Vanadium selenoether and selenolate complexes, potential single-source precursors for CVD of VSe₂ thin films

Andrew L. Hector,* Marek Jura, William Levason, Stuart D. Reid and Gillian Reid

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Reactions of VCl₄ with one mol equiv. of L–L (L–L = MeSe(CH₂)₂SeMe, MeSe(CH₂)₃SeMe, ⁿBuSe(CH₂)₂SeⁿBu) in anhydrous CH₂Cl₂ solution at room temperature give [VCl₄(L–L)] as very moisture-sensitive dark purple solids. Using VCl₄ and excess selenoether in gently refluxing CH₂Cl₂ leads to reduction to [VCl₃(L–L)] (L–L as above and o-C₆H₄(CH₂SeMe)₂), while VCl₄ reacts with excess SeMe₂ at room temperature to give [VCl₃(SeMe₂)₂]. All new complexes were characterised by microanalysis, IR and UV/visible spectroscopy and magnetic measurements. Reaction of [(Cp)₂VCl₂] with two mol equiv. of LiSe¹Bu in anhydrous thf gives the V^{IV} selenolate complex [(Cp)₂V(Se^tBu)₂] as a very moisture-sensitive brown solid. The new complexes have been investigated as possible reagents for deposition of vanadium selenide. While low pressure chemical vapour deposition (LPCVD) experiments showed that the diselenoether complexes were not sufficiently volatile for VSe₂ deposition, [VCl₃(SeMe₂)₂] gives very thin deposits of VSe₂. LPCVD studies on [(Cp)₂V(Se^tBu)₂] at 600 °C produce thicker black films of VSe₂. In all cases EDX measurements show that the films are Se deficient.

Introduction

Vanadium diselenide, VSe₂, is a member of the family of layered chalcogenides, ME_2 (M = Ti, Zr, Hf, Nb, Mo etc., E = S or Se), which are based upon strongly bound E-M-E layers, stacked with weak interlayer $E \cdots E$ interactions. As a result, these materials have important applications including solid state lubricants, battery cathodes, in solar energy cells, and in sensors. Vanadium diselenide, which is usually metal rich V_{1+x} Se₂, has received considerable attention, both in terms of intercalation reactions,^{1,2} and its highly unusual charge density wave properties.^{3,4} Although chemical vapour (I_2) transport has been used to prepare single crystals of VSe₂,⁵ the first successful use of chemical vapour deposition (CVD) approaches to make films of VSe₂ and related selenides have been reported only recently.6,7 Atmospheric pressure (AP)CVD of matt black films, with composition close to VSe2, was achieved using the dual source precursors [V(NMe2)4] and SetBu2.6 Single-source low pressure (LP)CVD of titanium diselenide films has been demonstrated using [TiCl₄(Se₂Et₂)₂], [TiCl₄(SeEt₂)₂],⁸ or [Ti{o-C₆H₄(CH₂SeMe)₂}],⁹ whilst ZrSe₂ and HfSe₂ films have been obtained very recently by us via LPCVD from $[(Cp)_2M(Se^tBu)_2]$ (M = Zr or Hf).¹⁰ We report here attempts to extend our recent studies^{9,10} to the production of VSe₂ films, and describe the study of some vanadium selenoether and selenolate ligand chemistry and LPCVD with selected complexes.

The early transition metal halides in their higher oxidation states are hard, oxophilic Lewis acids and their complexes with

soft neutral ligands, such as the heavier chalcogenoethers, are relatively little explored.¹¹ We have previously characterised diselenoether (e.g. MeSe(CH₂)₂SeMe, MeSe(CH₂)₃SeMe, o-C₆H₄(SeMe)₂, PhSe(CH₂)₂SePh, (L-L)) complexes of titanium(IV)¹² including the six-coordinate [TiX₄(L-L)] (X = Cl or Br), and the six- and eight-coordinate zirconium(IV) and hafnium(IV)¹³ complexes [MCl₄{MeSe(CH₂)₂SeMe}] and [MCl₄{MeSe(CH₂)₂SeMe}₂]. The Zr and Hf complexes are poorly soluble in non-coordinating solvents, whilst the diselenoethers are displaced by solvents containing nitrogen or oxygen donor functions, and all are exceedingly moisture sensitive. Very little is known about selenoether complexes of vanadium-the only examples in the literature are substituted carbonyl derivatives.¹¹ The vanadium(v) oxide halides VOX_3 and VO_2X (X = F or Cl) are immediately reduced by SeMe₂ or MeSe(CH₂)₂SeMe.¹⁴ There appear to be no vanadium halide examples with lower oxidation states, although thioether complexes of VII and VIII are well established,^{15–17} and we have recently characterised V^{IV} examples including $[VCl_4{RS(CH_2)_2SR}]$ and the tetrameric $[{VOCl_2{RS(CH_2)_2SR}}_4] (R = Me, Et, {^iPr etc.}).^{18}$

Experimental

All reactions were conducted under rigorously anhydrous conditions and under dry nitrogen using standard vacuum line, Schlenk and glove-box techniques. A fresh bottle of VCl₄ (Aldrich) was used as received (VCl₄ is a brown liquid which slowly loses Cl₂ on standing and deposits solid VCl₃). [(Cp)₂VCl₂] was obtained from Aldrich. Solvents were dried by distillation from CaH₂ (CH₂Cl₂ or MeCN) or Na/benzophenone ketyl (thf, hexane and diethyl ether). The selenoethers

School of Chemistry, University of Southampton, Southampton, UK SO17 1BJ. E-mail: A.L.Hector@soton.ac.uk

 $RSe(CH_2)_2SeR$ (R = Me, ⁿBu), MeSe(CH_2)_3SeMe, and o-C₆H₄(CH₂SeMe)₂ were made by literature methods,^{19,20} dried and stored over molecular sieves. SeMe₂ was obtained from Aldrich and was stored over molecular sieves. Physical measurements were made as previously^{14,18} and microanalytical data were obtained from the microanalytical laboratories of Strathclyde University or Medac Ltd. All measurements were made on freshly prepared samples.

Preparations

[VCl₄{MeSe(CH₂)₂SeMe}]. VCl₄ (0.19 g, 1.0 mmol) was dissolved in CH₂Cl₂ (15 mL). MeSe(CH₂)₂SeMe (0.22 g, 1.0 mmol) in CH₂Cl₂ (10 mL) was added slowly producing a very dark solution and precipitate. Concentration *in vacuo* to *ca*. 5 mL, followed by filtration produced a dark purple powder, which was dried *in vacuo*. Yield: 0.36 g, 88%. Calc. for C₄H₁₀Cl₄Se₂V (408.8): C, 11.8; H, 2.5. Found: C, 12.1; H, 2.6%. IR (Nujol) [cm⁻¹]: $\nu = 363$ (sh), 300(vs), 290(sh) (V–Cl). UV/Vis (diffuse reflectance in BaSO₄): E_{max} [cm⁻¹] = 17 850, 20 400, 29 000. μ_{eff} (298 K) = 1.76 μ_{B} .

The following compounds were made similarly.

[VCl₄{MeSe(CH₂)₃SeMe}]. Dark purple powder. Yield: 85%. Calc. for C₅H₁₂Cl₄Se₂V (442.8): C, 14.2; H, 2.9. Found: C, 13.7; H, 3.0%. IR (Nujol) [cm⁻¹]: $\nu = 363$ (sh) 337(vs,br), 328(sh) (V–Cl). UV/Vis (d.r. in BaSO₄): E_{max} [cm⁻¹] = 17700, 20 500, 28 600. μ_{eff} (298 K) = 1.70 μ_{B} .

[VCl₄{**"BuSe(CH₂)₂SeⁿBu}].** Dark purple powder. Yield: 81%. Calc. for C₁₀H₂₂Cl₄Se₂V (493.0): C, 24.4; H, 4.5. Found: C, 24.4; H, 4.1%. IR (Nujol) [cm⁻¹]: $\nu = 360(s), 300(vs)$ (V–Cl). UV/Vis (d.r. in BaSO₄): E_{max} [cm⁻¹] = 18 200, 20 400, 28 500(sh). μ_{eff} (298 K) = 1.75 μ_{B} .

[VCl₃{MeSe(CH₂)₃SeMe}]. VCl₄ (0.19 g, 1.0 mmol) was dissolved in CH₂Cl₂ (15 mL) and MeSe(CH₂)₃SeMe (0.46 g, 2.0 mmol) in CH₂Cl₂ (10 mL) was added slowly producing a very dark solution and precipitate. The solution was stirred under gentle reflux for 1 h, when it slowly became paler. Concentration *in vacuo* to *ca*. 5 mL produced a pale lilac solid, which was filtered off and dried *in vacuo*. Yield: 0.31 g, 81%. Calc. for C₅H₁₂Cl₃Se₂V (385.5): C, 15.6; H, 2.6. Found: C, 15.5; H, 2.9%. IR (Nujol) [cm⁻¹]: $\nu = 363$ (br), 270(m) (V–Cl). UV/Vis (d.r. in BaSO₄): E_{max} [cm⁻¹] = 11 500, 17 480, 30 150. μ_{eff} (298 K) = 2.50 μ_{B} .

[VCl₃{ⁿ**BuSe(CH₂)₂SeⁿBu}].** VCl₄ (0.19 g, 1.0 mmol) was dissolved in CH₂Cl₂ (15 mL) and ⁿBuSe(CH₂)₂SeⁿBu (0.44 g, 2.0 mmol) in CH₂Cl₂ (10 mL) was added, and the mixture was gently refluxed for 1 h. The initial dark precipitate slowly lightened in colour. The solution was cooled to room temperature, filtered, the precipitate was washed with CH₂Cl₂ (5 mL) and dried *in vacuo*. Dull lilac powder. Yield: 0.33 g, 72%. Calc. for C₁₀H₂₂Cl₃Se₂V (457.5): C, 26.3; H, 4.9. Found: C, 26.4; H, 4.7%. IR (Nujol) [cm⁻¹]: $\nu = 355(s)$, 300(s), 270(m,sh) (V–Cl). UV/Vis (d.r. in BaSO₄): E_{max} [cm⁻¹] = 11760, 17900, 27800(sh), 30500. μ_{eff} (298 K) = 2.66 μ_{B} .

[VCl₃{o-C₆H₄(CH₂SeMe)₂}]. VCl₄ (0.19 g, 1.0 mmol) was dissolved in CH₂Cl₂ (15 mL) and o-C₆H₄(CH₂SeMe)₂ (0.58 g, 2.0 mmol) in CH₂Cl₂ (10 mL) added. The initially dark

solution lightened quickly and rapidly deposited a lilac precipitate, which was separated after *ca.* 10 h by filtration, and dried *in vacuo.* Yield: 0.32 g, 73%. Calc. for $C_{10}H_{22}Cl_3Se_2V \cdot CH_2Cl_2$ (542.4): C, 24.4; H, 4.5. Found: C, 23.8; H, 4.4%. IR (Nujol) [cm⁻¹]: $\nu = 337(sh), 320(vs,br), 270(sh)$ (V–Cl). UV/Vis (d.r. in BaSO₄): E_{max} [cm⁻¹] = 11 500, 17 500, 20 000(sh), 29 400(sh). μ_{eff} (298 K) = 2.64 μ_B .

[VCl₃(SeMe₂)₂]. VCl₄ (0.19 g, 1.0 mmol) was dissolved in CH₂Cl₂ (20 mL) and SeMe₂ (0.33g, 3.0 mmol) in CH₂Cl₂ (5 mL) added slowly. A dark solution formed immediately, which then paled on stirring and deposited a pink solid. This was filtered off after *ca.* 15 min and dried *in vacuo.* Yield: 0.28 g, 68%. Calc. for C₄H₁₂Cl₃Se₂V (375.4): C, 12.8; H, 3.2. Found: C, 12.7; H, 3.2%. IR (Nujol) [cm⁻¹]: ν = 393(s) (V–Cl). UV/Vis (d.r. in BaSO₄): E_{max} [cm⁻¹] = 6000, 7200, 12 500, 16 400, 27 000(sh). μ_{eff} (298 K) = 2.65 μ_{B} .

Larger quantities were obtained by scaling up the reaction $(\times 3)$ without problems.

[(Cp)₂V(Se^tBu)₂]. To a frozen (77 K) suspension of Se powder (0.65 g, 8.3 mmol) in thf (30 mL) was added dropwise ^tBuLi (7.3 mL, 1.7 M in pentane). Upon warming to room temperature the solid dissolved to give a colourless solution. After a further 1 h of stirring, the resulting solution was added to a stirred suspension of [(Cp)₂VCl₂] (1.0 g, 4.0 mmol) in thf (20 mL) to give a brown mixture which was stirred at room temperature for 2 h. The volatiles were removed at reduced pressure, the brown solid extracted with Et₂O (50 mL) and filtered through Celite. The precipitate was washed with Et₂O $(3 \times 10 \text{ mL})$, and the Et₂O washings were combined and concentrated, ca. 10 mL. The brown solid which deposited was separated by decantation and dried in vacuo. Yield: 0.11 g, 25%. Further solid was obtained by evaporating the filtrate. The complex is extremely readily hydrolysed. Chemical tests showed it to contain significant amounts of residual LiCl, carried through in the ether extraction and leading to a poor fit of the microanalytical data on several samples. Attempts at recrystallisation and sublimation led to decomposition. UV/Vis (d.r. in BaSO₄): E_{max} [cm⁻¹] = 13 300, 22 320, 26 050.

Deposition and film characterisation

LPCVD experiments were carried out on selected samples in a 40 cm silica tube ($\sim 8 \text{ mm I.D.}$) sealed at one end. Approximately 100 mg of the precursor was placed at the sealed end followed by cut silica tiles ($15 \times 6 \times 1 \text{ mm}$) along most of the length of the tube. The tiles were cleaned with acid piranha etch and dried thoroughly prior to use. The entire assembly was placed in a 30 cm tube furnace with the part of the tube containing the precursor protruding from the other side, and the tube was evacuated to *ca.* 0.05 mbar. This vacuum was maintained throughout the deposition. The tube furnace was heated to 500 or 600 °C then the tube was slowly moved back through the furnace until the precursor showed signs of sublimation. Heating was continued for 1 h, then the furnace was transferred to the glove box.

Coated tiles were generally black in colour. Coatings were usually found to be very thin and so the thickest coatings were chosen for characterisation. The films were also soft, being easily scratched by metal tools as expected for these selenides,⁶ but were well adhered to the substrate surface. Powder X-ray diffraction data were collected with a Bruker D8 Advance with GADDS diffractometer using Cu-K_{α 1} radiation and an incident beam at a 5° angle to the substrate surface. Typically data were collected for 6–10 h. Scanning electron microscopy (SEM) used a Jeol JSM5910, with gold or carbon coated samples. Standardless quantitative energy dispersive X-ray (EDX) analyses used an Oxford Instruments Inca 300 probe.

Results and discussion

Following our previously described routes to MSe_2 (M = Ti, Zr and Hf) thin films,^{9,10} we have investigated similar approaches to VSe_2 via single-source precursor compounds based upon V^{III} and V^{IV} complexes involving neutral selenoether and anionic selenolate ligands. This led to the preparation and characterisation of the first complexes of VCl₄ and VCl₃ with selenoether ligands and synthesis of a V^{IV} selenolate. Deposition studies based upon selected compounds are described later.

Synthesis and characterisation

 $[VCl_4(L-L)]$ complexes. The reaction of VCl₄ with $MeSe(CH_2)_nSeMe$ (n = 2 or 3) in a 1 : 1 molar ratio, in anhydrous CH₂Cl₂ solution at room temperature produced very dark purple powders formulated on the basis of microanalyses, spectroscopic and magnetic measurements as $[VCl_4{MeSe(CH_2)_nSeMe}]$. The complexes are extremely readily hydrolysed in solution and the solids fume in air, and change colour due to hydrolysis. The isolated complexes are insoluble in chlorocarbons or toluene and reduced by MeCN, thf or acetone. Poor solubility in chlorocarbons and hydrolytic instability is also characteristic of Ti, and especially Zr and Hf analogues,^{12,13} but the easy reduction of the V^{IV} complexes is not found in Group 4 analogues. In an attempt to improve solubility, the complex of the *n*-butyl substituted diselenoether, ⁿBuSe(CH₂)₂SeⁿBu, was prepared, but this also gave a poorly soluble complex. The reaction of VCl₄ with o-C₆H₄(CH₂SeMe)₂ gave a dull lilac product directly, which was identified as a V^{III} complex (below). Similar species were produced on refluxing the reaction mixtures containing VCl₄ and 2 mol equiv. of $RSe(CH_2)_2SeR$ (R = Me or ⁿBu) in CH₂Cl₂. The reactions of VCl₄ with the monodentate SeMe₂ gave the V^{III} complex directly (below), with no evidence that V^{IV} species could be isolated. This dependence of the ability to form V^{IV} complexes on the selenoether denticity and architecture is generally similar to that found with thioethers,¹⁸ although the selenoether complexes appear less stable, reflecting the increasing softness and greater reducing power of the selenium donors.

The three [VCl₄(L–L)] (L–L = MeSe(CH₂)_nSeMe (n = 2 or 3), ⁿBuSe(CH₂)₂SeⁿBu) are paramagnetic with $\mu_{\text{eff}} \sim 1.7 \mu_{\text{B}}$ and exhibit several very strong features in the far IR spectra in the range 370–300 cm⁻¹ assigned as terminal ν (V–Cl) modes of *cis*-octahedral species (group theory predicts four IR active modes: 2A₁ + B₁ + B₂). Despite many attempts, their instability and poor solubility have prevented the growth of suitable crystals to confirm the structures, but there seems little doubt that they are closely analogous to the Group 4 complexes.^{12,13} The diffuse reflectance UV/visible spectra are dominated by two intense overlapping transitions at ~20 500 and 18 000 cm⁻¹, which we assign as $Cl(\pi) \rightarrow V(t_{2g})$ and $Se(\pi) \rightarrow V(t_{2g})$, respectively. There is no band evident that is assignable to the d–d transition ${}^{2}T_{2g} \rightarrow {}^{2}E_{g}$ expected in this region; it is clearly obscured by the charge transfer bands. The alternative assignment of the observed bands as the d–d transitions, with splitting caused by the lower than O_{h} symmetry, is ruled out by the absence of other bands <25 000 cm⁻¹ which could be the LMCT transitions. In the Ti^{IV} analogues $Se(\pi) \rightarrow Ti(t_{2g})$ are ~21 000 cm⁻¹ ¹² and the $Se(\pi) \rightarrow V(t_{2g})$ are expected to be at significantly lower energy in the more easily reduced V^{IV} complexes.

[VCl₃(SeMe₂)₂] and [VCl₃(L–L)] complexes. As indicated above, the [VCl₄(L–L)] complexes are easily reduced by refluxing the preparative solutions, giving pale lilac solids. We found that a 1 : 2 VCl₄ : L–L ratio gave pure samples of these lilac solids, [VCl₃(L–L)] (L–L = MeSe(CH₂)₃SeMe, ⁿBuSe(CH₂)₂SeⁿBu or *o*-C₆H₄(CH₂SeMe)₂), which were insoluble in chlorocarbons or MeCN and decomposed by alcohols. The V^{III} complexes are also moisture sensitive, turning blue-green in air, although much less readily hydrolysed than the V^{IV} analogues above.

As expected the diffuse reflectance UV/visible spectra are quite different to those of the V^{IV} complexes, showing weak features at ~ 11500 , 17500 and a strong, broad transition at \sim 30 000 cm⁻¹. The latter is assigned as a charge transfer band, but the weak features are assigned as the two d-d transitions of V^{III} in an octahedral environment, specifically ${}^{3}T_{1g}(F) \rightarrow {}^{3}T_{2g}(F)$ and ${}^{3}T_{1g}(F) \rightarrow {}^{3}T_{1g}(P)$.^{17,21,22} The complexes have room temperature magnetic moments of ~2.6 $\mu_{\rm B}$, confirming the presence of $d^2 V^{III}$. The IR spectra show only weak selenoether bands above 400 cm⁻¹, and several overlapping strong bands in the region 400-300 cm⁻¹, clearly in terminal V-Cl stretching modes. A weaker band $\sim 270 \text{ cm}^{-1}$ is tentatively assigned as a V-Cl bridging mode. The IR spectra and the UV/visible thus lead to a likely assignment as sixcoordinate chloride-bridged vanadium(III) complexes. In contrast, VCl₄ and SeMe₂ react in CH₂Cl₂ solution, irrespective of the reagent ratios used, to form pink [VCl₃(SeMe₂)₂]. This complex exhibits a broad V-Cl stretching vibration in the far IR spectrum at 393 cm⁻¹, and diffuse reflectance UV/visible transitions at 6000, 7200, 12500, 16400, 27000(sh). The UV/visible data are very similar to those reported for the $V^{\rm III}$ thioether complexes $[VCl_3(SR_2)_2]$ (R = Me, Et etc.)^{15,16} which are believed to have trigonal bipyramidal structures.

[(Cp)₂V(Se^tBu)₂]. The use of the *tert*-butyl selenolate follows from our previous work on Group 4 analogues,¹⁰ which were shown to have sufficient volatility to function as CVD precursors for MSe₂ (M = Ti, Zr, Hf). The V^{IV} selenolate complex was obtained from the reaction of [(Cp)₂VCl₂] with two equiv. of LiSe^tBu in anhydrous thf solution. After removal of the thf, the residue was extracted with diethyl ether and filtered. Concentration of the filtrate gave the



Fig. 1 X-Ray diffraction pattern of a VSe₂ film deposited at 600 °C from $[(Cp)_2V(Se^tBu)_2]$. Miller indices are labelled according to VSe₂ ($P\overline{3}m1$, 1T).²⁵

product as a paramagnetic, extremely moisture-sensitive orange-brown powder. It usually retained some LiCl from the preparation (confirmed by a flame test and a silver nitrate spot test), but since the complex is unstable in solution, attempts to purify it further by recrystallisation resulted in considerable decomposition, hence further purification was not attempted. Importantly, the deposition studies described below showed no chloride impurity in the films produced. The only prior reports of V^{IV} selenolates are $[(Cp)_2V(SePh_2)_2]^{23}$ and $[(Cp^{**})_2V(L-L)]$ (Cp^{**} = C₅H₄Me, C₅H₄Et; L–L = various heterocyclic diselenolates).²⁴

Deposition studies

In all of the examples attempted, incomplete sublimation of the vanadium selenoether and selenolate precursors was observed. Significant amounts of residue remained once the deposition was complete and the cold walls of the silica tube at the other end were coated with black and red deposits of elemental Se. The bidentate selenoether complexes did not produce films. However, LPCVD using [VCl₃(SeMe₂)₂] at 600 °C resulted in thin black films on the silica tiles through the furnace hot zone. SEM measurements showed low density growth of small crystallites, many of which were hexagonal plates with their faces parallel to the surface of the substrate. EDX measurements confirmed the presence of V and Se (V : Se = 1 : 0.9), together with Si and O from the substrate and a weak carbon peak. The PXD pattern was weak, but showed peaks assigned to VSe₂ with the typical $P\bar{3}m1$ (1T) structure.²⁵ Lowering the temperature to 500 °C did not improve the films.

Using [(Cp)₂V(Se^tBu)₂] resulted in films at 500 and 600 °C by LPCVD. Those produced at 600 °C were visibly thicker and diffracted well. PXD patterns identified the films as VSe₂, Fig. 1, and the lattice parameters were refined as a = 3.387(19) and c = 5.849(25) Å. Previous reports show the lattice parameters for bulk VSe₂ to be a = 3.355-3.358 and c = 6.107-6.134 Å, with selenium deficiency causing *a* to increase and *c* to decrease (*e.g.* 3.431 and 5.972 Å for VSe_{1.16}).²⁵ SEM measurements showed even growth of ~2 µm platelets perpendicular to the substrate surface, Fig. 2. This growth mode is typical of metal dichalcogenide films due to growth occurring along the *a* and *b* axes of these layered compounds.⁶⁻¹⁰ EDX measurements showed V and



Fig. 2 SEM image of a VSe_ film deposited at 600 $^\circ C$ from $[(Cp)_2V(Se^tBu)_2].$

Se (again with some Si and O evident from the substrate), indicating a Se-deficient composition of VSe_{1.55}. A weak carbon peak was also observed—by analogy with the films grown from $[(Cp)_2M(Se^tBu)_2]$ (M = Ti, Zr, Hf)¹⁰ a carbon content of ~15% can be expected in these films. The sample produced at 500 °C was poorly diffracting, but with a long collection time the broad 100, 011, 102, 110 and 111 reflections of the same VSe₂ phase were all visible. SEM showed less dense coverage of the tile than at 600 °C and EDX a composition of VSe_{1.4}.

A previous study of the APCVD of VSe₂ from V(NMe₂)₄ and Se^tBu₂ precursors found deposition of close to stoichiometric material with platelet crystallites growing perpendicular to the substrate.⁶ Using $[(Cp)_2V(Se^tBu)_2]$ by LPCVD the growth mode is the same but the films are Se deficient, either due to volatilisation of Se in the vacuum or a less favourable decomposition pathway.

Conclusions

The first series of V^{IV} and V^{III} selenoether complexes has been obtained and characterised. Deposition studies (LPCVD) show that, in general, these have insufficient volatility to serve as LPCVD precursors, although some deposition was achieved from [VCl₃(SeMe₂)₂]. This contrasts with previous work on similar TiCl₄ complexes.^{8,9} [(Cp)₂V(Se^IBu)₂], although both moisture-sensitive and easily reduced, does produce black, crystalline films of VSe₂ *via* LPCVD. Modifications of the co-ligands in vanadium selenolates may further improve them as precursors for VSe₂ deposition *via* AACVD or precursor injection techniques.

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