Niobium(v) and tantalum(v) halide chalcogenoether complexes – towards single source CVD precursors for ME₂ thin films†

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A series of pentavalent niobium and tantalum halide complexes with thio-, seleno- and telluro-ether ligands, [MCl₅][E₅(Bu₂)] (M = Nb, Ta; E = S, Se, Te), [TaX₅(SeMe₂)] (X = Cl, Br, F) and the dinuclear [MCl₅₂–(O–C₆H₄(CH₂SeBu₂))₆] (M = Nb, Ta), has been prepared and characterised by IR, ¹H, ¹³C{¹H}, ⁷⁷Se, ⁹³Nb and ¹²⁵Te NMR spectroscopy, as appropriate, and microanalyses. Confirmation of the tantalum(v)–telluroether coordination follows from the crystal structure of [TaCl₅(SeMe₂)], which represents the highest oxidation state transition metal complex with telluroether coordination structurally authenticated. The Ta(v) mono-telluroether complexes are much more stable than the Nb(v) analogues. In the presence of TaCl₅ the ditelluroether, CH₂(CH₂Te₆Bu₂), is decomposed; one of the products is the dealkylated [BuTe(CH₂)₃Tel–[TaCl₅], whose structure was determined crystalographically. Crystal structures of [MCl₅₂–(O–C₆H₄(CH₂SeBu₂))₆] (M = Nb, Ta) show ligand-bridged species. The complexes bearing β-hydrogen atoms on the terminal alkyl substituents have also been investigated as single source reagents for the deposition of ME₂ thin films via low pressure chemical vapour deposition. While the tantalum complexes proved to be unsuitable, the [NbCl₅][S₅(Bu₂)] and [NbCl₅][Se₅(Bu₂)] deposit NbS₂ and NbSe₂ as hexagonal platelets onto SiO₂ substrates at 750 °C and 650 °C, respectively. Grazing incidence and in-plane X-ray diffraction confirm both materials adopt the 3R-polytype (R3mnh), and the sulfide shows preferred orientation with the crystallographic c-axis perpendicular to the substrate. Scanning electron microscopy and Raman spectra are consistent with the X-ray data.

Introduction

Interest in methods for growing thin films of the layered early transition metal chalcogenides, ME₂ (E = S, Se, Te) has increased recently due to their structural relationship as inorganic analogues of graphene, but with the benefits of higher stability and tuneability of the inorganic materials compared with graphene. A wide range of materials and functional properties are accessible by varying M and E.¹ Controlling the dimensionality of these materials is of particular interest since it allows the anisotropy of the material properties to be maximized. Hence, 2D thin films of VSe₂, NbSe₂ and MoSe₂ are highly promising candidates for use in a variety of applications such as spintronics, energy storage, electrocatalysis, optoelectronics materials, environmental sensors and magnetic materials.²–⁷ Despite the attractions of these binary materials and their exciting applications, reliable methods for their deposition as thin films are still very limited, especially for E = Se and Te. Exfoliation from bulk samples has been employed recently to access ultrathin 2D films, including for VSe₂, TaE₂ (E = S, Se) and WSe₂.⁸–⁹ Chemical vapour deposition (CVD) is a versatile, scalable and low-cost deposition method that is used widely in commercial processes for thin film coatings.¹⁰–¹³ Typically for sulfides, either thiolate complexes have been employed as single source reagents or a volatile metal source has been used with excess thiol in a dual source approach. With regards to the heavier chalcogenides, some success has been achieved with selenolate complexes, e.g. [(η⁵-C₅H₅)₂M(SeBu₂)] for ME₂ (M = Ti, Zr, Hf),¹⁴ and with metal halide complexes of the neutral selenoether ligands, which form more easily handled single source

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precursors. However, outside of Group 4, single source CVD reagents for controlled growth of early transition metal chalcogenides are rare. Examples of telluroether complexes with these hard, strongly polarised, high oxidation state metals are extremely unusual, and none have been tested as single source precursors in CVD.

With regards to the Group 5 (Nb, Ta) binary chalcogenide materials, a small number of reports have used niobium thiolate complexes for CVD of NbS$_2$, while for NbSe$_2$, the only CVD-based route uses a dual source approach from NbCl$_5$ and excess Se$_2$Bu$_2$. Here we report the synthesis and spectroscopic properties of the distorted octahedral M(v) complexes [MCl$_5$(E$^n$Bu$_2$)] (M = Nb, Ta; E = S, Se, Te), [TaX$_5$(TeMe$_2$)] (X = Cl, Br, F) and the dinuclear [MCl$_5$(o-C$_6$H$_4$(CH$_2$SEt)$_2$)] (M = Nb, Ta), including the crystal structures of [TaCl$_5$(TeMe$_2$)] and [MCl$_5$(o-C$_6$H$_4$(CH$_2$SEt)$_2$)]. We also report investigations into their application as single source reagents for the deposition of the layered binary chalcogenides, ME$_2$, via low pressure CVD. Several NbX$_5$ and TaX$_5$ chalcogenoether complexes have been reported previously, however, in the present work E$^n$Bu, Et and o-xylyl organic groups were incorporated into the ligands specifically in an attempt to promote a low energy elimination pathway during the CVD process.

Results and discussion

The complexes [MCl$_5$(E$^n$Bu$_2$)] (E = S, Se, Te), [TaX$_5$(TeMe$_2$)] (X = Cl, Br) and the dinuclear [MCl$_5$(o-C$_6$H$_4$(CH$_2$SEt)$_2$)] (M = Nb, Ta) were prepared and isolated in good yield as orange-red products by direct reaction of MX$_5$ with the ligand in anhydrous CH$_2$Cl$_2$ at ambient temperature, except for the telluroether reactions which were performed at 0 °C (Scheme 1). The complexes with butyl-substituted ligands are viscous oils, whereas the complexes with ethyl and methyl substituted ligands are powdered solids. As expected for complexes of niobium(v) and tantalum(v) with soft donor ligands, the isolated compounds are very moisture sensitive, particularly in solution. However, other than the NbCl$_5$(Te$^n$Bu$_2$)], they are stable for months when stored in a N$_2$ purged glove box. The choice of ligand was driven by the objective to utilise them as single source CVD reagents, hence where possible, substituents with β-hydrogen atoms were chosen to take advantage of the low energy β-hydride elimination pathway, as well as to lower the lattice energy for the material, leading to favourable volatility. Far IR spectroscopy confirms the local C$_{4v}$ symmetry associated with the [MCl$_5$(L)] moiety, typically showing the expected three M—Cl stretching vibrations, consistent with earlier work. In addition to microanalytical data, $^1$H, $^{13}$C($^1$H), $^{77}$Se($^1$H), $^{125}$Te($^1$H) and $^{93}$Nb NMR spectroscopy are fully consistent with the stated formulations.

The Nb(v) telluroether complexes are particularly unstable, changing colour over a few hours at room temperature even under N$_2$, possibly through reduction of the metal by internal redox chemistry involving the telluroether. In contrast, the Ta(v) complexes with the mono-telluroether ligands form in excellent yield, and are readily handled under N$_2$ and may be stored for several months in a freezer (−18 °C). This probably reflects the increased stability of the +5 oxidation state for Ta over Nb, so that the Ta complexes are less susceptible to reduction by the telluroether. It is notable that the +5 oxidation state present in the tantalum telluroether complexes represents the highest known for any telluroether complex.

Further, the [TaCl$_5$(TeMe$_2$)] that we report here (vide infra) is the first crystallographically characterised telluroether complex of any metal ion from Groups 1 to 5 of the periodic table. In view of the unexpected stability of the [TaX$_5$(TeR$_2$)] (X = Cl, Br) complexes reported here, and our recent work exploring TaF$_5$ complexes with soft donor ligands such as phosphines or thio- and selenoethers, we have also investigated reaction of TaF$_5$ and TeMe$_2$ in a 1:1 molar ratio in CH$_2$Cl$_2$ at 0 °C. This initially produced a light yellow solution, and following filtration to remove minor insoluble material, the solvent was removed in vacuo to give a light yellow solid. This product is very unstable and darkens over a few hours even when stored as a solid under a dry N$_2$ atmosphere, hindering its full characterisation. This is likely to be a result of the weak binding of the soft telluroether to the very hard TaF$_5$ moiety. Spectroscopic data were therefore obtained from freshly prepared samples. The IR spectrum (Nujol) shows peaks at 6415, 6185 and 607sh cm$^{-1}$ assigned to Ta—F stretching modes, consistent with the C$_{4v}$ symmetry ($2a_u + e$) expected for [TaF$_5$(TeMe$_2$)]. The $^1$H NMR spectrum of a freshly prepared solution in CD$_2$Cl$_2$ shows a singlet at δ = 2.49 assigned to the neutral pentfluoro complex, [TaF$_5$(TeMe$_2$)]. A second, much weaker singlet at 2.57 ppm is due to Me$_2$TeF$_2$, formed by fluorination of the telluroether by TaF$_5$. A weak, but sharp, singlet in

![Scheme 1](image-url)
the $^{19}$F($^1$H) NMR spectrum at $-132.0$ ppm is also due to Me$_2$TeF$_2$; this is accompanied by a much more intense, broad resonance at ca. 73 ppm. Cooling this solution to $-90$ °C leads to the broad resonance shifting to 41.2 ppm and sharpening significantly. This is similar to the behaviour observed for [TaF$_5$(SeMe$_2$)]$^{16}$ and is attributed to the presence of the rather unstable complex [TaF$_5$(TeMe$_2$)], which is extensively dissociated at room temperature. At $-90$ °C the low temperature limiting spectrum has not yet been reached, hence distinct resonances for the equatorial and axial Fs are not observed. Further $^{19}$F($^1$H) NMR resonances at 117.6, 71.5 and $-82$ ppm (in a 1 : 8 : 2 ratio) grew in over ca. 30 minutes, and are attributed to [Ta$_2$F$_{11}$].$^{21}$ The $^{125}$Te NMR resonance for [TaF$_5$(Me$_2$Te)] was not observed, most likely due to the instability of the compound over the long accumulation time.

Confirmation of the Ta(v)-telluroether coordination follows from a single crystal X-ray structure determination of [TaCl$_5$(TeMe$_2$)]. The structure shows (Fig. 1) the expected distorted octahedral coordination at Ta(v), with $d$(Ta–Te) = 2.964(3) Å, and $d$(Ta–Cl) lying in the range 2.290(9) to 2.306(6) Å. The Ta–Cl trans to TeMe$_2$ lies at the lower end of the range, but is not significantly different from Ta–Cl trans to Cl. While there are no other tantalum(v)-telluroether species with which to compare the Ta–Te bond distance, the isomorphous [TaCl$_5$(SeMe$_2$)] shows $d$(Ta–Se) = 2.7992(8) Å.$^{16}$

Attempts to coordinate TaCl$_3$ to the ditelluroether, CH$_2$(CH$_2$Te'tBu)$_2$, led instead to significant Te–C bond scission and multiple products (based upon NMR spectroscopic data) – Scheme 2. One of these formed small orange crystals by cooling a CH$_2$Cl$_2$ solution in the freezer for several days. A structure determination was therefore attempted. The diffraction data were weak, and the C atoms determined less accurately, however the study was sufficient to establish this product as a [TaCl$_6$]$^-$ salt of the cationic cyclic organotellurium species [BuTe(CH$_2$)$_3$Te]$^+$ shown in Fig. 2 below. It is likely that this cation is formed by elimination of a tBu group, followed by nucleophilic attack of the anionic Te terminus on the other Te group, forming the Te–Te bond. Similar reactivity of other telluroethers has been observed in the presence of other strongly Lewis acidic metal halides, including AlX$_3$.$^{22}$

Structure determinations were also undertaken for [(MCl$_5$)$_2$($
\text{O-C$_6$H$_4$(CH$_2$SEt)$_2$}$) (M = Nb and Ta) which are isostructural, both containing six-coordinate M(v) with the ligand bridging the two MCl$_5$ units. The Ta complex is shown in Fig. 3 and the Nb analogue is presented in the ESI.† The M–Cl and M–S bond distances are comparable to other thioether complexes of these ions.$^{15,16}$

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**Fig. 1** View of the structure of [TaCl$_5$(TeMe$_2$)] with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ta1–Cl1 = 2.290(9), Ta1–Cl2 = 2.306(6), Ta1–Cl3 = 2.298(9), Ta1–Cl4 = 2.303(10), Ta1–Te1 = 2.964(3), Cl1–Ta1–Te1 = 179.1(2). Symmetry operation a = $-x$, $y$, $z$.

**Fig. 2** View of the structure of [BuTe(CH$_2$)$_3$Te][TaCl$_6$] with ellipsoids shown at the 50% probability level. Note that the data quality is poor, hence structural comparisons should be treated with caution.

\[
\begin{align*}
2\text{TaCl}_3 + & \text{BuTe} + \text{TeBu} \\
\rightarrow & \text{[TaCl$_6$]} + \text{other decomposition products}
\end{align*}
\]
CVD experiments

The complexes [MCl₅(SBu₂)] and [(MCl₅)₂(η₂-C₆H₄(CH₂SeEt)₂)] (M = Nb, Ta) were all tested as potential single source CVD precursors at a range of temperatures around 600–750 °C (at a pressure ca. 0.05 mmHg). No significant deposition was observed at lower temperature. In general, none of the Ta reagents showed significant deposition (except for [TaCl₅(C₆H₄(CH₂SeEt)₂)] which deposited some crystalline tellurium). However, while the dinuclear Nb(v) species appeared to be insufficiently volatile to give significant deposition, LPCVD experiments using both [NbCl₅(SBu₂)] (T ca. 750 °C) and [NbCl₅(SeBu₂)] (T ca. 650 °C) led to formation of reflective dark brown/black films onto the SiO₂ substrates. The thickest deposits were identified towards the centre of the hot zone and these were therefore selected for further characterisation.

The films obtained from [NbCl₅(SBu₂)] show diffraction patterns consistent with NbS₂; the best fit being for NbS₂ in space group R3m (3R-type NbS₂) (Fig. 4). In some early samples minor peaks associated with niobium oxide (Nb₂O₅) were observed, however, these did not increase in intensity upon prolonged exposure (for several months) of the deposits to the atmosphere, and could be eliminated by rigorous drying of the CVD equipment and using high purity precursors. Hence it seems likely that this was a result of trace hydrolysis of the precursor. The diffraction pattern is similar to that identified by Winter and co-workers using [NbCl₅(PrSSiPr)₂][NbCl₄] as a single source precursor for LPCVD of 3R-NbS₂, also with some Nb₂O₅ impurity. Lattice parameters determined by Rietveld refinement of the grazing incidence XRD pattern are: a = 3.3343(14) Å and c = 17.820(11) Å \( \left( R_{wp} = 5.3\%, R_p = 3.5\% \right) \), see ESI†. These are close to literature values for bulk NbS₂ of \( a = 3.3303(3) \text{ Å, } c = 17.918(2) \text{ Å} \).\(^{23}\)

Notably comparison of the grazing incidence and in-plane XRD patterns (Fig. 4) shows considerable intensity variations for several of the diffraction peaks, consistent with preferred orientation. Specifically, the 003 reflection that is strongest in the grazing incidence XRD pattern is almost completely suppressed in the in-plane XRD pattern, while the 101, 012 and 110 reflections are highly suppressed in the grazing incidence XRD, but dominate the in-plane XRD pattern. A symmetric \( \theta–2\theta \) scan resulted in a very weak pattern due to the thinness of the film studied, but the combination of the grazing incidence and in-plane patterns strongly suggests crystallites are largely aligned with the <001> axis at the film surface normal such that the a and b crystallographic directions are parallel with the surface.

The Raman spectrum recorded from the deposited film is also consistent with the 3R-NbS₂ polytype (ESI†).\(^{25}\) Scanning electron microscopy (SEM) images (Fig. 5) reveal that the NbS₂ films have a regular morphology formed of microcrystalline platelets mostly aligned with the ab plane parallel to the substrate.
strate, as suggested by the XRD data. EDX data measured at an accelerating voltage of 5 kV to minimise break-through to the substrate still show significant Si and O in addition to peaks due to Nb and S, indicating that the films are thin; importantly, however, there is no evidence for any residual Cl in the films. Accurate quantification of the Nb:S ratio by EDX is hampered by overlap of the Nb L\textsubscript{\alpha} and S K\textsubscript{\alpha} peaks.

Films obtained using the [NbCl\textsubscript{5}(Se\textsubscript{n}Bu\textsubscript{2})] precursor appear shiny and dark brown/black. Grazing incidence XRD data on our films were consistent with NbSe\textsubscript{2} (space group R\textsubscript{3}m; 3R-NbSe\textsubscript{2}, Fig. 6).\textsuperscript{26} Again, some samples showed small amounts of Nb\textsubscript{2}O\textsubscript{5} impurity,\textsuperscript{27} which could be eliminated by careful exclusion of trace moisture from the CVD rig prior to introduction of the [NbCl\textsubscript{5}(Se\textsubscript{n}Bu\textsubscript{2})]. A previous study by Parkin and co-workers\textsuperscript{12a} using dual source APCVD from NbCl\textsubscript{5} and excess Se\textsubscript{n}Bu\textsubscript{2} found dark-green or dark-purple films of the 2H-NbSe\textsubscript{2} phase. The 3R phase observed here differs from the 2H phase only in the stacking sequence of the layers of edge-linked NbSe\textsubscript{6} trigonal prisms, the 2H phase has a 2-layer stacking sequence and the 3R phase has a 3-layer sequence. Rietveld refinement of the grazing incidence XRD data [ESI] gave lattice parameters \(a = 3.4469(9)\), \(c = 18.940(14)\) Å (\(R_{wp} = 6.4\%\), \(R_p = 4.5\%\)), which compare with literature values of \(a = 3.45(1)\), \(c = 18.880(40)\) Å.\textsuperscript{26} While significant enhancement of the 003 reflection is again observed in the grazing incidence XRD and the 101 and 110 are clearly enhanced in the in-plane pattern, suggesting the same type of <001> preferred orientation, this is less pronounced than for the NbS\textsubscript{2} above.

Raman spectra recorded for the films deposited at 600 and 650 °C (Fig. 7) are consistent with NbSe\textsubscript{2}, showing a broad peak at \(~189\) cm\textsuperscript{-1}, which has been assigned to a lattice distortion, and a stronger, sharper peak at 228 cm\textsuperscript{-1} with a shoulder at ca. 237 cm\textsuperscript{-1} assigned to the A\textsubscript{1g} active phonon and the E\textsubscript{2g} phonon mode, respectively.\textsuperscript{28} Measurements taken at several locations on the sample showed no significant variation.

SEM images (Fig. 8) show that the NbSe\textsubscript{2} thin films are formed of hexagonal plate-like microcrystals growing out from and covering the surface of the substrate. The partial orientation identified in the XRD measurements is not as obvious here, although the enhancement of the <001> direction can be understood in terms of the observation that in general the plates do not appear to be growing perpendicular to the surface.

EDX data show the Nb:Se ratio is \(1 : 1.7\) (22.40\%:38.35\%), and like the sulfide films, there is no evidence for any Cl impurity, despite the Cl\textsuperscript{-} ligands present in the precursor compounds, although significant substrate peaks are seen. WDX data were also recorded for this NbSe\textsubscript{2} thin film, giving an Nb:Se ratio = 1:1.9, however, accurate quantification of the carbon content was not possible due to the occurrence of other Nb emission peaks at similar energy to the C peak.
Conclusions

A selected set of Nb(v) and Ta(v) complexes with chalcogenoether coordination has been prepared and the Et and 17-butoxy substituted derivatives have been evaluated as possible single source CVD candidates for ME2 thin films. Successful growth of NbS2 and NbSe2 thin films has been demonstrated using the [NbCl5(E2Bu2)] (E = S or Se) systems; this was rather unexpected based upon both the M:E ratio in the precursor (1:1) vs. the metal dichalcogenide phase (1:2), and the utilization of the +5 oxidation state in the precursor vs. +4 in the ME2. NbS2 exhibits strong <001> preferred orientation in these thin films, whereas NbSe2 exhibits enhancement of some peaks in the XRD pattern, but to a lesser degree. The instability of the niobium(v) telluroether complexes eliminated the possibility of testing these as reagents in LPCVD.

The first detailed characterization of Ta(v) telluroether complexes are described, including [TaCl5(SeMe2)], which is the first crystallographically authenticated early transition metal halide telluroether complex. The tantalum(v) chalcogenoether complexes did not produce TaE2 via LPVD. There are several possible reasons for this, including the higher molecular weights associated with the Ta complexes, and hence their lower volatilities, such that the difference between the evaporation temperature and the deposition temperature is too small for an effective CVD reagent. Further work investigating alternative precursors and deposition methods will help to elucidate the key factors involved.

Experimental

Infrared spectra were recorded as Nujol mulls or thin films between CsI plates using a Perkin Elmer Spectrum 100 over the range 4000–200 cm⁻¹. 1H and 13C{1H} NMR spectra were recorded from CDCl3 or CD2Cl2 solutions using a Bruker DPX400 spectrometer. 77Se{1H}, 125Te{1H} and 93Nb NMR spectra were recorded using a Bruker DPX400 spectrometer. 77Se{1H}, 125Te{1H} and 93Nb NMR data due sample degradation over the long spectral acquisition time. 1H NMR (CDCl3, 298 K): δ = 0.98 (t, [3H], CH3), 1.50 (m, [2H], CH2), 1.83 (m, [2H], CH2), 3.14 (br, [2H], SeCH3). 13C{1H} NMR (CDCl3, 298 K): 23.05 (CH3), 31.05 (CH2), 36.62 (br, SeCH2). 77Se{1H} NMR (CDCl3, 298 K): δ = 169. IR (Nujol, cm⁻¹): 16645, 16640, 340 cm⁻¹, 2145, 2014, 1387, 740 sh (Nb-Cl).

Atmospheric deposition of [NbCl5(SeBu2)]2. NbCl5 (0.27 g, 1.0 mmol) was suspended in anhydrous CH2Cl2 (10 mL) at room temperature, and a solution of SeBu2 (0.24 g, 1.0 mmol) in CH2Cl2 (4 mL) added with stirring. The solution was stirred for 10 min. the volatiles were removed and the remaining blue oil was dried in vacuo. The compound appeared to change colour over a few hours, hence spectroscopic data were obtained from a freshly prepared sample, but we were unable to obtain either microanalytical data (outsourced) or 125Te{1H} NMR data due to sample degradation over the long spectral acquisition time. 1H NMR (CDCl3, 298 K): δ = 0.98 (t, [6H], CH3), 1.48 (m, [4H], CH2), 1.87 (m, [4H], CH2), 3.13 (s, [4H], CH2). 93Nb NMR (CDCl3, 298 K): δ = 169. IR (Nujol, cm⁻¹): 340 m, 367 s, 388 sh (Nb-Cl).

Preparations

[NbCl5(S2Bu2)]. NbCl5 (0.41 g, 1.5 mmol) was suspended in anhydrous CH2Cl2 (10 mL) at room temperature, and a solution of S2Bu2 (0.22 g, 1.5 mmol) in CH2Cl2 (2 mL) added with stirring. The solution was stirred for 30 min. The volatiles were removed in vacuo, leaving an orange oil. Yield: 0.43 g, 69%. Required for C8H18Cl5NbS2: C, 18.79%; H, 2.37%. Found: C, 18.79; H, 2.37. 1H NMR (CDCl3, 298 K): δ = 0.98 (t, [3H], CH3), 1.50 (m, [2H], CH2), 1.83 (m, [2H], CH2), 3.14 (br, [2H], SeCH3). 13C{1H} NMR (CDCl3, 298 K): δ = 13.49 (CH3), 22.83 (CH2), 31.05 (CH2), 36.62 (br, SeCH2). 77Se{1H} NMR (CDCl3, 298 K): δ = 273.6. 93Nb NMR (CDCl3, 298 K): δ = 123. IR (Nujol, cm⁻¹): 340 m, 372 s, 394 sh (Nb-Cl)
leaving a yellow/orange oil. Yield: 0.31 g, 69%. Required for 
C₄H₁₀Cl₅STa: C, 15.43; H, 1.79%. Found: C, 17.08; H, 3.48%.

\[ \text{TaCl}_5\text{(SeCH}_2\text{)} \text{]. TaCl}_5 \text{ (0.36 g, 1.0 mmol) was suspended} \]

in vacuo to around 5 mL, hexane (5 mmol) was added, causing a rapid colour change to yellow. The solution was concentrated in vacuo to around 5 mL, hexane (5 mmol) was added, causing precipitation of a yellow solid, which was collected by filtration. The filtrate was placed in the freezer (−18 °C) where single crystals grew over a few days. Yield: 0.11 g, 45%. Required for 
C₄H₁₀Cl₅STa: C, 10.72; H, 2.25%. Found: C, 10.56; H, 2.16%.

\[ \text{in vacuo} \text{. The solution was filtered and all volatiles were then removed} \]

1H NMR (CDCl₃, 298 K): 0.99 (t, [6H], CH₃), 1.49 (m, [4H], CH₂), 1.84 (m, [4H], CH₂), 7.43 (m, [4H], aromatic-CH). IR (Nujol, cm⁻¹): 343 s, 366 m sh, 392 m (TaCl). 1H NMR (CDCl₃, 298 K): 0.98 (t, [3H], CH₃), 1.50 (m, [2H], CH₂CH₃), 1.78 (m, [2H], CH₂), 3.22 (t, [2H], SCH₂), 13C{¹H} NMR (CDCl₃, 298 K): δ: 13.47 (CH₃), 22.76 (CH₂), 31.05 (CH₂), 36.76 (CH₂). 125Te{¹H} NMR (CDCl₃, 298 K): δ: 13.38 (CH₃), 21.46 (TeCH₃), 24.81 (CH₃), 31.74 (CH₂). 125Te{¹H} NMR (CH₂Cl₂, 298 K): δ: 268. IR (thin film, cm⁻¹): 317 s, 335 s, 392 m (Ta-Cl).

\[ \text{TaCl}_5\text{(S}^\text{Bu}_2\text{)} \text{]. TaCl}_5 \text{ (0.18 g, 0.5 mmol) was suspended} \]

in anhydrous CH₂Cl₂ (5 mL) at room temperature, and S²Bu (0.99 mL, 0.5 mmol) was added with stirring. The solution turned yellow immediately and was stirred for 1 h. The solution was filtered and all volatiles were then removed in vacuo to leave a yellow oil. Yield: 0.34 g, 61%. Required for C₂H₆Br₅TaTe: C, 4.66; H, 1.17%. Found: C, 5.03; H, 1.35%. 1H NMR (CDCl₃, 298 K): δ: 2.48 (s, CH₃). 13C{¹H} NMR (CDCl₃, 298 K): δ: −1.93 (CH₃). 125Te{¹H} NMR (CH₂Cl₂, 298 K): δ: 102. IR (Nujol, cm⁻¹): 300 sh, 338 s, 379 m (Ta-Cl). Crystals suitable for X-ray structure determination were obtained by cooling a CH₂Cl₂ solution in the freezer (−18 °C) for 2 days.

\[ \text{TaBr}_3\text{(TeMe}_2\text{)} \text{]. Method as for [TaCl}_5\text{(TeMe}_2\text{)} \text{] above. Deep} \]

red powdered solid. Yield: 65%. Required for C₄H₉Br₅TaTe: C, 3.25; H, 0.82%. Found: C, 3.50; H, 1.16%. 1H NMR (CDCl₃, 298 K): δ: 2.55 (s, CH₃). 13C{¹H} NMR (CDCl₃, 298 K): δ: 1.12 (CH₃). 125Te{¹H} NMR (CH₂Cl₂, 298 K): δ: 107. IR (Nujol, cm⁻¹): 221 m br, 230 sh (Ta-Br).

\[ \text{TaF}_5\text{(TeMe}_2\text{)} \text{]. TaF}_5 \text{ (0.28 g, 1.0 mmol) and TeMe}_2 \text{ (0.16 g,} \]

1.0 mmol) were weighed inside a glove box. The TaF₅ was suspended in anhydrous CH₂Cl₂ (3 mL) and the Me₂Te was mixed with anhydrous CH₂Cl₂ (2 mL); both solutions were then cooled in an ice bath. The Me₂Te solution was then added to the TaF₅ solution, causing a colour change to yellow green. After stirring for ca. 15 min. the colour changed to lemon. All volatiles were then removed in vacuo leaving a light yellow solid. IR (Nujol, cm⁻¹): 641 sh, 618 s, 607 sh (Ta-F). 1H NMR (CDCl₃, 298 K): δ 2.50 (s, CH₃, major), 2.57 (s, Me₂TeF₂, minor). 19F{¹H} NMR (CDCl₃, 298 K): δ = 73 (br, [TaF₅(TeMe₂)]), major), −132.0 (s, Me₂TeF₂, minor); (178 K): δ = 41.2 (s, [TaF₅(TeMe₂)]), major), −132.0 (s, Me₂TeF₂, minor). 125Te{¹H} NMR (CDCl₃, 298 K): no resonances observed.

\[ \text{Attempted preparation of [} \text{TaCl}_5\text{(CH}_2\text{CH}_2\text{TeMe}_2\text{)} \text{]. TaCl}_5 \text{ (0.18 g, 0.5 mmol) was suspended} \]

in CH₂Cl₂ (7 mL) at 0 °C (ice bath) under N₂. C₂H₆Cl₅TaTe: C, 4.61 g, 0.25 mmol) in CH₂Cl₂ (3 mL) at 0 °C was added dropwise. The solution turned dark red immediately and stirring was maintained for 15 min. The volatiles were then removed in vacuo leaving a dark red-orange viscous oil. 1H NMR spectroscopy (CDCl₃) showed multiple ¹Bu resonances, indicative of a mixture of products suggesting decomposition. A few small, weakly diffracting crystals of [BuTe(THF)₃]₆[TaCl₅] were obtained by cooling a CH₂Cl₂ solution of this product mixture in the freezer (−18 °C) for ca. one week.

\[ \text{X-ray experimental} \]

Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals suitable for single crystal X-ray analysis were obtained as described. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (i = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 µm focus) with the crystal held at 100 K (N₂ cryostream). Structure solution and refinements were performed with SHELX(S/L)-97. Open Access Article. Published on 18 September 2014. Downloaded on 5/10/2020 8:04:28 AM. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.
model, except for \([\text{TaCl}_5(\text{o-C}_6\text{H}_4(\text{CH}_2\text{SEt})_2))]\), in which the H atom positions were calculated. The diffraction data obtained for the decomposition product, \([\text{BuTe}(\text{CH}_2)_2]\)–[\text{TaCl}_5], were weak and showed some evidence of twinning. Correspondingly the final structure solution is of only modest quality, with higher than normal residuals. The heavy atoms required restraints for satisfactory refinement. While the structure serves to confirm the identity of the compound, a decomposition product, comparison of geometric parameters is not warranted.

**LPCVD general procedure**

The single source precursor (0.02–0.10 g) was loaded into the end of silica tubes in an N2 purged glove box. Then the silica substrates (∼1 × 8 × 20 mm² or 0.5 × 8 × 12 mm²) also were loaded in the tube and placed end-to-end. The tube was set in a furnace so that the substrates were in the heated zone and the precursor was ca. 2 cm away from the start of the heated zone. The tube was evacuated to 0.5 mm Hg, and the furnace was heated to the requisite temperature between 600 and 800 °C. The tube was then moved gradually into the furnace so that the precursor moved closer to the hot zone until it began to evaporate. The position of the sample was maintained until the all the precursor had evaporated. The tube was then cooled to room temperature and the tiles were unloaded inside a dry N2-purged glove box, where they were stored for further characterisation. LPCVD from \([\text{NbCl}_5(\text{S}_2\text{Bu}_3))]\) and \([\text{NbCl}_4(\text{Se}_2\text{Bu}_3))]\) resulted in deposition of a reflective black film on tiles positioned in the hotter region of the furnace, with thinner deposits at either end.

**Film characterisation**

Scanning electron microscopy (SEM) was performed on samples at an accelerating voltage of 15 kV using a JEOL JSM5910 or at accelerating voltage from 5 kV to 15 kV using a Philips XL30 ESEM. Energy dispersive X-ray (EDX) data were obtained with an Oxford INCA x-act X-ray detector (JSM5910) or Thermofisher Ultradry NSS 3 (XL30). X-ray diffraction (XRD) patterns were collected in grazing incidence mode (θ/2θ, 20 = 0.5°, 2θ scan with the detector scanning in the film plane) using a Rigaku SmartLab diffractometer (Cu-Kα, λ = 1.5418 Å) with parallel X-ray beam and a DTex Ultra 250 1D detector. Phase matching used the PDFXL2 software package and diffraction patterns from ICSD. Raman spectra of the deposited films were acquired with a Renishaw 2000 microscope instrument equipped with a 632.8 nm He–Ne laser and Prior XYZ stage controller. The diameter of the laser spot was 1 μm. Typically, a single 120 s acquisition was used to acquire spectra.

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**References**