatment of [$Nb_2Cl_4S_3(tht)_4$] with $PPh_3$ extracts one sulfur from the disulfide bridge to give [$Nb_2Cl_4S_2(tht)_4$] which has Nb-Nb = 2.868(2) Å [47]. The sulfido-bridged complexes can be accessed directly by reaction of [$NbX_4(MeCN)_2$] with $Sb_2S_3$ in MeCN to produce [$Nb_2X_4S_2(MeCN)_4$] [48]. Crystal structures were obtained for the solvated complexes, [$Nb_2Cl_4S_2(MeCN)_4$]·nMeCN (n = 2, 3) which had identical metal cores with Nb-Nb = 2.872(3) Å (Fig. 7).

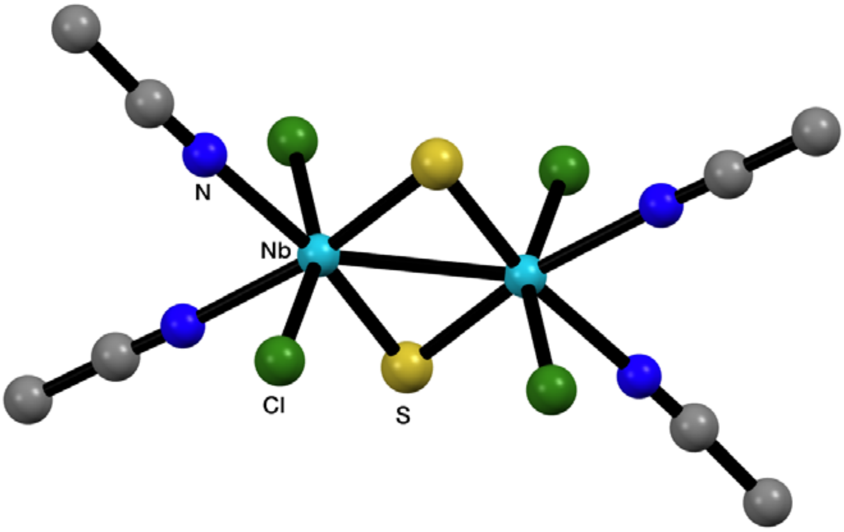


*Fig. 7: Structure of [$Nb_2Cl_4$(μ-S$)_2(MeCN)_4$] redrawn from Ref. [48].*

Simple complexes derived from the selenide halides are fewer in number (Table 1) and it appears that redox chemistry is even more likely here than in the sulfide halide systems. Thus, the reactions of $NbSeX_3$ (X = Cl, Br) with $SMe_2$, tht or $PhS(CH_2)_2SPh$ gave mixtures of green and red complexes, which proved to be difficult to separate cleanly and identify [41]. Recrystallisation of the $NbSeCl_3$–$SMe_2$ product from $CS_2$ gave red crystals identified by an X-ray structure determination as $[Nb_2Cl_4(\mu\text{-}Se_2)_2(SMe_2)_4]$. Its structure is shown in Fig. 8 and contains two diselenide bridges, with Nb–Nb = 2.962(3) Å [41]. Subsequently, the structure of $[Nb_2Cl_4(\mu\text{-}Se_2)_2(tht)_4]$ was also determined and is very similar, as expected [49].

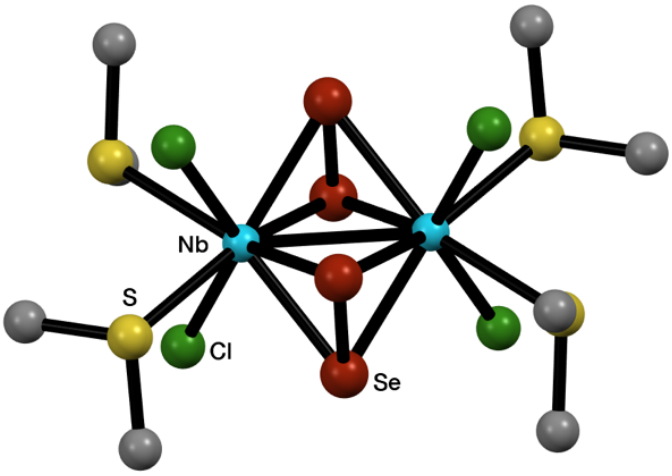


*Fig. 8: Structure of $[Nb_2Cl_4(\mu\text{-}Se_2)_2(SMe_2)_4]$ redrawn from Ref. [41].*

A tetranuclear species $[Nb_4Br_{10}Se_3(MeCN)_4]$ was obtained from the reaction of $[NbBr_4(MeCN)_2]$ and $Sb_2Se_3$ [50]. The structure shows an $(MeCN)_2Br_2Nb(\mu\text{-}Se_2)(\mu\text{-}Se)NbBr_2(MeCN)_2$ core linked to two $NbBr_3$ units above and below (Fig. 9). The Se-bridged core has a σ-bonded Nb(IV)-Nb(IV) unit with Nb–Nb = 2.886(1) Å, with $NbBr_3$ units above and below the plane.

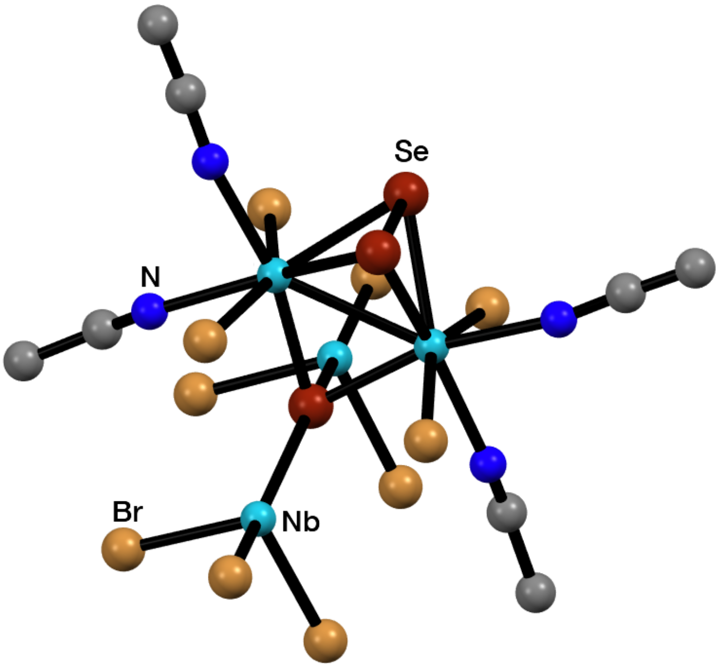


*Fig. 9: Structure of [$Nb_4Br_{10}Se_3(MeCN)_4$] redrawn from Ref. [50].*

The synthetic chemistry of reduced niobium chalcogenide halides is clearly complicated, and the species identified have often relied on structures determined from single crystals separated from mixtures, and it seems highly likely that other, as yet unidentified complexes, are also present. Several other chalcogenide halides, which are not known to give complexes with neutral ligands have also been described [6,7].

Although not made from chalcogenide halides, there are a number of dimeric complexes of niobium with S/Se and X ligands, some examples of which are mentioned briefly here. These include [$Nb_2Cl_4(\mu\text{-}S)_2(PMe_3)_4$] a Nb-Nb dimer with two sulfide bridges made from [$NbCl_4(thf)_2$], $Li_2S$ and $PMe_3$ in thf [52]. In other cases, the S/Se comes from fragmentation of thio- or seleno-ether ligands. For example, the Nb(IV) dimer [$Nb_2Cl_4(\mu\text{-}S)_2(SMe_2)_4$] was originally identified as Nb(III) and formulated as [$Nb_2Cl_6(SMe_2)_4$] [53]. Similarly, the reaction of $NbCl_4$ with $MeS(CH_2)_3SMe$ in $CH_2Cl_2$ solution over several weeks, gave red crystals of [$NbCl_4\{MeS(CH_2)_3SMe\}$], alongside a few yellow crystals identified by their crystal structure as [$Nb_2Cl_4(\mu\text{-}S)_2\{MeS(CH_2)_3SMe\}_2$], with a Nb-Nb single bond [54]. More extensive rearrangement of the neutral ligand occurred in the reaction of $NbCl_4$ with $o\text{-}C_6H_4(CH_2SeMe)_2$, when the major product was [$Nb_2Cl_4(\mu\text{-}Se)_2\{o\text{-}C_6H_4(CH_2)_2Se\}_4$], where the diselenoether had been cleaved to $Se^{2-}$ and 1,3-dihydrobenzo[c]selenophane ($o\text{-}C_6H_4(CH_2)_2Se$) formed by ring closure [54].

### 3.3 Tantalum

$TaSF_3$ has not been obtained, and whilst $TaOF_3$ is known [20], attempts to prepare complexes with neutral ligands have been unsuccessful thus far [21]. The tantalum(V) sulfide halides have been much less studied than the niobium systems and also appear to involve simpler chemistry, in that reduction to tantalum(IV) is not observed (Scheme 2 and Table 2). Little is known about the tantalum selenide halides and they warrant detailed study.

The $TaEX_3$ (E = S, Se) were made by reaction of $MX_5$ with $Sb_2E_3$ in $CS_2$ over 3 days [6,22,23,56] although only very limited detail is available about the selenide halide syntheses. The anion $[TaSCl_5]^{2-}$ has been obtained as $[PPh_4]^+$ [24] and $Cs^+$ [57] salts; the latter has the $K_2[PtCl_6]$ structure. The anion is also present in the compound $[Cp_8Ta_6S_{10}][TaSCl_5]$ [58]. Unusual anions containing a coordinated dioxane ligand, $[TaSCl_4(dioxane)]^-$ and $[(TaSCl_4)_2(\mu\text{-dioxane})]^{2-}$ (Fig. 10) were obtained from reaction of $TaCl_5$, $Na_2S_4$ and 15-crown-5 in $CH_2Cl_2$, with the dioxane derived from degradation of the crown ether [55]. Both contain square pyramidal $TaSCl_4$ units with the dioxane coordinated *trans* to the sulfur. The dimer also contains co-crystallised $S_8$.

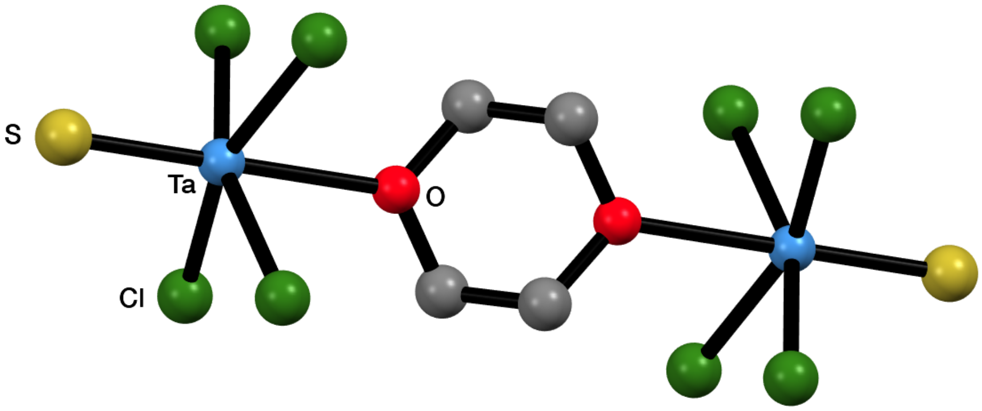
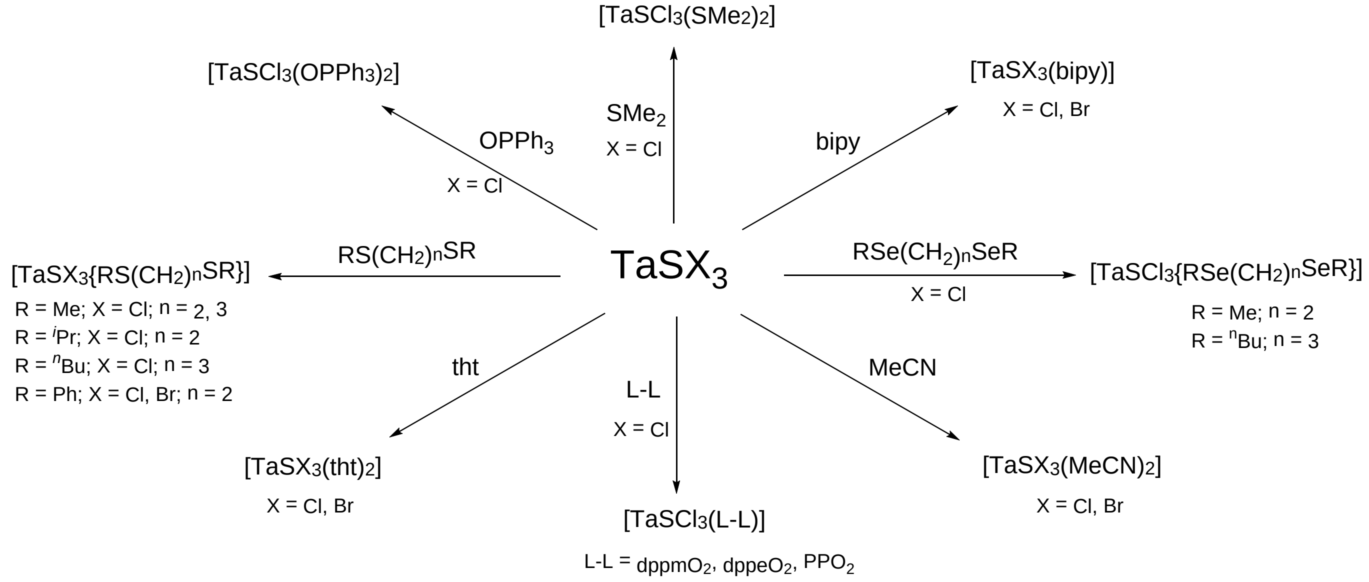


*Fig. 10: Structure of $[(TaSCl_4)_2(\mu\text{-dioxane})]^{2-}$ redrawn from Ref. [55].*



*Scheme 2: Selected complexes of $TaSX_3$.*

Table 2 Neutral ligand complexes of $TaEX_3$ (E = S, Se; X = Cl, Br)

| Complex | Notes | Reference |
|---|---|---|
| $[TaSCl_4(dioxane)]^-$ | X-ray structure | 55 |
| $[(TaSCl_4)_2(\mu\text{-dioxane})]^{2-}$ | X-ray structure | 55 |
| $[TaSX_3(SMe_2)_2]$ | X = Cl, Br | 56 |
| $[TaSX_3(tht)_2]$ | X = Cl, Br | 56 |
| $[TaSX_3(MeCN)_2]$ | X = Cl, Br X-ray structure X = Cl | 9, 33, 56, 60 |
| $[TaSX_3\{PhS(CH_2)_2SPh\}]$ | X = Cl, Br X-ray structure X = Cl | 56, 60 |
| $[TaSCl_3\{RS(CH_2)_2SR\}]$, R = Me, $^iPr$ | X-ray structure (both) | 60 |
| $[TaSCl_3\{RS(CH_2)_3SR\}]$, R = Me, $^nBu$ | X-ray structure R = $^nBu$ | 60 |
| $[TaSCl_3\{MeSe(CH_2)_2SeMe\}]$ | X-ray structure | 60 |
| $[TaSCl_3\{^nBuSe(CH_2)_3Se^nBu\}]$ | | 60 |
| $[TaSCl_3(OPPh_3)_2]$ | X-ray structure | 59 |
| $[TaSCl_3(phen)]$ | X-ray structure | 59 |
| $[TaSCl_3(bipy)]$ | | 59 |
| $[TaSCl_3(dppmO_2)]$ | | 59 |
| $[TaSCl_3(dppeO_2)]$ | X-ray structure | 59 |
| $[TaSCl_3(ppO_2)]$ | | 59 |

The yellow [$TaSX_3(MeCN)_2$] were obtained by prolonged reaction (17 days) of $TaSX_3$ with MeCN at 70°C, whilst similar reactions with a large excess of $SMe_2$ or tht gave red [$TaSX_3(SMe_2)_2$] or [$TaSX_3(tht)_2$], respectively [56]. The presence of a strong band in the IR spectra in the range 500–520 $cm^{-1}$, assigned at υ(Ta=S), is consistent with simple octahedral adducts. Only a single resonance is seen in the $^1H$ NMR spectra of the MeCN and $SMe_2$ complexes, probably indicating fast exchange. The structure of [$TaSCl_3(MeCN)_2$], obtained from $TaCl_5$ and $S(SiMe_3)_2$ in MeCN solution, showed the nitrile ligands positioned *trans* to S/Cl [59].

A series of yellow phosphine oxide complexes, [$TaSCl_3(OPPh_3)_2$] and [$TaSCl_3$(L-L)] (L-L = $dppmO_2$, $dppeO_2$, $ppO_2$), were prepared by treatment of a mixture of the phosphine oxide and $TaCl_5$ in $CH_2Cl_2$ with $S(SiMe_3)_2$ [59]. The structure of [$TaSCl_3(dppeO_2)$] is shown in Fig. 11, and $^1H$ and $^{31}P\{^1H\}$ NMR and IR spectroscopic data confirm that all have the neutral ligand lying *trans* to S/Cl. The yellow diimine complexes, [$TaSCl_3$(phen)] and [$TaSCl_3$(bipy)], were obtained similarly and also have the neutral diimines *trans* S/Cl, shown by resonances indicating inequivalent rings in their $^1H$ NMR spectra.

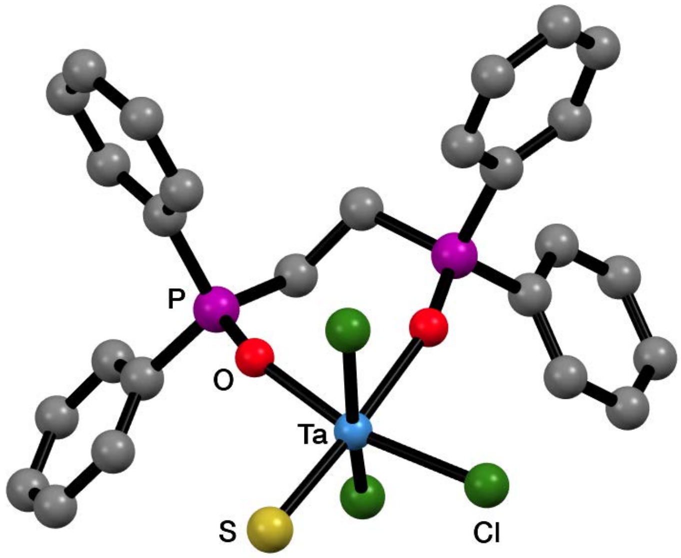


*Fig. 11: Structure of [$TaSCl_3(dppeO_2)$] redrawn from Ref. [59].*

Trace hydrolysis in solution of the [$TaSCl_3$(phen)] gave X-ray quality crystals, which were found to be the dimer [$\{TaSCl_2(phen)\}_2(\mu\text{-}O)$] with a linear oxido-bridge (Fig. 12). A corresponding series of complexes with $TaOCl_3$ was also prepared [59] and comparisons suggest that the sulfide chloride complexes are rather less stable than the oxide chloride analogues, although common spectroscopic parameters show only small differences.

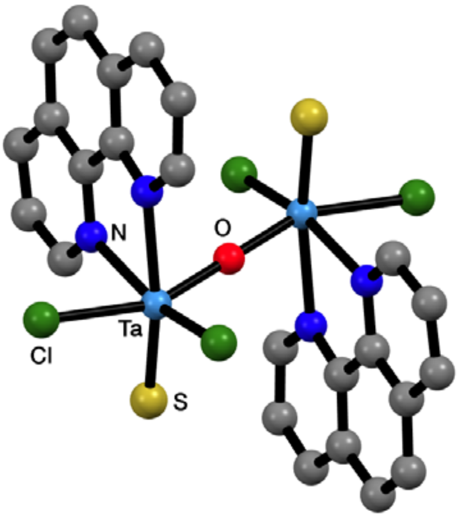


*Fig. 12: Structure of* $[\{TaSCl_2(phen)\}_2(\mu\text{-}O)]$ *redrawn from Ref. [59].*

Attempts to obtain dithioether complexes from reaction with $[TaSCl_3(MeCN)_2]$ failed, as the MeCN was not cleanly substituted. However, reaction of $TaCl_5$, the dithioether and $S(SiMe_3)_2$ in $CH_2Cl_2$ gave $[TaSCl_3(\text{dithioether})]$ (dithioether = $RS(CH_2)_2SR$: R = Me, ${}^{i}Pr$, Ph; $RS(CH_2)_3SR$: R = Me, ${}^{n}Bu$). Crystal structures were obtained for several complexes, all of which had the dithioether positioned *trans* to S/Cl [60]. In several cases the S/Cl showed disorder, but the structure of $[TaSCl_3\{{}^{n}BuS(CH_2)_3S{}^{n}Bu\}]$ appears free from such disorder and is shown in Fig. 13. The room temperature ${}^{1}H$ NMR spectrum of $[TaSCl_3\{PhS(CH_2)_2SPh\}]$ shows only a single $CH_2$ resonance, indicative of fast exchange, but upon cooling the solution, two resonances appear as exchange slows, as required for the structure present. The complexes of the alkyl substituted $RS(CH_2)_2SR$ show two RS- and two $CH_2$ resonances in their ${}^{1}H$ NMR spectra at ambient temperatures, showing exchange is slow on the NMR timescale, and on cooling the solutions below ~ 250 K more complicated splittings develop due to the slowing of pyramidal inversion at S; these effects are reversable on warming [60].

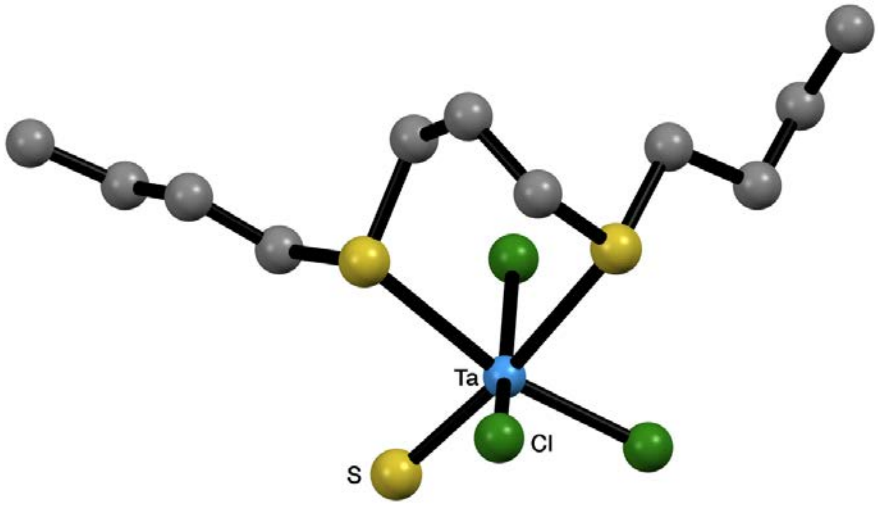


*Fig. 13: Structure of* $[TaSCl_3\{^nBuS(CH_2)_3S^nBu\}]$ *redrawn from Ref. [60].*

Two deeply coloured analogues with diselenoethers $[TaSCl_3\{MeSe(CH_2)_2SeMe\}]$ and $[TaSCl_3\{^nBuSe(CH_2)_3Se^nBu\}]$ were also isolated. The structure of the former was determined and showed the expected octahedral geometry, again with S/Cl disorder in plane [60]. The $^1H$ and $^{77}Se$ NMR spectra of $[TaSCl_3\{^nBuSe(CH_2)_3Se^nBu\}]$ in $CD_2Cl_2$ solution were little different to those of the free diselenoether suggesting extensive dissociation in solution.

Tantalum complexes with thioether ligands containing both sulfide and chloride anions were obtained from degradation of the thioether in some reactions with tantalum chloride. As $Cl^-$ and $S^{2-}$ are isoelectronic and therefore not easily distinguished by their scattering power for X-rays, failure to recognise this, caused some confusion in the literature [53]. Compounds originally formulated $[Ta_2Cl_6(SMe_2)_4]$ and $[Ta_2Cl_6\{EtS(CH_2)_2SEt\}_2]$ were reformulated by Cotton [53] as $[Ta_2Cl_4(\mu\text{-}S)_2(SMe_2)_4]$ and $[Ta_2Cl_4(\mu\text{-}S)_2\{EtS(CH_2)_2SEt\}_2]$ and are therefore Ta(IV) complexes with single Ta-Ta bonds, not Ta(III) with Ta=Ta double bonds. Other similar complexes are $[Ta_2Cl_4(\mu\text{-}S)_2(PR_3)_4]$ ($R_3$ = $Me_3$ [52], $Me_2Ph$ [53]), $[Ta_4S_4Cl_8(PMe_3)_6]$ [52] and $[Ta_2Cl_4(\mu\text{-}Se)_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}_2]$ (Fig. 14) [61].

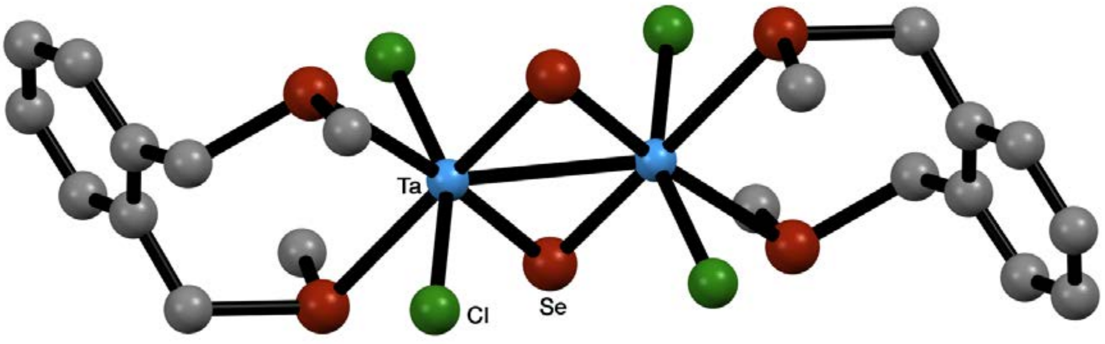


*Fig. 14: Structure of [$Ta_2Cl_4(\mu\text{-}Se)_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}_2$] redrawn from Ref. [61].*

### 3.4 Molybdenum

The synthesis of $MoEF_4$ (E = S, Se) by heating $MoF_6$ with $Sb_2E_3$ was reported in 1979 [62], and more recently $MoSF_4$ has been obtained by reaction of $MoF_6$ and $S(SiMe_3)_2$ in $CFCl_3$ at low temperatures [63]. However, there are no reports of any complexes. The $MoECl_4$ do not appear to exist. A considerable number of molybdenum sulfide chlorides were reported in the older literature, including $MoSCl_3$, $MoS_2Cl_2$, $Mo_2S_2Cl_3$ and $Mo_3S_7Cl_4$. These were made by a variety of methods including heating $MoCl_5$ or $MoCl_3$ with sulfur, $MoCl_5$ with $Sb_2S_3$, $MoS_2$ with $S_2Cl_2$, and $Mo(CO)_6$ with $SCl_2$, with the ratio of Mo:S in the reactants and the temperature regime controlling the product formed [6,7,64,65,66]. Low temperature preparations included $MoSCl_3$ from $MoCl_5$ using $Sb_2S_3$ in $CS_2$ or $S(SiMe_3)_2$ in $CH_2Cl_2$ [9,10,22]. Similar sulfide bromide and selenide chloride species were reported [6,7]. The purity of the products was often not clear and the structures unknown. More recent studies reported two structural forms of $MoSCl_3$, made from $MoCl_3$ and sulfur in a temperature gradient [67]. The high temperature α-form and the lower temperature β-form are 1-dimensional polymers with $Mo_2$ dimers connected by two chlorides in the former and by three in the latter, and both contain $(S_2)^{2-}$ groups (Fig. 15). $MoSeCl_3$ is made similarly from $MoCl_3$ and Se and has the α-$MoSCl_3$ structure. X-ray photoelectron spectroscopy shows all three contain Mo(IV) [67]. Two other structurally characterised sulfide chlorides are $MoS_2Cl_3$ and $Mo_3S_7Cl_4$ [68]. The former contains $Mo_2$ units, the latter $Mo_3$ triangles, both with $S^{2-}$ and $[S_2]^{2-}$ ligands. The lower oxidation states and the presence of disulfide groups has obvious implications for their ability to form Mo(V), [$MoSCl_3(L)_n$] coordination complexes. In fact, despite attempts to react $MoSCl_3$ with MeCN, diimines, etc. [69], no complexes of type $[MoSCl_3(L)_2]$ have been definitively identified crystallographically, and $MoSeCl_3$ did not appear to react with the same ligands even under prolonged reflux.

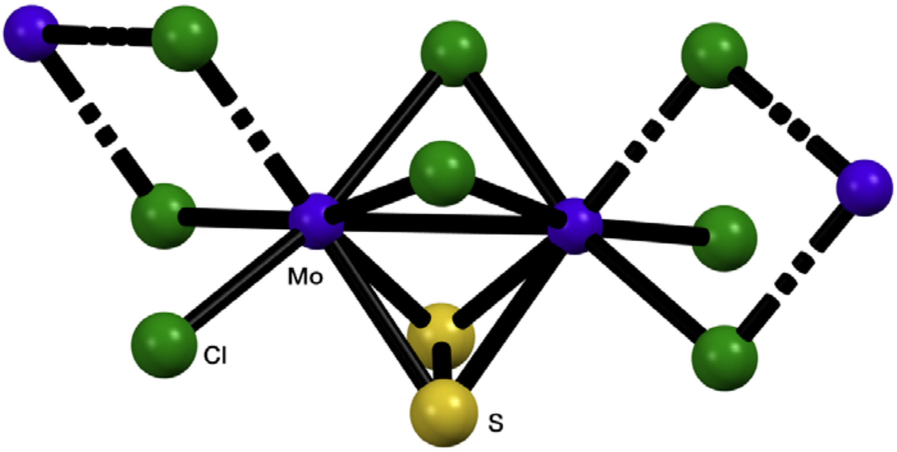


*Fig. 15: Part of the chain structure of α-$MoSCl_3$ redrawn from Ref. [67].*

There are a large number of molybdenum chalcogenide dimers ($Mo_2$) and clusters with triangular and cubane $Mo_3$, $Mo_4$ and octahedral and raft type $Mo_6$ frameworks, containing bridging $S^{2-}$, $Se^{2-}$, $(S_2)^{2-}$, and $(Se_2)^{2-}$, which often have terminal vertices occupied by neutral ligands or halides. This area has been reviewed several times [70,71,72,73], and is not considered in the present article.

### 3.5 Tungsten

Six chalcogenide halides of W(VI) are known, $WEX_4$ (E = S, Se; X = F, Cl, Br).

$WSF_4$ is formed by heating $WF_6$ with S or $Sb_2S_3$ [74,75], by reaction of $WF_6$ with $Sb_2S_3$ in anhydrous HF [76] or with $S(SiMe_3)_2$ in $CH_2Cl_2$[77]. $WSeF_4$ is made similarly from $WF_6$ and Se [75] or $Sb_2Se_3$ [78]. The structure of $WSF_4$ contains chains of square pyramidal molecules weakly F-bridged [75,76]. In the gas phase, both $WSF_4$ and $WSeF_4$ are square pyramidal monomers, demonstrated by electron diffraction studies [79,80] and matrix isolation IR spectroscopy [78]. Two fluoroanions are known, $[WSF_5]^-$ and $[F_4SW(\mu\text{-}F)WSF_4]^-$ [81,82,83], but the only characterised complexes with neutral ligands are $[WSF_4(MeCN)]$ [75,76] and $[WSF_4(py)]$ (Fig. 16) [84].

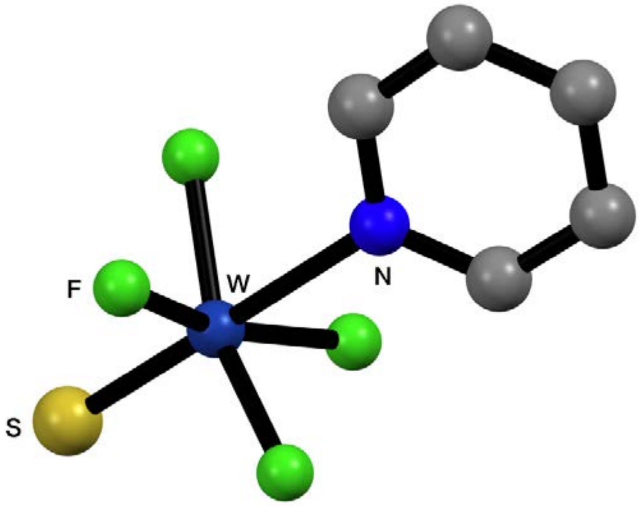
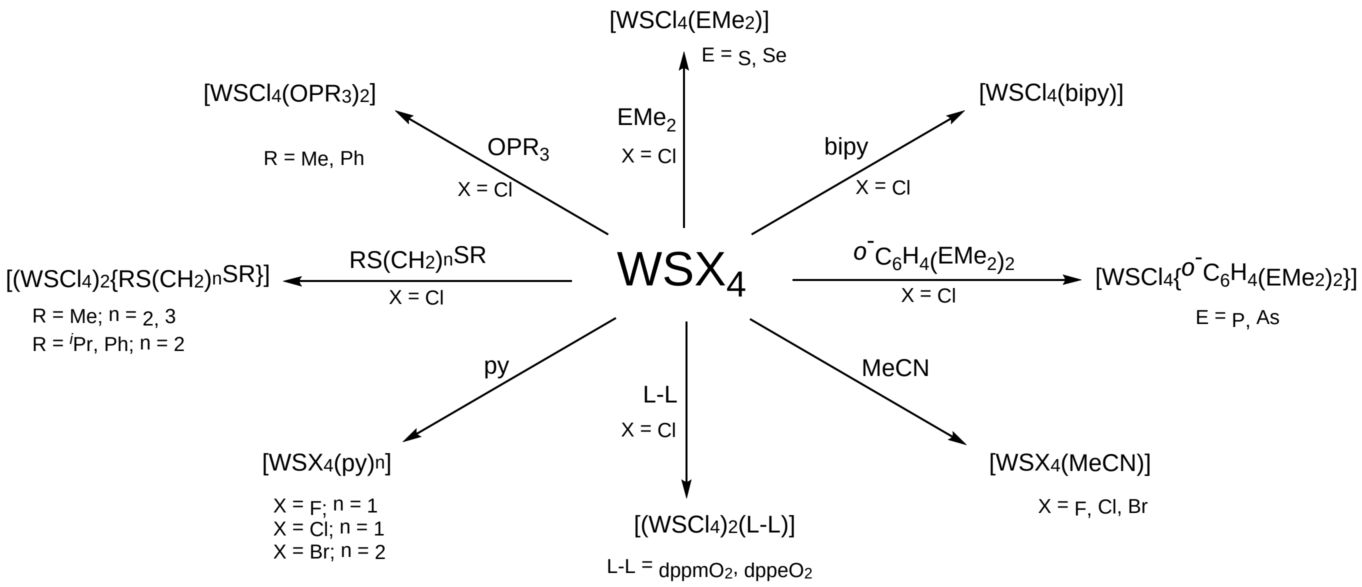


*Fig. 16: Structure of [$WSF_4$(py)] redrawn from Ref. [84].*

The corresponding tungsten oxide fluoride, $WOF_4$, forms both 1:1 and 2:1; complexes with pyridine [85]; that $WSF_4$ only forms a 1:1 adduct even in excess pyridine indicates the sulfide fluoride is a weaker Lewis acid. The [$WSeF_4$(MeCN)], which is mentioned without characterisation details [75], is the only report of an adduct of the selenide fluoride.

The red $WSCl_4$ and green $WSBr_4$ can be prepared by heating the appropriate $WX_6$ with sulfur or $Sb_2S_3$ [64], or, for $WSCl_4$, by reaction of W, $S_2Cl_2$ and S [86], or from $WS_2$ and $Cl_2$ [63]. Reaction of $WCl_6$ and $S(SiMe_3)_2$ in $CH_2Cl_2$ or toluene at ambient temperatures is a convenient alternative [10]. The $WSeX_4$ have usually been made by heating $WX_6$ with $Sb_2Se_3$ [63]. The crystal structures of $WSX_4$ show square pyramidal units weakly linked into dimers, [$X_3SW(\mu\text{-}X)_2WSX_3$], by halide bridges [87]. A polymorph of $WSCl_4$ is a tetramer in which the dimer core is linked by single chlorine bridges to two further $WSCl_4$ molecules [$Cl_4SW(\mu\text{-}Cl)SCl_2W(\mu\text{-}Cl)_2WCl_2S(\mu\text{-}Cl)WSCl_4$] [86]. The reaction of $W(CO)_6$ with $S_2Cl_2$ under reflux and with irradiation gave dark red crystals of [$WSCl_4$]·$S_8$, which contains co-crystallised monomeric $WSCl_4$ and cyclooctasulfur [88]. Electron diffraction studies of the vapours show that all four $WEX_4$ exist as $C_{4v}$ monomers in the gas phase [89,90], a result confirmed by matrix isolation IR spectroscopy [78]. The structures of dark green crystals of [Q][$WSCl_5$] (Q = $Ph_4As$ or $PPh_3(CH_2Ph)$) made from $WSCl_4$ and the appropriate [Q]Cl in $CH_2Cl_2$ solution, have been determined [30,91,92].

The red, very moisture sensitive $WSCl_4$ is probably the best known of the metal chalcogenide halides, and its coordination chemistry is well established (Scheme 3, Table 3); in most cases it adds a donor group *trans* to the W=S to complete distorted octahedral coordination.



*Scheme 3: Selected $WSX_4$ complexes.*

Table 3 Neutral ligand complexes of $WEX_4$

| Compound | Notes | reference |
|---|---|---|
| $[WSF_4(MeCN)]$ | | 75,76 |
| $[WSF_4(py)]$ | | 84 |
| $[WSX_4(MeCN)]$ | X = Cl, Br | 33 |
| $[WSCl_4(thf)]$ | | 93 |
| $[(WSX_4)_2(dioxane)]$ | X = Cl, Br | 93 |
| $[WSX_4(thioxane)]$ | X = Cl, Br; S-coordinated thioxane | 93 |
| $[WSCl_4(thf)]\cdot S_8$ | X-ray structure | 96 |
| $[WSCl_4(py)]$ | | 93, 94 |
| $[WSBr_4(py)_2]$ | | 93 |
| $[WSCl_4(Ph_3PO)]$ | | 33, 94 |
| $[WSCl_4(Me_3PO)]$ | | 94 |
| $[(WSCl_4)_2(dppmO_2)]$ | | 94 |
| $[(WSCl_4)_2(dppeO_2)]$ | X-ray structure | 94 |
| $[WSCl_4(bipy)]$ | 7-coordinate | 94 |
| $[(WSX_4)_2\{MeS(CH_2)_2SMe\}]$ | X = Cl, Br; X-ray structure X = Cl | 93, 95, 99 |
| $[(WSCl_4)_2\{MeS(CH_2)_3SMe\}]$ | X-ray structure | 95 |
| $[(WSCl_4)_2\{{}^iPrS(CH_2)_2S^iPr\}]$ | X-ray structure | 95 |

| | | |
|---|---|---|
| $[(WSCl_4)_2\{PhS(CH_2)_2SPh\}]$ | X-ray structure | 95 |
| $[WSCl_4(SMe_2)]$ | | 95 |
| $[WSCl_4(SeMe_2)]$ | | 95 |
| $[WSCl_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ | 7-coordinate; X-ray structure | 97 |
| $[WSCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$ | 7-coordinate | 97 |
| $[WSeCl_4(thf)]$ | | 93 |
| $[WSeCl_4(MeCN)]$ | | 93 |
| $[(WSeX_4)_2(dioxane)]$ | X = Cl, Br | 93 |
| $[WSeCl_4(thioxane)]$ | S-coordinated thioxane | 93 |
| $[WSeCl_4(py)]$ | | 93 |
| $[WSeBr_4(py)_2]$ | unlikely to be 7-coordinate | 93 |

The majority of the complexes of $WSCl_4$ and $WSeCl_4$ are prepared by mixing the chalcogenide chloride and the ligand in benzene, toluene or $CH_2Cl_2$ solution [93,94,95], but the corresponding bromides were poorly soluble and Soxlet extraction was more successful here [93]. Attempts to make the complexes of $WSCl_4$ by "one pot" reactions of $WCl_6$, $S(SiMe_3)_2$ and the neutral ligand were less reliable and often gave impure products [94].

The resulting complexes are readily hydrolysed, both as solids and in solution [94]. Reduction to W(V) complexes was also observed in some cases and these are discussed further below [93,94,97]. Several phosphine oxide complexes of both $WOCl_4$ and $WSCl_4$ of types $[WE'Cl_4(OPR_3)]$ (R = Me, Ph; E' = O, S) and $[(WE'Cl_4)_2(\mu\text{-}L\text{-}L)]$ (L-L = $dppmO_2$, $dppeO_2$) were prepared and comparison of their structural and spectroscopic properties ($^{1}$H, $^{31}$P{$^{1}$H} NMR, IR etc) showed only small differences. The sulfide chloride complexes seemed rather less robust than the oxide analogues, probably indicating that towards hard ligands at least, the $WOCl_4$ is the stronger Lewis acid [94]. The structure of the brown $[(WSCl_4)_2(dppeO_2)]$ is a centrosymmetric dimer with the tungsten lying out of the $WCl_4$ plane towards the sulfide ligand (Fig. 17) [94]. The pyridine complex $[WSCl_4(py)]$ is a six-coordinate octahedral species [93,94], but the bromide is reported to form a 2:1 complex [93]; this is unlikely to be seven-coordinate. The red $[WSCl_4(bipy)]$ is seven-coordinate, probably pentagonal bipyramidal, based upon the IR and $^{1}$H NMR spectra, but attempts to obtain crystals for an X-ray study resulted in crystals of the W(V) complex due to slow reduction in solution (below) [94]. The corresponding $WOCl_4$ / 2,2'-bipyridyl system, which produces a green diamagnetic complex, $[WOCl_4(bipy)]$, from reaction in $CH_2Cl_2$ solution at room temperature, but under more forcing conditions forms $[WOCl_3(bipy)]$, appears analogous [93,94,98].

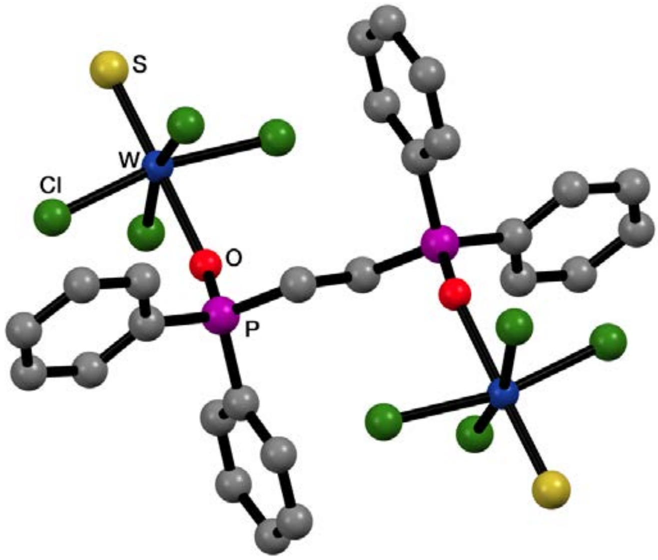


*Fig. 17: Structure of [(WSCl$_4$)$_2$(μ-dppeO$_2$)] redrawn from Ref. [94].*

Red-brown, moisture sensitive thioether complexes, [(WSCl$_4$)$_2${μ-RS(CH$_2$)$_2$SR}] (R = Me, $^i$Pr, Ph), were obtained by reaction of the dithioether and WSCl$_4$ in a 1:2 ratio in CH$_2$Cl$_2$ at ambient temperatures and with rapid isolation of the products [95]. Use of excess ligand or longer reaction times bring about reduction to W(V). The brown [WSCl$_4$(EMe$_2$)] (E = S, Se) were also isolated, but attempts to obtain [(WSCl$_4$)$_2${MeSe(CH$_2$)$_2$SeMe}] or the complex with SPh$_2$ were unsuccessful [95]. All the dithioether complexes have ligand bridged dimer structures (Fig. 18) [95,99]. Some of these thioether complexes have been used as LPCVD reagents for the production of WS$_2$ thin films (Section 4).

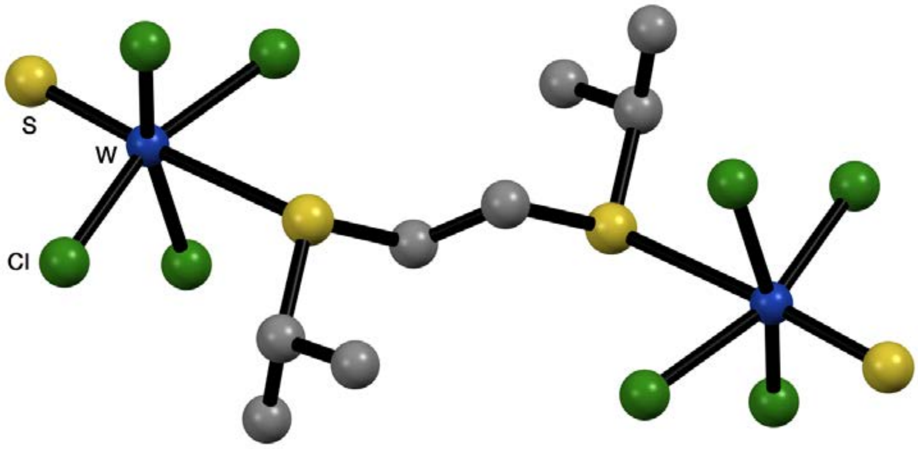


*Fig. 18: Structure of [(WSCl$_4$)$_2${μ-$^i$PrS(CH$_2$)$_2$S$^i$Pr}] redrawn from Ref. [95].*

The reaction of WE'Cl$_4$ (E' = O, S, Se) in toluene with a large excess of PPh$_3$ over several days results in removal of the E' (as Ph$_3$PE') and yellow *trans*-[WCl$_4$(PPh$_3$)$_2$] is isolated in high yield [100]. In contrast, reaction of $WSCl_4$ with $o$-$C_6H_4(QMe_2)_2$ (Q = P, As) in $CH_2Cl_2$ at room temperature produced red-brown [$WSCl_4\{o$-$C_6H_4(QMe_2)_2\}$], which are stable solids under anhydrous conditions, but readily hydrolysed in air, especially in solution [97]. Slow decomposition in $CH_2Cl_2$ solution generated a number of products, which include the sulfur-free, eight-coordinate tungsten(V) cations [$WCl_4\{o$-$C_6H_4(QMe_2)_2\}_2]^+$.

The X-ray structure of [$WSCl_4\{o$-$C_6H_4(PMe_2)_2\}$] (Fig. 19) shows an unusual seven-coordinate pentagonal bipyramidal molecule with axial S/Cl and with the d(W=S) longer than in six-coordinate complexes of $WSCl_4$ [97]. The unusual seven-coordination is also present in [$WOCl_4\{o$-$C_6H_4(AsMe_2)_2\}$] [97] and [$WOF_4\{o$-$C_6H_4(PMe_2)_2\}$] [101].

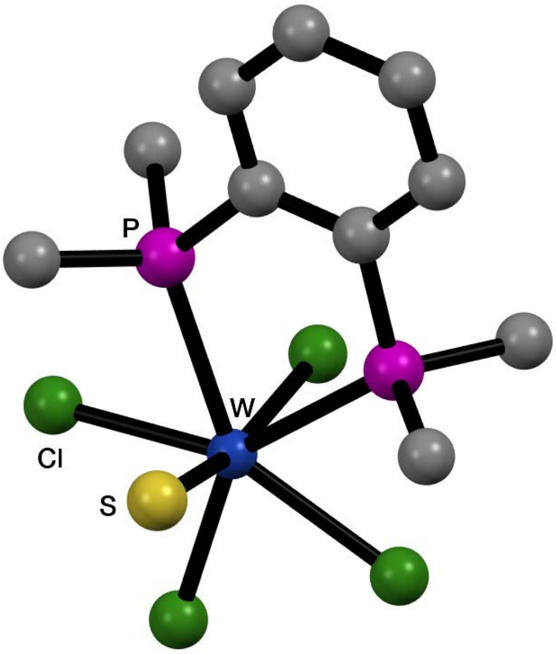


*Fig. 19: Structure of [$WSCl_4\{o$-$C_6H_4(PMe_2)_2\}$] redrawn from Ref. [97].*

Cleavage of an R-O bond in $RO(CH_2)_2OR$ (R = Me, Et, Pr, Ph) occurs on reaction with $WE'Cl_4$ (E' = O, S, Se) in $CHCl_3$ solution, to form the alkoxide complexes [$WE'Cl_3\{O(CH_2)_2OR\}$] [102]; the X-ray structure of [$WSeCl_3\{O(CH_2)_2OMe\}$] showed the Se to be *trans* to the -OMe group [103]. The $WE'Cl_4$ are alkylated by $MgMe_2$ to unstable [$WE'Cl_3Me$], which are stabilised by coordination to a variety of N- and O-donor ligands [104].

The second tungsten(VI) sulfide chloride, $WS_2Cl_2$, can be made from $WSCl_4$ and $S(SiMe_3)_2$ [10], or from $WCl_6$ and $H_2S$ in $CS_2$ [63]. It reacts with [$PPh_4$]Cl in a 2:1 ratio in $CH_2Cl_2$ to give black crystals of *cis*-[$PPh_4$]$_2$[$WS_2Cl_4$]·$2CH_2Cl_2$, whilst from a 1:1 ratio the product is [$PPh_4$][$WS_2Cl_3$] [105]. Little is known about the coordination chemistry of $WS_2Cl_2$, although it is reduced to W(V) by pyridine [106].

In contrast to the molybdenum systems, a number of molecular complexes derived from W(V) chalcogenide chloride have been characterised, although these are often obtained by reduction of $WSCl_4$ rather than from W(V) starting materials. The $WEX_3$ (X = Cl, Br) are formed on heating $WX_5$ with $Sb_2E_3$ [64] and $WSCl_3$ by reduction of $WSCl_4$ with $C_2Cl_4$ [30]. Generally, they fail to react with neutral ligands. Reaction of $WSCl_3$ with $[Ph_4P]Cl$ in $CH_2Cl_2$ produces $[Ph_4P]_2[W_2S_2Cl_8]$, which is believed to be sulfur-bridged [30,105]. The same anion is formed by reaction of $WCl_5$ with $[Et_4N]SH$ [105]. However, reduction of $[WSCl_5]^-$ in the presence of $[Ph_4P]I$ generates $[Ph_4P][WSCl_4]$, whose crystal structure reveals a square pyramidal monomer anion [30,105]. From $[Ph_4As]Cl$ and $WSeCl_3$, the brown $[Ph_4As]_2[Cl_4W(\mu\text{-}Se)(\mu\text{-}Se_2)WCl_4]$ was isolated, which has a W-W single bond (2.862(3) Å) [107].

$WS_2Cl_2$ reacts with excess pyridine to give $[W_2S_4Cl_2(py)_4]$, which has both bridging and terminal W-S links (Fig. 20) [106].

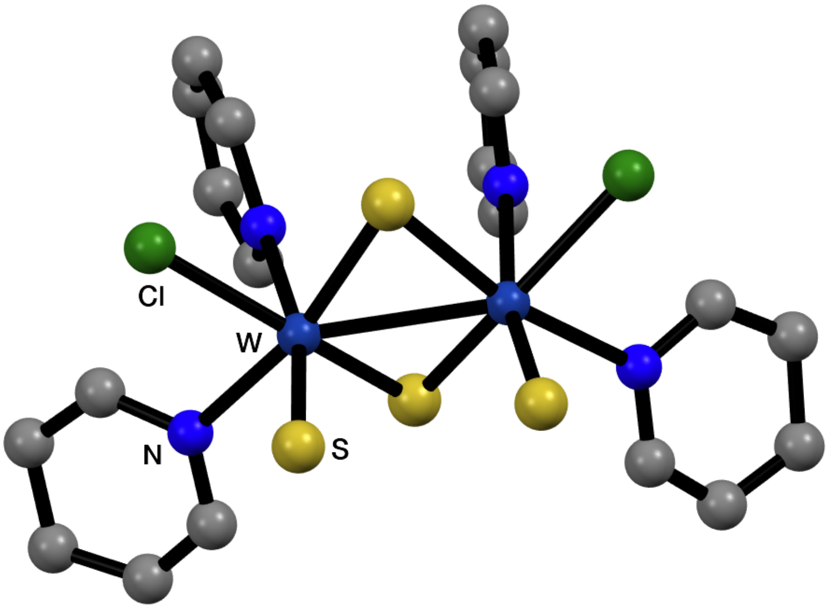


*Fig. 20: Structure of $[W_2Cl_2S_2(\mu\text{-}S)_2(py)_4]$ redrawn from Ref. [106].*

Melting 2,2'-bipyridyl with $WSCl_4$ gave $[WSCl_3(bipy)]$ [93]; crystals of this complex were isolated from a solution of $[WSCl_4(bipy)]$ in $CH_2Cl_2$ after standing for several days, and had the structure shown in Fig. 21 [94]. Reduction of the metal centre also occurs on reaction of $WSCl_4$ with an excess of dithioether or if long reaction times are used [95,108] producing red-brown paramagnetic $[WSCl_3\{RS(CH_2)_2SR\}]$ (R = Me, $^i$Pr), which have the dithioether *trans* to S/Cl (Fig. 21). The W=S bond lengths are little different between the W(VI) and W(V) complexes, although the W-S are shorter in the W(V) complexes.

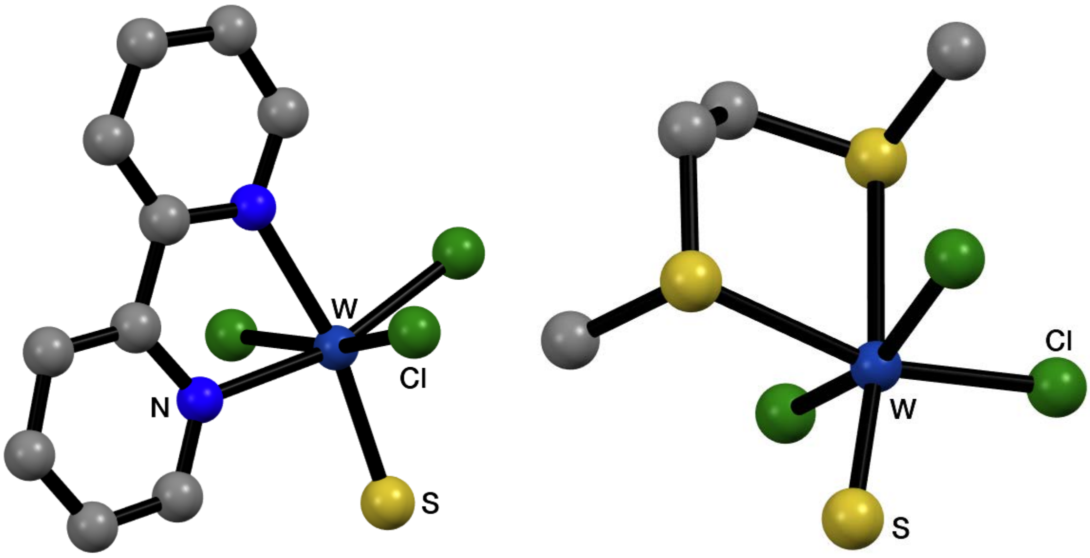


*Fig. 21: Structure of [$WSCl_3$(bipy)] (left) redrawn from Ref. [94] and structure of [$WSCl_3\{MeS(CH_2)_2SMe\}$] (right) redrawn from Ref. [95].*

Although not made from chalcogenide halides, there are a number of other tungsten complexes with S/Cl ligands, including [$WSCl_2(PMePh_2)_3$] and [$WS(CO)Cl_2(MePh_2P)_2$], made by reaction of [$WCl_2(PMePh_2)_4$] and $Ph_2MePS$ or COS, respectively [109]. The former complex also results from reaction of [$WCl_2(PMePh_2)_4$] with thiols [110].

Tungsten forms a range of cluster compounds based upon triangular $W_3$, cubane $W_4$, and raft and octahedral $W_6$ cores, with bridging chalcogenide or dichalcogenide groups, terminal halides and terminal neutral ligands [70,71,72,73]. The $W_3S_7X_4$ (X = Cl, Br) made from the elements (48 h, 425°C) are key starting materials for the $W_3$ compounds [111].

### 3.6 Other Metals

Although a series of rhenium sulfide chlorides have been reported, characterisation is generally poor [6,7, 112] and no chloroanions or neutral ligand complexes seem to have been described. Similarly, $ReSF_4$ and $ReSF_5$ have been made from $ReF_6$ or $ReF_7$ and $Sb_2S_3$, respectively [75,113]. The structure of $ReSF_4$ contains octahedral rhenium linked into chains by *cis* fluoride bridges [75], which suggests that some complexes of type [$ReSF_4$(L)] with N-donor bases (L) should be obtainable.

Sulfide fluorides of the platinum metals with M=S links are unknown, in marked contrast to the range of oxide fluorides of osmium. The brown $RuSCl_4$, obtained from $RuO_4$ and $SCl_2$ in $CCl_4$ [114], is unlikely to be a simple Ru(VI) compound and its structure is unknown. Reaction of $OsF_6$ or $IrF_6$ with $B_2S_3$ gave the fluorosulfonium salts $[SF_3][MF_6]$ rather than sulfide fluorides, whilst $Sb_2S_3$ in anhydrous HF reduced the hexafluorides to lower fluorides with formation of $SbF_3$ [115]. A variety of sulfur/chlorine compounds of osmium, iridium and ruthenium have been reported [116], including $[SCl_3]_2[OsCl_6]$, $[SCl_3]_2[RuCl_3(SCl_2)_3]$, and $[SCl_3]_2[IrCl_4(SCl_2)_2]$ but the structures show these to be trichlorosulfonium salts, not sulfide chlorides.

## 4. Applications

Layered transition metal dichalcogenides are an important family of materials with tuneable band gaps and important applications in electronics, photonics and catalysis [117]. Methods to obtain thin films of these materials include exfoliation from the bulk samples, sulfurisation (or selenisation) of metal or metal oxide films previously deposited on a suitable substrate, atomic layer deposition, and chemical vapour deposition (CVD) [118]. Chemical vapour deposition, in particular, is a versatile, scalable and low-cost deposition method, already widely used in industry for thin film coatings. Dual source CVD is based upon combining two (usually volatile) chemicals, which each contain one of the required elements, and passing the mixture over heated substrates, where they decompose, depositing the $ME_2$ film [119]. An example of this approach is the deposition of $NbSe_2$ from $NbCl_5$ and $Se^nBu_2$ [120]. On the other hand, single source, low pressure CVD (the "low pressure" is necessary to achieve vapourisation of the complex) uses a single molecular reagent, which contains both of the elements to be deposited in the same molecule. For example, $NbSe_2$ has been deposited by LPCVD using $[NbCl_5(Se^nBu_2)]$ [121]. Single source precursors can offer advantages in terms of controlling the stoichiometry of the final film, most cost-effective use of reagents, and in some cases the ability to selectively deposit the $ME_2$ onto particular regions of a micro- or nano-patterned substrates [122]. Neutral metal chalcogenide halides and their complexes are in principle potential single source CVD reagents, since they contain both the metal and chalcogen. The report of the electron diffraction study of $NbSCl_3$ [26] shows it vapourises on heating, but passing this vapour over heated silica substrates in the temperature range 400-750°C, failed to produce any niobium sulfide deposit [25]. However, the use of thioether complexes of $NbSCl_3$ proved more successful [25]. The complexes, $[NbSCl_3(S^nBu_2)]$ and $[NbSCl_3\{^nBuS(CH_2)_3S^nBu\}]$ were selected for this work since the $^nBu$ groups contain β-hydrogens, which offer a low energy decomposition pathway (β-hydride elimination). Black reflective films were produced on silica substrates by LPCVD from $[NbSCl_3(S^nBu_2)]$ at 700°C / 0.05 mmHg, which were identified as 3R-type $NbS_2$ (the 3R refers to the stacking of the layers in the film) by grazing incidence X-ray diffraction (XRD) (Fig. 22). A scanning electron microscope image of the deposit shows polycrystalline $NbS_2$ (Fig. 23). 3R-type $NbS_2$ films were also produced by LPCVD of [$NbSCl_3\{^nBuS(CH_2)_3S^nBu\}$] [25]. The [$NbSe_2Cl_3(Se^nBu_2)$] similarly deposited 2H-$NbSe_2$ films by LPCVD at 650°C and energy dispersive X-ray spectroscopy showed no chlorine content in the resultant films [25].

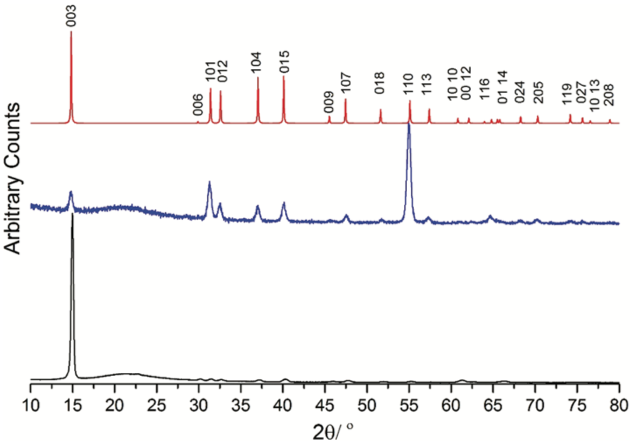


*Fig. 22: In plane X-ray diffraction (blue), grazing incidence (incidence angle = 1°) XRD (black) from the* $NbS_2$ *thin film deposited by low pressure CVD using [*$NbSCl_3(S^nBu_2)$*] at 700 °C, and the XRD (red) of bulk* $NbS_2$ *from Ref. [25] with permission from the Royal Society of Chemistry.*

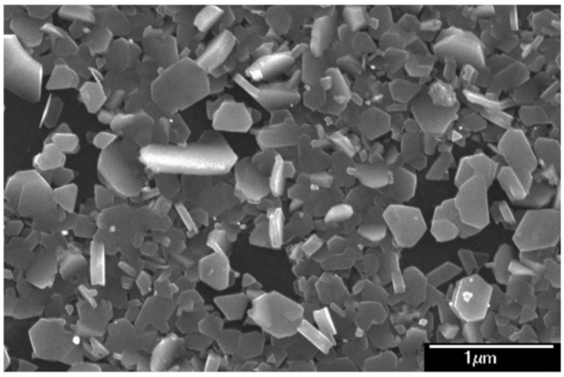


*Fig. 23: Scanning electron microscope image of polycrystalline* $NbS_2$ *film deposited by low pressure CVD from [*$NbSCl_3(S^nBu_2)$*] at 700 °C, from Ref. [25] with permission from the Royal Society of Chemistry.*

Curiously, attempts to deposit $TaS_2$ films from the analogous precursor, [$TaSCl_3\{^nBuS(CH_2)_3S^nBu\}$], failed [60]. Similarly, [$TaSCl_3\{^nBuSe(CH_2)_3Se^nBu\}$] gave only red deposits that were identified as elemental selenium by powder XRD analysis. Obviously, the change from Nb to Ta involves an increase in the molecular weight of the precursor complex by some 88 a.m.u., which might reduce volatility, but this seems unlikely to be the only cause of the failure. Comparison of the chemistry of the niobium and tantalum pentahalide and sulfide trichloride complexes [25,60,121] suggests the niobium species are rather more robust, probably due to tantalum(V) being a harder Lewis acid and binding the softer thioether ligands less strongly. The greater chemical stability of Ta(V) towards reduction may also hinder the decomposition to form $TaS_2$. Designing successful single source LPCVD reagents at the present state of development and understanding involves some degree of trial and error to achieve all the necessary characteristics for deposition of the target material. Further studies of related tantalum chalcogenide systems may shed more light on the requirements for successful CVD precursors for $TaE_2$ films.

In the case of tungsten dichalcogenides, the first single source LPCVD reagents for deposition of $WS_2$ has been reported very recently [95]. $[(WSCl_4)_2\{\mu\text{-}{}^iPrS(CH_2)_2S^iPr\}]$ at 590-620°C / 0.1 mmHg gave thin bronze films shown by scanning electron microscopy (Fig. 24), grazing incidence XRD analysis and Raman spectroscopy (Fig. 25) to be 4H $WS_2$ [95]. The film deposition was achieved despite the relatively high molecular weight of the dinuclear precursor (supporting the hypothesis that the MWt of the precursor is not the critical factor hindering the $TaE_2$ deposition as discussed above); a significant residue of dark material is left in the precursor bulb.

The subtlety of the parameters involved in determining the key design features for an effective LPCVD precursor is shown by the fact that no deposit at all was observed under the same conditions using the mononuclear tungsten(V) complex, $[WSCl_3\{{}^iPrS(CH_2)_2S^iPr\}]$, despite the fact that it has a M.Wt. almost half that (500 versus 894) of the (successful) tungsten(VI) dimer complex.

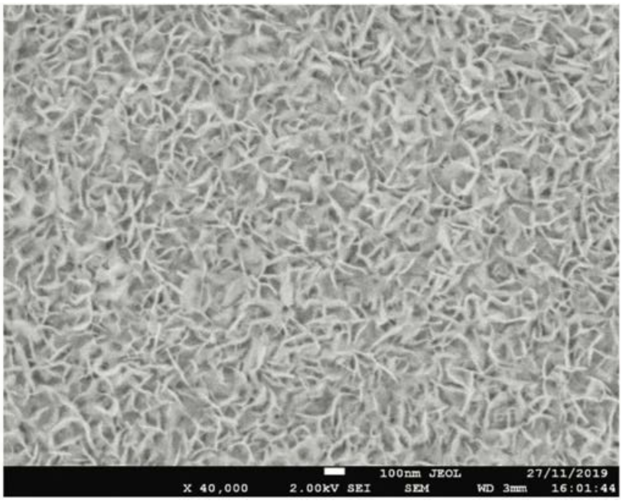


*Fig. 24: Scanning electron microscope image of a continuous* $WS_2$ *thin film produced by low pressure CVD using* $[(WSCl_4)_2\{\mu\text{-}{}^iPrS(CH_2)_2S^iPr\}]$ *from Ref. [95] with permission from the Royal Society of Chemistry.*

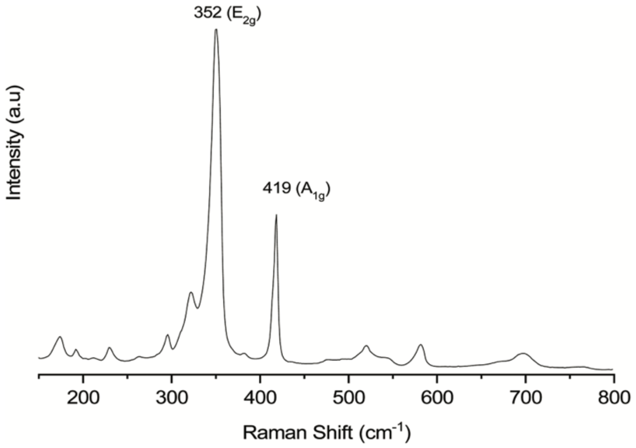


*Fig. 25: Raman spectrum of the $WS_2$ film obtained using $[(WSCl_4)_2\{\mu\text{-}^iPrS(CH_2)_2S^iPr\}]$ from Ref. [95] with permission from the Royal Society of Chemistry.*

The investigations of transition metal chalcogenide halide complexes as LPCVD reagents are clearly at an early stage and further work is necessary to refine the systems and evaluate their utility for this application.

## 5. Conclusions and Outlook

The existing literature described in Section 3 shows that the coordination chemistry of transition metal chalcogenide halides is essentially limited to a few systems, *viz* $NbEX_3$ (E = S, Se; X = Cl, Br), $TaSCl_3$ and $WSCl_4$, leaving considerable scope for new work and to reveal properties, trends and possible applications.

For the chalcogenide fluorides, only two complexes have been described, both based upon $WSF_4$ [76,84]. Further examples with hard N- and O-donor ligands (*cf.* $[WOF_4(L)_2]$ [123]) are expected to be reasonably stable, as should analogues with $WSeF_4$. Whether complexes with softer donor ligands, such as alkyl phosphines, could be prepared is less easy to predict; the very sensitive $[WOF_4(\text{diphosphine})]$ [101] may have (probably less stable) analogues with $WSF_4$. Complexes of $MoSF_4$ with N- and O-donor ligands are anticipated to be less stable than their tungsten(VI) analogues, but again, comparison with the known $[MoOF_4(L)]$ [124] would lead one to expect that such complexes will form under appropriate (and rigorously anhydrous) conditions. Similarly, the ready preparation of vanadium oxide fluoride complexes [125,126] suggests that complexes of $VSF_2$, and possible even $VSF_3$ would be worthy of investigation, although the absence of the parent chalcogenide fluorides and of other chalcogen halides of vanadium (section 3.1) in the literature is very surprising.

Of the other metals, rhenium appears a likely candidate, with complexes of $ReSF_4$ being most likely to be able to be formed. The major barrier to development of chalcogenide fluoride chemistry is likely to be that few laboratories have the facilities necessary to handle the metal fluorides needed for their synthesis, rather than inherent instability of the complexes.

Turning to the transition metal chalcogenide chloride and bromide systems, the selenides are much less thoroughly studied than the sulfides, with only complexes derived from $NbSeX_3$ (Section 3.2) investigated in any detail. Study of $TaSeX_3$ and $WSeX_4$ complexes would enable comparisons of the Lewis acidity with those of the corresponding sulfides; they also have the possibility of using $^{77}Se$ NMR spectroscopy as a sensitive probe to elucidate the reaction chemistry. The chalcogenide bromides are expected to be poorer Lewis acids than the corresponding chlorides, and the metal centres more prone to reduction, but some study here would contribute to the overall establishment of stability patterns.

Redox chemistry has been explored in some detail in the niobium systems (Section 3.2). This is an area where the oxide halide and chalcogenide halide chemistry are fundamentally different, in that reduction of the metal oxidation state in the latter leads to species with $(E\text{-}E)^{2-}$ (E = S, Se) ligands, whereas peroxide analogues do not form in this way in the oxide halide systems.

The chemistry of the molybdenum systems also warrants re-examination. The literature (Section 3.3) contains a few examples of complexes formulated as $[MoSCl_3(L)_2]$ (L = MeCN, dioxane, etc.) [69] made from $MoSCl_3$, but none have been authenticated by X-ray crystallographic analysis; $MoSeCl_3$ appears not to form complexes with neutral ligands. The $MoSCl_3$ made by high temperature routes contain Mo(IV) and disufide groups [67], but the structure of the $MoSCl_3$ [10] made by low temperature routes has not been established. If this is a genuine molybdenum(V) compound, then some $[Mo^{V}SCl_3(L)_2]$ species may be obtainable, but it is clear that molybdenum sulfide halide chemistry is dominated by that of Mo-Mo dimers and clusters. Some complexes of tungsten(V) such as $[WSCl_3(dithioether)]$ or $[WSCl_3(bipy)]$ are clearly established, but they have been obtained by reduction of the $WSCl_4$ complexes rather than directly via $WSCl_3$ [93,95,108].

From the coordination chemistry perspective, the general paucity of chalcogenide halide complexes with phosphine or arsine ligands is surprising, since these play a major role in oxide halide chemistry. The reports of the seven-coordinate $[NbSCl_3(PMe_3)_3]$[37] and $[WSCl_4(L\text{-}L)]$ (L-L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$) [97] demonstrate that under appropriate conditions, such complexes can be formed. Possibly the reports that phosphines desulfurise some sulfide halide complexes [47, 100] (with production of $SPR_3$) deterred further studies, although it should be pointed out that the desulfurisation took days to accomplish, whereas under the correct conditions, complexation is usually much faster.

Several of the thioether complexes of $NbSCl_3$ and $WSCl_4$ have been shown to function as single source LPCVD reagents for the production of the corresponding $MS_2$ semi-conducting thin films. Single source precursors potentially give more control over the deposition process, including morphology and thickness of the films and may be valuable reagents for the generation of nanowires, nanoparticles or for use in other deposition techniques, such as aerosol assisted CVD. In the longer term it should be possible to develop reagents for deposition of $WSe_2$ from $WSeCl_4$ complexes, and maybe even identify reagents that could be used for other early d-block dichalcogenides.

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## Declaration of Interest

The authors have no interests to declare.

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