Chalcogenoether complexes of tantalum(V) sulfide trichloride – synthesis, properties and structures

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Abstract

The complexes [$TaSCl_3$(L-L)] (L-L = $MeSCH_2CH_2SMe$, ${}^iPrSCH_2CH_2S^iPr$, $PhSCH_2CH_2SPh$, ${}^nBuSCH_2CH_2CH_2S^nBu$, $MeSCH_2CH_2CH_2SMe$, $MeSeCH_2CH_2SeMe$ ${}^nBuSeCH_2CH_2CH_2Se^nBu$) have been synthesised and isolated in good yield as powdered solids by the reaction of $TaCl_5$ with the appropriate chalcogenoether in a 1:1 molar ratio in anhydrous CH_2Cl_2 solution at room temperature, followed by the addition of a CH_2Cl_2 solution containing one mol. equiv. of $S(SiMe_3)_2$. The isolated complexes were characterised by IR, ${}^1H$ and ${}^{77}Se\{{}^1H\}$ NMR spectroscopy, as appropriate, and elemental analysis. Single crystal X-ray structure analyses for [$TaSCl_3(MeSCH_2CH_2SMe)$], [$TaSCl_3(MeSeCH_2CH_2SeMe)$], [$TaSCl_3({}^iPrSCH_2CH_2S^iPr)$] and [$TaSCl_3({}^nBuSCH_2CH_2CH_2S^nBu)$] have been obtained. The data are compared with the previously described Nb(V) analogues. In contrast to the corresponding [$NbSCl_3(E^nBu_2)$] (E = S, Se), attempts to isolate [$TaSCl_3(E^nBu_2)$] were unsuccessful. Low pressure chemical vapour deposition (LPCVD) experiments using [$TaSCl_3({}^nBuSCH_2CH_2CH_2S^nBu)$] did not lead to any deposition, whilst similar experiments using [$TaSCl_3({}^nBuSeCH_2CH_2CH_2Se^nBu)$] produced only elemental Se films, with no evidence for any deposition of tantalum sulfide or selenide films.

Keywords: tantalum sulfide trichloride, thioether, selenoether, crystal structure

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1. Introduction

The early 4d and 5d metals in their higher oxidation states form sulfide and selenide halides which are modest Lewis acids, forming complexes with neutral ligands from groups 15 and 16, although they have received much less study than the corresponding oxide halides [1,2,3]. The $TaECl_3$ (E = S, Se) were first obtained some 50 years ago by reaction of $TaCl_5$ with Sb_2E_3 or Bi_2E_3 in CS_2 [3,4] but in marked contrast to the $NbECl_3$ [5,6,7,8], have been little studied, and the structures of the

$TaECl_3$ species appear to be unknown. A very small number of complexes of $TaECl_3$ have been described, including $[TaSCl_3(MeCN)_2]$ [4,6], $[TaSCl_3(SMe_2)_2]$ [4], $[TaSCl_3\{PhS(CH_2)_2SPh\}]$ [4] and the anions $[TaSCl_4(\kappa^1\text{-}1,4\text{-dioxane})]^-$ and $[(TaSCl_4)_2(\mu\text{-}1,4\text{-dioxane})]^{2-}$ [9] of which the last three were authenticated by X-ray crystallographic studies. We have recently reported a comparison of the complexes of $TaOCl_3$ and $TaSCl_3$ with hard O- and N-donor ligands, including the white $[TaOCl_3(OPPh_3)_2]$, $[TaOCl_3(L\text{-}L)]$ (L-L = 1,10-phenanthroline, 2,2'-bipyridyl, $Ph_2P(O)CH_2P(O)Ph_2$, $Ph_2P(O)CH_2CH_2P(O)Ph_2$ and $o\text{-}C_6H_4(P(O)Ph_2)_2$), which were prepared from $TaCl_5$, $O(SiMe_3)_2$ and the ligands in anhydrous CH_2Cl_2 solution; the yellow $[TaSCl_3(OPPh_3)_2]$ and $[TaSCl_3(L\text{-}L)]$ made similarly using $S(SiMe_3)_2$ [10]. X-ray crystal structures were obtained for $[TaSCl_3(1,10\text{-phen})]$, $[TaSCl_3(OPPh_3)_2]$, $[TaSCl_3\{Ph_2P(O)CH_2CH_2P(O)Ph_2\}]$ and $[TaSCl_3(MeCN)_2]$, which all contain *mer*-chlorines, with the neutral ligands *trans* to S/Cl.

Layered transition metal dichalcogenides ME_2 (M = Nb, Ta, V, W, Mo etc; E = S, Se or Te) are inorganic analogues of graphene and their band gaps and other properties for various applications can be tuned by varying the chalcogen or the metal [11],[12]. In recent studies we have examined a range of thio- and seleno-ether complexes of niobium and tantalum halides as potential single source low pressure chemical vapour deposition (LPCVD) reagents for the production of thin films of the transition metal dichalcogenides [13-15]. Thus, $[NbCl_5(E^nBu_2)]$ produced thin films of the 3R-polytype (R3mh) of NbS_2 and $NbSe_2$; the butyl-substituents provide a β-hydride decomposition route facilitating cleavage of the ligands in an accessible temperature range. Similar LPCVD experiments using the niobium sulfide trichloride complexes, $[NbSCl_3(S^nBu_2)$ and $[NbSCl_3\{^nBuS(CH_2)_3S^nBu\}]$, produced 3R-$NbS_2$, whilst $[NbSe_2Cl_3(Se^nBu_2)]$ produced 2H-$NbSe_2$ thin films [8]. On the other hand, none of the corresponding tantalum complexes were found to be suitable LPCVD reagents, and single source precursors to TaE_2 remain to be developed. Here we report the synthesis, spectroscopic and structural characterization of a series of complexes of $TaSCl_3$ with thio- and seleno-ethers, along with the results from LPCVD experiments using selected examples.

2. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1}. ^1H and $^{77}Se\{^1H\}$ NMR spectra were recorded from CD_2Cl_2 solutions using a Bruker AV400 spectrometer and referenced to TMS via the residual solvent resonance and external neat $SeMe_2$, respectively. Microanalyses were undertaken at

Medac. Hexane was dried by distillation from sodium prior to use, and CH_2Cl_2 by distillation from CaH_2. All preparations were carried out under rigorously anhydrous conditions *via* a dry dinitrogen atmosphere and standard Schlenk and glovebox techniques. $TaCl_5$ and $S(Me_3Si)_2$ were obtained from Sigma-Aldrich and used as received. The thioether and selenoether ligands were made as described [16,17,18.19].

2.1 [TaSCl₃(PhSCH₂CH₂SPh)]·CH₂Cl₂

$TaCl_5$ (0.30 g, 0.84 mmol) was stirred in dichloromethane (5 mL). A solution of $PhSCH_2CH_2SPh$ (0.21 g, 0.84 mmol) in dichloromethane (1 mL) was added and stirred for 2 h, causing a colour change to yellow. $S(Me_3Si)_2$ (0.15 g, 0.84 mmol) dissolved in dichloromethane was then added to the reaction mixture and stirred for 2 h, giving a dark orange solution. The solvent was removed *in vacuo* and the resulting orange-brown solid was washed with n-hexane (2 mL). Yield: 0.28 g, 59%. Required for $C_{14}H_{14}Cl_3S_3Ta\cdot CH_2Cl_2$ (650.7): C, 27.69; H, 2.4. Found: C, 27.78, 2.30 %. ^1H NMR (CD_2Cl_2, 295 K): 3.84 (br s, [4H], CH_2), 7.37-7.50 (m, [10H], Ph); (203 K): 3.75 (br s, [2H], CH_2), 4.09 (br s, [2H], CH_2), 7.36-7.64 (m, [10H], Ph. IR spectrum (Nujol mull)/cm^{-1}: 519, 513 (Ta=S), 360s, 320m (br, Ta-Cl).

2.2 [TaSCl₃(MeSCH₂CH₂SMe)]

Method 1: $TaCl_5$ (0.30 g, 0.84 mmol) was stirred in anhydrous CH_2Cl_2 (5 mL). A solution of $MeSCH_2CH_2SMe$ (0.11 g, 0.84 mmol) in CH_2Cl_2 (5 mL) was added and the reaction stirred for 30 min., giving a yellow solution immediately on addition of the ligand. $S(SiMe_3)_2$ (0.15 g, 0.84 mmol) dissolved in CH_2Cl_2 (1 mL), was then added to the reaction mixture, causing a colour change from bright yellow to straw coloured with some solid precipitating. The reaction was stirred for a further 16 h, during which time the solid all dissolved and the solution became darker. The solution was filtered and then concentrated and a dark brown solid was precipitated with n-hexane (2 mL), collected by filtration and dried *in vacuo*. Yield 0.24 g, 66 %. Orange crystals were obtained by layering a dichloromethane solution of the product with hexane. Required for $C_4H_{10}Cl_3S_3Ta$ (441.3): C, 10.88; H, 2.28 %. Found: C, 11.23; H, 2.65 %. ^1H NMR (CD_2Cl_2, 295 K): 2.27 (s, [3H], Me), 2.89 (s, [3H], Me), 3.08 (br m, [2H], CH_2), 3.47 (br m, [2H], CH_2). IR (Nujol)/cm^{-1}: 508 s (Ta=S), 327 m, 352 s (Ta-Cl).

2.3 [TaSCl₃(ⁱPrSCH₂CH₂SⁱPr)]

$TaCl_5$ (0.30 g, 0.837 mmol) was stirred in CH_2Cl_2 (5 mL). A solution of $^iPrSCH_2CH_2S^iPr$ (0.19 g, 0.84 mmol) in CH_2Cl_2 (5 mL) was added and stirred for 16 h, giving a yellow solution. $S(SiMe_3)_2$ (0.15 g, 0.84 mmol) dissolved in CH_2Cl_2 (1 mL) was then added to the reaction mixture and stirred for 2 days, during which the solution turned from yellow to brown to black. The solution was concentrated and the dark solid was precipitated with n-hexane, collected by filtration, washed with n-hexane and dried *in vacuo.* Yield 0.32 g, 77 %. Dark purple crystals were obtained by layering a solution of the product in CH_2Cl_2 with hexane. Required for $C_8H_{18}Cl_3S_3Ta$ (497.4): C, 19.30; H, 3.65. Found: C, 18.73; H, 3.50 %. ^1H NMR (CD_2Cl_2, 295 K): δ = 1.34 (d, [6H], ^3J = 8 Hz, CH_3), 1.61 (d, [6H], ^3J = 8 Hz, CH_3), 3.05 (m, [2H], CH_2), 3.24 (septet, [1H], ^3J = 8 Hz, CH), 3.49 (m, [2H], CH_2), 3.58 (septet [1H], ^3J = 8 Hz, CH). IR spectrum (Nujol)/cm^{-1}: 509 (Ta=S), 329 s, 351 m (Ta-Cl).

2.4 [$TaSCl_3(MeSCH_2CH_2CH_2SMe)$]

$TaCl_5$ (0.30 g, 0.84 mmol) was stirred in CH_2Cl_2 (5 mL). A solution of $MeSCH_2CH_2CH_2SMe$ (0.115 g, 0.84 mmol) in CH_2Cl_2 (5 mL) was added and stirred for 4 h. The solution turned yellow on addition of the ligand. $S(SiMe_3)_2$ (0.149 g, 0.84 mmol) dissolved in CH_2Cl_2 (1 mL) was then added to the reaction mixture and stirred for 16 h. The solution turned from bright yellow to dark green. Dark green crystals were obtained from a CH_2Cl_2 solution of the product layered with hexane. Yield 0.243 g, 64 %. Required for $C_5H_{12}Cl_3S_3Ta$ (455.3): C, 13.18; H, 2.65. Found: C, 13.40; H, 2.64 %. ^1H NMR (CD_2Cl_2, 295 K): δ = 2.08 (br s, [3H], Me), 2.24 (s, [3H], Me) 2.58 (br s, [2H], CH_2), 3.01 (br s, [2H], CH_2), 3.32 (br s, [2H], CH_2). IR spectrum (Nujol)/cm^{-1}: 507 m (Ta=S), 326 br, s (Ta-Cl).

2.5 [$TaSCl_3(^nBuSCH_2CH_2CH_2S^nBu)$]

$TaCl_5$ (0.30 g, 0.84 mmol) was stirred in CH_2Cl_2 (5 mL). A solution of $^nBuSCH_2CH_2CH_2S^nBu$ (0.185 g, 0.84 mmol) in CH_2Cl_2 (5 mL) was added and stirred for 4 h. The solution turned yellow after stirring for 20 mins. $S(SiMe_3)_2$ (0.15 g, 0.84 mmol), dissolved in CH_2Cl_2 (1 mL) was then added to the reaction mixture and stirred for16 h; after 30 mins. the solution had turned from yellow to black. A dark solid was precipitated by the addition of n-hexane, collected by filtration, washed with n-hexane and dried in vacuo. Yield 0.211 g, 47 %. Required for $C_{11}H_{24}Cl_3S_3Ta$ (539.8): C, 24.47; H, 4.48. Found: C, 24.33; H, 4.70 %. ^1H NMR (CD_2Cl_2): 0.91 (m, [3H], CH_3), 0.93 (m, [3H], CH_3), 1.41 (vbr, m, [6H], CH_2), 1.55 (br, [4H], CH_2), 2.51 (m [2H], CH_2), 2.59 (br, [2H], CH_2), 3.07 (v br [2H], CH_2), 3.31 (v br [2H], CH_2). IR spectrum (Nujol)/cm^{-1}: 508 (Ta=S), 340sh, 328 (br, Ta-Cl).

2.6 [$TaSCl_3(MeSeCH_2CH_2SeMe)$]

$TaCl_5$ (0.30 g, 0.837 mmol) was stirred in CH_2Cl_2 (5 mL). A solution of $MeSeCH_2CH_2SeMe$ (0.181 g, 0.837 mmol) in CH_2Cl_2 (5 mL) was added and stirred for 3 h, giving a yellow solution. $S(SiMe_3)_2$ (0.149 g, 0.84 mmol) dissolved in CH_2Cl_2 (1 mL) was then added to the reaction mixture and stirred for 3 h, causing a colour change to brown then black. The solution was concentrated and a black solid and dark purple crystals were formed by addition of a layer of n-hexane (2 mL). These were collected by filtration and dried *in vacuo*. Yield 0.37 g, 82 %. Required for $C_4H_{10}Cl_3SSe_2Ta.CH_2Cl_2$ (620.35): C, 9.68; H, 1.95. Found: C, 9.55; H, 1.94 %. ^1H NMR (CD_2Cl_2): δ = 2.15 (s, [3H], Me), 2.74 (s, [3H], Me), 3.13 (br m, [2H], CH_2), 3.63 (br m, [2H], CH_2). $^{77}Se\{^1H\}$ NMR (CD_2Cl_2, 295 K): 144 (s, [Se]), 186 (s,[Se]). IR spectrum (Nujol)/cm^{-1}: 326 s, 348 m (Ta-Cl), 507 s (Ta=S).

2.7 [$TaSCl_3(^nBuSeCH_2CH_2CH_2Se^nBu)$]

$TaCl_5$ (0.30 g, 0.84 mmol) was stirred in CH_2Cl_2 (5 mL). A solution of $^nBuSeCH_2CH_2CH_2Se^nBu$ (0.26 g, 0.84 mmol) in CH_2Cl_2 (5 mL) was added and stirred for 4 h. The solution turned yellow after 30 mins. $S(SiMe_3)_2$ (0.15 g, 0.84 mmol) dissolved in CH_2Cl_2 (1 mL) was then added to the reaction mixture and stirred for 16 h, during which the solution turned from yellow to black. The solvent was removed *in vacuo* leaving a dark oil, which was washed with hexane and afforded a black solid. Yield 0.28 g, 52 %. Required for $C_{11}H_{24}Cl_3SSe_2Ta.CH_2Cl_2$ (718.5): C, 20.06; H, 3.65. Found: C, 19.86; H, 3.67 %. ^1H NMR (CD_2Cl_2, 295 K): δ = 0.93 (t, [6H], CH_3), 1.43 (m, [4H], CH_2), 1.66 (m, [4H], CH_2), 1.99 (br, [2H], CH_2), 2.34 (br, [2H], CH_2), 2.58 (br, [2H], CH_2), 2.62 (br, [2H], CH_2), 2.62 (br, [2H]), 3.19 (br, [2H], CH_2). $^{77}Se\{^1H\}$ NMR (CH_2Cl_2, 298 K): no resonance. IR spectrum (Nujol)/cm^{-1}: 331, 307 (br, Ta-Cl), 508 (Ta=S).

2.8 X-Ray experimental

Data collections for single crystal X-ray analyses used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K (N_2 cryostream). Crystallographic parameters are in the (Table 1). Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2014/7 [20], H atoms were added and refined with a riding model.

3. Results and Discussion

Addition of the one mol. equivalent of the dithioethers $PhSCH_2CH_2SPh$, $MeSCH_2CH_2SMe$, $MeSCH_2CH_2CH_2SMe$ $^nBuSCH_2CH_2CH_2S^nBu$ or $^iPrSCH_2CH_2S^iPr$ to $TaCl_5$ in anhydrous CH_2Cl_2 gave bright yellow solutions. Treatment of these solutions with one mol. equivalent of $S(SiMe_3)_2$ in CH_2Cl_2 caused the colours to darken and work up gave dark solids with microanalyses confirming the composition as [$TaSCl_3$(dithioether)]. The colours of the solids isolated with a specific dithioether were observed to be rather variable although the IR and NMR spectra indicated all batches contained the same species. The solid complexes also darken and become sticky over time in the glove box. Similar colour variation has been observed in the $NbSCl_3$ systems [7,8,21] and was attributed to the presence of small amounts of disulfide ($[S_2]^{2-}$) ligands in some samples, formed by a redox-disproportionation reaction, and formation of complexes such as [$Nb_2Cl_4S_3(tht)_4$] (tht = tetrahydrothiophene) [7]. Similar disulfide species have not been identified thus far in the tantalum thiochloride systems, but this appears a likely explanation for the colour variation in the complexes reported here. For several of the complexes the single crystals selected for the X-ray analysis were also intensely coloured, e.g. orange-brown for [$TaSCl_3(MeSCH_2CH_2SMe)$], purple for [$TaSCl_3(^iPrSCH_2CH_2S^iPr)$], dark green for [$TaSCl_3(MeSCH_2CH_2CH_2SMe)$]. Attempts to prepare the complexes from [$TaSCl_3(MeCN)_2$] [10] were not successful, with the MeCN not being cleanly substituted. The addition of the appropriate diselenoethers, $MeSeCH_2CH_2SeMe$ or $^nBuSeCH_2CH_2CH_2Se^nBu$ to a solution of $TaCl_5$ in CH_2Cl_2, followed by $S(SiMe_3)_2$, gave the purple-black [$TaSCl_3$(diselenoether)], but attempts to isolate [$TaSCl_3(MeSeCH_2CH_2CH_2SeMe)$] were unsuccessful.

Crystals of [$TaSCl_3(^nBuSCH_2CH_2CH_2S^nBu)$] were obtained from a CH_2Cl_2 solution layered with *n*-hexane. The structure is shown in Figure 1 and reveals six-coordinate tantalum with *mer*-chlorines and the dithioether, which has the *meso*-conformation, *trans* to S/Cl. The d(Ta-S1) = 2.199(3) Å and d(Ta-Cl2) = 2.283(3) Å, whilst the axial Ta-Cl are significantly longer (2.360(2), 2.345(2) Å). Disorder of the S and Cl *trans* to the neutral ligands in complexes of the type [$MSCl_3(L)_2$] (M = Nb, Ta) is common [5,8,9,22], and since S^{2-} and Cl^- are isoelectronic and have very similar scattering power, it is not possible to completely rule out *some* disorder in such systems. However, in the case of [$TaSCl_3(^nBuSCH_2CH_2CH_2S^nBu)$], the structure appears disorder-free, with the difference in Ta=S and Ta-Cl2 much as expected. It is notable that the Ta-$S_{thioether}$ distances are also significantly different d(Ta1–S3) = 2.684(2) and d(Ta1–S2) = 2.791(2) Å, which is attributed to the *trans* influence Ta=S > Ta-Cl. The complex adopts the DL stereoisomer.

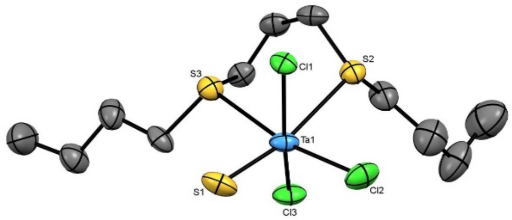

Figure 1 View of the structure of [$TaSCl_3(^nBuSCH_2CH_2CH_2S^nBu)$] with numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ta1–Cl1 = 2.360(2), Ta1–S3 = 2.684(2), Ta1–Cl3 = 2.345(2), Ta1–S1 = 2.199(3), Ta1–S2 = 2.791(2), Ta1–Cl2 = 2.283(3), Cl1–Ta1–S3 = 82.12(7), Cl1–Ta1–S2 = 75.16(7), S3–Ta1–S2 = 80.59(7), Cl3–Ta1–Cl1 = 156.78(8), Cl3–Ta1–S3 = 82.87(8), Cl3–Ta1–S2 = 84.99(8), S1–Ta1–Cl1 = 97.24(8), S1–Ta1–S3 = 90.45(10), S1–Ta1–Cl3 = 100.49(9), S1–Ta1–S2 = 168.90(9), S1–Ta1–Cl2 = 103.81(11), Cl2–Ta1–Cl1 = 95.64(9), Cl2–Ta1–S3 = 165.74(9), Cl2–Ta1–Cl3 = 94.56(9), Cl2–Ta1–S2 = 85.22(9).

X-ray structures were also determined for [$TaSCl_3(MeSCH_2CH_2SMe)$] and [$TaSCl_3(^iPrSCH_2CH_2S^iPr)$] (Figures 2 and 3), and here the very similar "Ta=S" and "Ta-Cl_{transS}" and the similar Ta-S distances to the dithioether ligands clearly show that disorder is present. Attempts to model the disorder by splitting the site occupancies were unsuccessful, and whilst the structures serve to confirm the basic geometries, comparisons of the metrical data are unreliable. The coordinated dithioethers in both structures are the *DL* diastereoisomer.

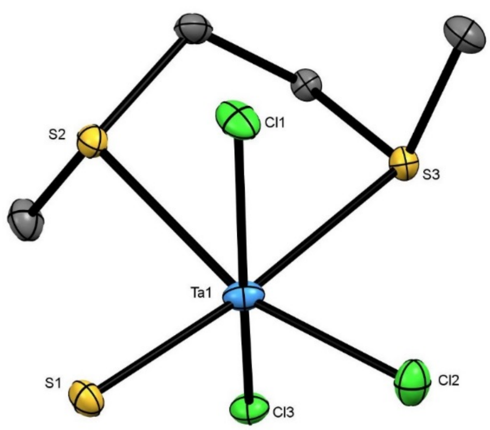

Figure 2 View of the structure of [$TaSCl_3(MeSCH_2CH_2SMe)$] with numbering scheme adopted. Ellipsoids are shown at the 50% probability level. Note that S1 and Cl2 are disordered. Selected bond lengths (Å) and angles (°): Ta1–S3 = 2.7243(13), Ta1–Cl3 = 2.3600(12), Ta1–S1 = 2.2301(13), Ta1–Cl2 = 2.2642(13), Ta1–S2 = 2.6993(12), Ta1–Cl1 = 2.3522(13), Cl3–Ta1–S3 = 76.71(4), Cl3–Ta1–S2 = 84.72(4), S1–Ta1–S3 168.01(5), S1–Ta1–Cl3 = 96.24(5), S1–Ta1–Cl2 = 105.79(5), S1–Ta1–S2 = 91.23(4), S1–Ta1–Cl1 = 97.98(5), Cl2–Ta1–S3 = 84.83(5), Cl2–Ta1–Cl3 = 96.45(5),

Cl2–Ta1–S2 = 162.66(5), Cl2–Ta1–Cl1 = 96.37(5), S2–Ta1–S3 = 78.58(4), Cl1–Ta1–S3 = 86.10(4), Cl1–Ta1–Cl3 = 157.48(5), Cl1–Ta1–S2 = 77.61(4);

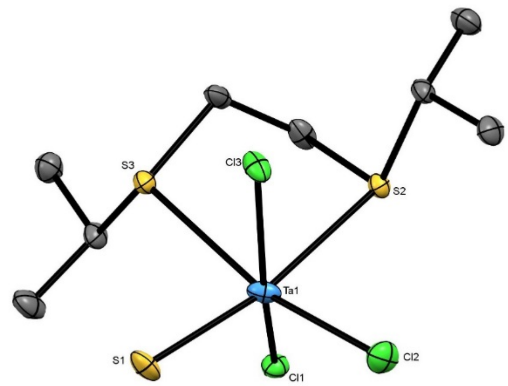

Figure 3 View of the structure of [$TaSCl_3$($^iPrSCH_2CH_2S^iPr$)] with numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Note that S1 and Cl2 are disordered Selected bond lengths (Å) and angles (°): Ta1–Cl1 = 2.3509(4), Ta1–Cl3 = 2.3559(5), Ta1–Cl2 = 2.2442(5), Ta1–S2 = 2.7487(5), Ta1–S3 = 2.7375(5), Ta1–S1 = 2.2339(5), Cl1–Ta1–Cl3 = 155.464(17), Cl1–Ta1–S2 = 76.447(15), Cl1–Ta1–S3 = 85.118(15), Cl3–Ta1–S2 = 83.485(15), Cl3–Ta1–S3 = 77.214(15), Cl2–Ta1–Cl1 = 97.282(17), Cl2–Ta1–Cl3 = 96.615(18), Cl2–Ta1–S2 89.812(17), Cl2–Ta1–S3 = 167.641(17), S3–Ta1–S2 = 78.929(14), S1–Ta1–Cl1 = 98.236(17), S1–Ta1–Cl3 = 97.905(18), S1–Ta1–Cl2 = 103.941(19), S1–Ta1–S2 = 165.867(16), S1–Ta1–S3 = 87.635(17).

The structure present in the dark purple crystals of [$TaSCl_3(MeSeCH_2CH_2SeMe)$] (Figure 4) shows a similar geometry to the dithioether complexes, with S/Cl disorder *trans* to the diselenoether.

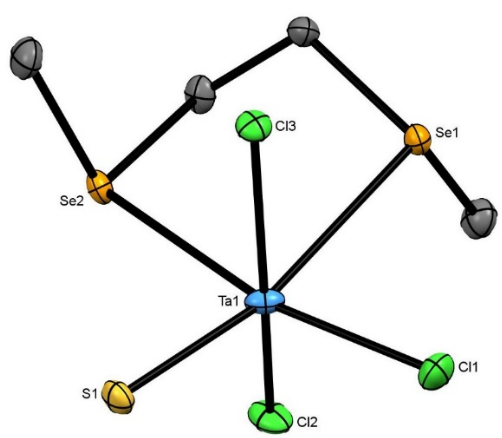

Figure 3 View of the structure of [$TaSCl_3(MeSeCH_2CH_2SeMe)$] with numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Note that S1 and Cl1 are disordered Selected bond lengths (Å) and angles (°): Ta1–Se1 = 2.8412(5), Ta1–Se2 = 2.8050(5), Ta1–Cl3 = 2.3592(11), Ta1–Cl1 = 2.2671(12), Ta1–Cl2 = 2.3543(12), Ta1–S1 =

2.2293(12), Se2–Ta1–Se1 = 80.046(14), Cl3–Ta1–Se1 = 76.31(3), Cl3–Ta1–Se2 = 85.05(3), Cl1–Ta1–Se1 = 83.77(4), Cl1–Ta1–Se2 = 162.78(4), Cl1–Ta1–Cl3 = 96.85(5), Cl1–Ta1–Cl2 = 96.26(5), Cl2–Ta1–Se1 = 86.58(3), Cl2–Ta1–Se2 = 77.01(3), Cl2–Ta1–Cl3 = 157.11(4), S1–Ta1–Se1 = 168.12(3), S1–Ta1–Se2 = 90.35(3), S1–Ta1–Cl3 = 96.05(4), S1–Ta1–Cl1 = 106.41(5), S1–Ta1–Cl2 = 98.13(4).

The spectroscopic data are similar to those reported for the corresponding niobium systems [8]. In the IR spectra the ν(Ta=S) is found as a medium intensity feature ~ 505-510 cm^{-1}, except for [$TaSCl_3(PhSCH_2CH_2SPh)$] where there are two bands at 513, 519 cm^{-1}, neither corresponds to any dithioether ligand modes, and the splitting is presumably due to a solid state effect. Two bands were also noted for this complex in the original study [4]. The ν(Ta-Cl) are assigned as (usually two) bands which lie in the range 305-360 cm^{-1}. The ^{1}H NMR spectrum of [$TaSCl_3(PhSCH_2CH_2SPh)$] in CD_2Cl_2 at 295K shows a single $\delta(CH_2)$ resonance indicating fast exchange, but on cooling the solution to 223K two $\delta(CH_2)$ resonances are present consistent with the expected structure, as the exchange slows. The ^{1}H NMR spectra of the dithioalkane complexes mostly show two RS- and two SCH_2 (backbone) resonances at room temperature as broad singlets distinguishing the donor groups which are inequivalent in these structures, and consistent with stronger donation in the alkyl substituted ligands. Cooling of the solutions, further results in the reversible appearance of more complex resonance patterns, no doubt due to the slowing of pyramidal inversion at the coordinated sulfur, but these are too complex to assign and are not reported. The IR and ^{1}H NMR spectra of [$TaSCl_3(MeSeCH_2CH_2SeMe)$], which contains a five-membered chelate ring, are broadly similar to those of the dithioether analogue and the $^{77}Se\{^{1}H\}$ NMR spectrum of the diselenahexane complex shows two δ(Se) resonances due to the selenium *trans* to Cl and S. A small amount of Me_2Se_2 is also evident (266 ppm); this is most likely a result of some elimination of $-CH_2CH_2-$ from the ligand backbone in solution [23]. However the ^{1}H NMR spectrum of [$TaSCl_3(^{n}BuSeCH_2CH_2CH_2Se^{n}Bu)$] is little different that of the free diselenoether, and the complex fails to exhibit a $\delta(^{77}Se)$ resonance, which are consistent with extensive dissociation in the case of the larger (six-membered) chelate ring complex.

Complexes with *n*-butyl substituents were targeted as potential single source CVD reagents (below) since these can, in principle, undergo β-hydride elimination on heating. Unfortunately, the reaction of $TaCl_5$, $S(SiMe_3)_2$ and the monodentate ligands $S^{n}Bu_2$ or $Se^{n}Bu_2$ in anhydrous CH_2Cl_2 solution, produced black powders with highly variable analytical composition, and these lacked any IR spectral evidence for a Ta=S feature. In solution the ^{1}H (and for the selenoether compound) the ^{77}Se NMR spectra showed features only due the uncoordinated chalcogenoether, and the nature of these black products is unknown. In the niobium systems, $[NbSCl_3(SR_2)]$ (R = Me, ^nBu) and $[NbSCl_3(Se^nBu_2)]$ were prepared and the structure of the SMe_2 complex determined [8]. It is a dimer $[Nb_2S_2Cl_4(\mu\text{-}Cl)_2(SMe_2)_2]$ with the sulphides terminal in plane and with *syn* axial SMe_2 ligands. A red 2:1 complex $[TaSCl_3(SMe_2)_2]$ has been described, but with very limited characterisation [4].

Finally, attempts to deposit TaE_2 thin films by low pressure CVD were carried out using the equipment described for the niobium analogues [8] (see Supporting Information) and $[TaSCl_3(^nBuSCH_2CH_2CH_2S^nBu)]$ and $[TaSCl_3(^nBuSeCH_2CH_2CH_2Se^nBu)]$ as reagents. Unfortunately, the newly prepared thioether complex gave no deposit, while the selenoether reagent produced only red elemental selenium films (as demonstrated through grazing incidence X-ray diffraction (GIXRD) and scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis, with no evidence for any TaE_2 (see Supplementary Information).

4 Conclusions

The preparations and characterisation of a series of very unusual Ta(V) sulfide trichloride complexes with soft, neutral dithioether and diselenoether co-ligands is reported, including crystal structures of representative examples, all of which display distorted octahedral coordination with the bidentate ligand lying *trans* to S/Cl. Except where there is S/Cl disorder evident in the crystal structures, the higher *trans* influence of the sulfide vs. chloride is clearly manifested in the $Ta\text{-}S_{thioether}$ bond distances and the spectroscopic data are in accord with the solid state structures. The products obtained from similar reactions with the monodentate ligands E^nBu_2 (E = S, Se) were irreproducible and could not be identified.

Investigation of the ^nBu-bearing dithioether and diselenoether complexes as potential CVD precursors for tantalum sulfide/selenide thin film growth proved unsuccessful, the thioether regent yielding no deposit (contrasting with the corresponding niobium(V) complex, which gave NbS_2 films), while the selenoether complex yielded only elemental selenium. Introducing tantalum in place of niobium has the obvious consequence of increasing the molecular weight of the corresponding complex by 88 a.m.u.. However, this is unlikely to be the major cause of the failure of the Ta(V) complexes to function as CVD reagents for TaS_2, since, based upon the coordination chemistry, the $TaOCl_3$ and $TaSCl_3$ complexes generally appear to be significantly less stable than the niobium analogues, reflecting the harder Lewis acidity of Ta(V) [4,6,7,8,10].

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Conflicts of interest

The authors have no conflicts to declare.

Appendix A. Supplementary Data.

CCDC 1899988 [$TaSCl_3(MeSeCH_2CH_2SeMe)$], CCDC 1899989 [$TaSCl_3({}^nBuSCH_2CH_2CH_2S^nBu)$], CCDC 1899990 [$TaSCl_3({}^iPrSCH_2CH_2S^iPr)$], CCDC 1899991 [$TaSCl_3(MeSCH_2CH_2SMe)$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK. Other supplementary materials include IR and NMR spectra for the complexes. Details of the low pressure CVD experiments are also provided.

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Table 1 X-ray crystallographic data[a]

Compound	$[TaSCl_3(MeSCH_2CH_2SMe)]$	$[TaSCl_3(MeSeCH_2CH_2SeMe)]$	$[TaSCl_3({}^iPrSCH_2CH_2S{}^iPr)]$
Formula	$C_4H_{10}Cl_3S_3Ta$	$C_4H_{10}Cl_3SSe_2Ta$	$C_8H_{18}Cl_3S_3Ta$
M	441.60	535.40	497.70
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group (no.)	$P2_1$ (4)	$P2_1$ (4)	$P2_1/c$ (14)
a /Å	7.22174(15)	7.3780(3)	8.7703(2)
b /Å	11.36725(15	11.4853(4)	9.1766(2)
c /Å	7.93897(16)	8.0629(3)	19.7147(4)
α /°	90	90	90
β /°	115.595(3)	115.924(5)	98.565(2)
γ /°	90	90	90
U /$Å^3$	587.77(2)	614.49(5)	1568.97(6)
Z	2	2	4
μ(Mo-$K_α$) /mm^{-1}	10.508	15.635	7.886
F(000)	412	484	952
Total number reflns	5355	12183	32686
R_{int}	0.018	0.030	0.023
Unique reflns	2267	2412	3090
No. of params, restraints	102, 1	102, 1	140, 0
GOF	1.069	1.036	1.071
R_1, wR_2 [$I > 2σ(I)$][b]	0.015, 0.034	0.012, 0.030	0.011, 0.026
R_1, wR_2 (all data)	0.015, 0.034	0.012, 0.030	0.013, 0.026

[a] Common items: T = 293 K; wavelength (Mo-$K_α$) = 0.71073 Å; θ(max) = 27.5°; [b] $R_1 = Σ||Fo|-|Fc||/Σ|Fo|$; $wR_2=[Σw(Fo^2-Fc^2)^2/ΣwFo^4]^{1/2}$

Table 1 continued.

Compound	$[TaSCl_3(^nBuSCH_2CH_2CH_2S^nBu)]$
Formula	$C_{11}H_{24}Cl_3S_3Ta$
M	539.78
Crystal system	Tetragonal
Space group (no.)	$P\,4_1$ (76)
a /Å	9.65170(10)
b /Å	9.65170(10)
c /Å	19.9311(3)
α /°	90
β /°	90
γ /°	90
U /$Å^3$	1856.69(5)
Z	4
μ(Mo-K_α) /mm^{-1}	6.672
F(000)	1048
Total number reflns	40170
R_{int}	0.071
Unique reflns	3642
No. of params, restraints	165, 1
GOF	1.068
R_1, wR_2 [I > 2σ(I)][b]	0.027, 0.064
R_1, wR_2 (all data)	0.029, 0.065