Thioether complexes of WSCl₄, WOCl₄ and WSCl₃ and evaluation of thiochloride complexes as CVD precursors for WS₂ thin films

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Abstract

The red-brown [(WSCl₄)₂{µ-RS(CH₂)₂SR}] (R = Me, Ph, iPr) and [(WSCl₄)₂{µ-MeS(CH₂)₃SMe}] have been made by reaction of WSCl₄ with the thioether in a 2:1 molar ratio, in anhydrous CH₂Cl₂ solution, and characterised by microanalysis, IR, UV/Vis and ¹H NMR spectroscopy. The X-ray structures of the four dithioether complexes reveal square pyramidal WSCl₄ units and bridging dithioethers with W=S trans to thioether sulfur. Paramagnetic W(V) complexes, [WSCl₃{RS(CH₂)₂SR}] (R = Me, iPr), have been made similarly using a 1:≥1 ratio of reactants or longer reaction times. The W(VI) complexes, [WSCl₄(SMe₂)] and [WSCl₄(SeMe₂)], are also described. Analogous complexes of WOCl₄, [(WOCl₄)₂{RS(CH₂)₂SR}] (R = Ph, iPr), have been made similarly from WOCl₄, but reactions using MeS(CH₂)ₙSMe (n = 2, 3) led to reduction to W(V), forming [WOCl₃{MeS(CH₂)ₙSMe}], both of which were identified crystallographically. Curiously, they are geometric isomers: [WOCl₃{MeS(CH₂)₃SMe}] has the dithioether trans Cl/Cl whereas in [WOCl₃{MeS(CH₂)₂SMe}] it is trans O/Cl.

Remarkably, low pressure chemical vapour deposition (CVD) experiments using the dinuclear W(VI) species, [(WSCl₄)₂{PrS(CH₂)₂SPr}]], as a single source precursor produced thin films of 4H-WS₂, identified by grazing incidence X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and Raman spectroscopy; the tungsten thiochloride complex is the first single source low pressure CVD precursor for WS₂. In contrast, the mononuclear W(V) complex, [WSCl₃{PrS(CH₂)₂SPr}], does not deposit WS₂ under similar conditions.

Introduction

The synthesis and some limited coordination chemistry of early 4d and 5d thiohalides, including NbSX₃, TaSX₃, WSX₄, MoSCl₃ and WSX₃ (X = Cl or Br), was first explored in the period 1965-1985,
much of it by Fowles, Rice and Drew,\textsuperscript{1-3} who showed the thiohalides were moderate Lewis acids towards neutral N- or O-donor ligands. Their chemistry was generally similar to that of the corresponding oxide halides, although the thiohalide species seemed more limited and less stable. Complexes of WOF\textsubscript{4} and WSF\textsubscript{4} have been explored more recently,\textsuperscript{4,5} but MSF\textsubscript{3} (M = Nb or Ta) are unknown. We recently reported a series of thioether complexes of NbSCl\textsubscript{3}, of type [NbSCl\textsubscript{3}(SR\textsubscript{2})] (R = Me, \textsuperscript{t}Bu), obtained from reaction of NbCl\textsubscript{5}, SR\textsubscript{2} and S(SiMe\textsubscript{3})\textsubscript{2} in CH\textsubscript{2}Cl\textsubscript{2}.\textsuperscript{6} The structure of the [Nb\textsubscript{2}S\textsubscript{2}Cl\textsubscript{6}(SMe\textsubscript{2})\textsubscript{2}] revealed a Cl-bridged dimer with the SMe\textsubscript{2} ligands disposed syn. The six-coordinate dithioether analogues, [NbSCl\textsubscript{3}(L-L)] (L-L = MeS(CH\textsubscript{2})\textsubscript{2}SMe, MeS(CH\textsubscript{2})\textsubscript{3}SMe, \textsuperscript{t}PrS(CH\textsubscript{2})\textsubscript{2}S\textsuperscript{t}Pr and \textsuperscript{t}BuS(CH\textsubscript{2})\textsubscript{3}S\textsuperscript{t}Bu), were obtained from reaction of L-L with preformed [NbSCl\textsubscript{3}(MeCN)\textsubscript{2}]. We also showed that selected examples can function as single source precursors for low pressure chemical vapour deposition (LPCVD) of thin films of 3R-NbS\textsubscript{2}.\textsuperscript{6} These were the first examples of single source LPCVD reagents using complexes based upon thiohalide M=S units. However, attempts to use analogous thioether complexes of TaSCl\textsubscript{3} did not produce TaS\textsubscript{2} deposition.\textsuperscript{7}

We have reported elsewhere the synthesis, spectroscopic properties and X-ray crystal structures of a range of six-coordinate complexes of WSCl\textsubscript{4} (and analogues with WOCl\textsubscript{4}) with some hard donor phosphine oxides and pyridyl ligands,\textsuperscript{8} and highly unusual, seven-coordinate (pentagonal bipyramidal) W(VI) complexes with phosphine and arsine coordination, [WECl\textsubscript{4}{\textsuperscript{o}-C\textsubscript{6}H\textsubscript{4}(QMe\textsubscript{2})\textsubscript{2}}] (E = O, S, Q = P, As).\textsuperscript{9}

Layered early transition metal dichalcogenides, ME\textsubscript{2} (M = Nb, Ta, V, W, etc.; E = S, Se or Te) are more stable inorganic analogues of graphene, and their properties and band gaps can be tuned by varying the metal and the chalcogen.\textsuperscript{10} Applications of these materials include in optoelectronics, spintronics, sensors, electrocatalysis and magnetic materials.\textsuperscript{10-12} Chemical vapour deposition (CVD) is a low cost and versatile method to deposit such films, using either dual or single source precursors, with single source precursors offering the prospect of better control of film stoichiometry and efficient use of reagents.\textsuperscript{13,14} To our knowledge there are no single source precursors for low pressure CVD of WS\textsubscript{2}. Aerosol-assisted CVD (AACVD) of WS\textsubscript{2} from the dithiocarbamate complex, [WS(S\textsubscript{2})(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}], and of Mo\textsubscript{1-x}W\textsubscript{x}S\textsubscript{2} from a mixture of [WS\textsubscript{3}S\textsubscript{2}CN(Et\textsubscript{2})\textsubscript{2}]\textsubscript{2} and [Mo(S\textsubscript{2}CN(Et\textsubscript{2})\textsubscript{2})\textsubscript{4}] have been reported very recently.\textsuperscript{15} Routes to WS\textsubscript{2} films typically include sulphurisation of WO\textsubscript{3} at elevated temperature, or using dual source precursors, such as WF\textsubscript{6} and H\textsubscript{2}S, or WCl\textsubscript{6}, WOCl\textsubscript{4} or W(CO)\textsubscript{6} with thiols.\textsuperscript{16}

Here we report the synthesis, spectroscopic and structural studies of a series of thioether complexes of WSCl\textsubscript{4} and WSCl\textsubscript{3} alongside a comparative study of their WOCl\textsubscript{4} analogues. We also report on our
evaluation of \([([\text{WSCl}_4]_2\text{PrS(CH}_2\text{)}_2\text{S}\text{Pr}])\) and \([\text{WSCl}_3\text{PrS(CH}_2\text{)}_2\text{S}\text{Pr}])\) as potential single source precursors for the growth of WS\(_2\) thin films by low pressure CVD.

Previous work has shown that the reaction of WSCl\(_4\) with 0.5 equivalents of MeS(CH\(_2\))\(_3\)SMe forms \([([\text{WSCl}_4]_2\text{MeS(CH}_2\text{)}_2\text{SMe}))\),\(^{17}\) the crystal structure of which showed the dithioether bridge linking two six-coordinate tungsten centres.\(^{18}\) Use of an excess of the dithioether or long reaction times caused reduction to tungsten(V) with a chelating dithioether ligand, as in \([\text{WSCl}_3\text{MeS(CH}_2\text{)}_2\text{SMe}])\).\(^{19}\)

**Experimental**

Syntheses were performed using standard Schlenk and glove-box techniques under a dry N\(_2\) atmosphere. WCl\(_6\) (Acros organics), O(SiMe\(_3\))\(_2\) and S(SiMe\(_3\))\(_2\) (Sigma-Aldrich) were used as received. Solvents were dried by distillation from CaH\(_2\) (CH\(_2\)Cl\(_2\), MeCN) or Na/benzophenone ketyl (toluene, n-hexane). The monodentate ligands (SMe\(_2\), SPh\(_2\), SeMe\(_2\)) were obtained from Sigma-Aldrich or Strem and dried over molecular sieve. The dithioethers,\(^{20}\) WOCl\(_4\) and WSCl\(_4\) were made as described elsewhere.\(^{8,21}\)

Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer in the range 4000–200 cm\(^{-1}\), with samples prepared as Nujol mulls between CsI plates. \(^1\)H NMR spectra were recorded using a Bruker AV 400 spectrometer and referenced to the residual protio-resonance of the solvent. \(^{77}\)Se\(^{1}\)H) NMR spectra were obtained from CD\(_2\)Cl\(_2\) solutions using a Bruker AV 400 spectrometer and referenced to neat SeMe\(_2\). Spectra were recorded at 295 K unless indicated otherwise. UV/visible spectra were recorded as powdered solids, using the diffuse reflectance attachment of a PerkinElmer 750S spectrometer. Microanalyses on new compounds were undertaken by London Metropolitan University.

\([([\text{WSCl}_4]_2\text{MeS(CH}_2\text{)}_2\text{SMe}])\): A solution of 2,5-dithiahexane (0.026 g, 0.21 mmol) in dichloromethane (5 mL) was slowly added to a suspension of WSCl\(_4\) (0.150 g., 0.42 mmol) in dichloromethane (5 mL). The dark red solution was then stirred for 1 h, concentrated in vacuo to ~ 3 mL, filtered, and the red/brown solid dried in vacuo. Yield: 0.050 g, 28%. Required for C\(_4\)H\(_{10}\)Cl\(_8\)S\(_4\)W\(_2\) (837.7): C: 5.74, H: 1.25. Found: C: 5.83, H: 1.19%. IR spectrum (Nujol / cm\(^{-1}\)): 534s W=S, 376m, 335s W -Cl. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta = 2.98\) (s, [2H], CH\(_2\)), 2.32 (s, [3H], CH\(_3\)). UV/Vis spectrum (diffuse reflectance) / cm\(^{-1}\): 35,350, 32,250 sh, 20,200.

\([([\text{WSCl}_4]_2\text{MeS(CH}_2\text{)}_3\text{SMe}])\): Prepared similarly using 2,6-dithiaheptane (0.029 g, 0.21 mmol) and WSCl\(_4\) (0.150 g, 0.42 mmol). Red/brown solid. Yield: 0.096 g, 54%. Required for C\(_5\)H\(_{12}\)Cl\(_8\)Se\(_2\)W\(_2\) (851.7): C: 7.05, H: 1.42. Found: C: 7.24, H: 1.53%. IR spectrum (Nujol / cm\(^{-1}\)): 529s W=S, 360m, 332s W-Cl.
\[^1\text{H}\text{ NMR} (\text{CD}_2\text{Cl}_2): \delta = 2.72 \text{ (s br, } [4\text{H}], \text{SCH}_2), 2.20 \text{ (s br, } [6\text{H}], \text{CH}_3), 2.03 \text{ (s br, } [2\text{H}], \text{CH}_2). \text{ UV/Vis spectrum (diffuse reflectance) / cm}^{-1}: 34,750, 32,200, 20,000.  \\
\{(\text{WSCl}_4)\text{2}\{\text{PrS(CH}_2)_2\text{SPr}\}\}: \text{Prepared similarly using 1,2-bis(isopropylthio)ethane (0.037 g, 0.21 mmol) and WSCl}_4 (0.150 g, 0.42 mmol). \text{Red/brown solid. Yield: 0.101 g, 54%. Required for C}_8\text{H}_{18}\text{Cl}_8\text{S}_4\text{W}_2 (893.8): C: 10.75, H: 2.03. Found: C: 10.90, H: 1.95. IR spectrum (Nujol / cm}^{-1}: 543s W=S, 370m 341s W-Cl. \[^1\text{H}\text{ NMR} (\text{CD}_2\text{Cl}_2): \delta = 3.15 \text{ (sep, } [2\text{H}], \text{CH}, 8\text{Hz}), 2.86 \text{ (s, } [2\text{H}], \text{CH}_2), 1.32 \text{ (d, } [6\text{H}], 8\text{Hz, CH}_3). \text{ UV/Vis spectrum (diffuse reflectance) / cm}^{-1}: 36,500, 32,250, 20,800.  \\
\{(\text{WSCl}_4)\text{2}\{\text{PhS(CH}_2)_2\text{SPh}\}\}: \text{Made similarly using 1,2-bis(phenylthio)ethane (0.052 g, 0.21 mmol) and WSCl}_4 (0.150 g, 0.42 mmol) in toluene. \text{Dark red solid. Yield: 0.090 g, 45%. Required for C}_{14}\text{H}_{14}\text{Cl}_8\text{S}_4\text{W}_2 (961.8): C: 17.48, H: 1.47. Found: C: 17.52, H: 1.60%. IR spectrum (Nujol / cm}^{-1}: 539s W=S, 355m, 337s W-Cl. \[^1\text{H}\text{ NMR} (\text{CD}_2\text{Cl}_2): \delta = 7.33 \text{ (br, } [10\text{H}], \text{Ph}), 3.20 \text{ (s br, } [4\text{H}], \text{CH}_2).  \\
\{(\text{WS}_2\text{Cl}_4)\text{2}\cdot \text{CH}_2\text{Cl}_2\}: \text{Made similarly using dimethylsulfide (0.026 g, 0.42 mmol) and WSCl}_4 (0.150 g, 0.42 mmol). \text{Brown/red solid. Yield: 0.101 g, 48%. Required for C}_2\text{H}_6\text{Cl}_4\text{S}_2\text{W} \cdot \text{CH}_2\text{Cl}_2 (504.78): C: 7.14, H: 1.60. Found: C: 7.26, H: 1.73%. IR spectrum (Nujol / cm}^{-1}: 538s W=S, 347s W-Cl. \[^1\text{H}\text{ NMR} (\text{CD}_2\text{Cl}_2): \delta = 2.32 \text{ (s, br, SMe}_2), 5.32 \text{ (s, CH}_2\text{Cl}_2).  \\
\{(\text{WS}_2\text{Cl}_4)\text{2}\cdot \text{SeMe}_2\}: \text{Made similarly using dimethylselenide (0.046 g, 0.42 mmol) and WSCl}_4 (0.150 g, 0.42 mmol). \text{Brown solid. Yield: 0.134 g, 68%. Required for C}_2\text{H}_6\text{Cl}_4\text{SeW} \cdot \text{CH}_2\text{Cl}_2 (466.75): C: 5.15, H: 1.30. Found: C: 5.22, H: 1.36%. IR spectrum (Nujol / cm}^{-1}: 525s W=S, 331m W-Cl. \[^1\text{H}\text{ NMR} (\text{CD}_2\text{Cl}_2): \delta = 2.23 \text{ (s). 77\text{Se}[^1\text{H}]\text{ NMR} (\text{CD}_2\text{Cl}_2, 295 K): no resonance; (183 K): \delta = +81.3.  \\
\{(\text{WO}_4\text{Cl}_4)\text{2}\{\text{PhS(CH}_2)_2\text{SPh}\}\}: \text{Made similarly using 1,2-bis(phenylthio)ethane (0.054 g, 0.22 mmol) and WOCl}_4 (0.150 g, 0.44 mmol). \text{Dark pink solid. Yield: 0.070 g, 34%. Required for C}_{14}\text{H}_{14}\text{Cl}_8\text{O}_2\text{S}_2\text{W}_2 (929.69): C: 18.09, H: 1.52. Found: C: 18.18, H: 1.60%. IR spectrum (Nujol / cm}^{-1}: 992s, 982s W=O, 356s W-Cl. \[^1\text{H}\text{ NMR} (\text{CD}_2\text{Cl}_2): \delta = 7.39 \text{ (m, } [10\text{H}], \text{Ph}), 3.43 \text{ (s, } [4\text{H}], \text{CH}_2).  \\
\{(\text{WO}_4\text{Cl}_4)\text{2}\{\text{PrS(CH}_2)_2\text{SPr}\}\}: \text{Made similarly using 1,2-bis(isopropylthio)ethane (0.039 g, 0.22 mmol) and WOCl}_4 (0.150 g, 0.44 mmol). \text{Greenish-brown solid. Yield: 0.089 g, 47%. Required for C}_8\text{H}_{18}\text{Cl}_8\text{O}_2\text{S}_2\text{W}_2 (861.6): C: 11.15, H: 2.11 Found: C: 11.24, H: 2.14%. IR spectrum (Nujol / cm}^{-1}: 998s W=O, 352s W-Cl. \[^1\text{H}\text{ NMR} (\text{CD}_2\text{Cl}_2): \delta = 3.20 \text{ (sep, } [2\text{H}], 8\text{Hz, CH}_3).  \\
\{(\text{WO}_4\text{Cl}_4)\text{2}\cdot \text{SMe}_2\}: \text{Made similarly using dimethylsulfide (0.027 g, 0.44 mmol) and WOCl}_4 (0.150 g, 0.44 mmol). \text{Brown-yellow solid. Yield: 0.096 g, 54%. Required for C}_2\text{H}_6\text{Cl}_4\text{OSW} (403.8): C: 5.95, H: 1.50.}
Found: C: 5.86, H: 1.39%. IR spectrum (Nujol / cm\(^{-1}\)): 993s, W=O, 352s W-Cl. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta = 2.54\) (s, br).

**[WSCl\(_3\){MeS(CH\(_2\)_2SMe}]**]: Made similarly using 2,5-dithiahexane (0.051 g, 0.42 mmol) and WSCl\(_4\) (0.150 g, 0.42 mmol). Red/brown solid. Yield: 0.070 g, 37%. Required for C\(_4\)H\(_{10}\)Cl\(_3\)S\(_3\)W (444.5): C: 10.81, H: 2.27. Found: C: 11.07, H: 2.26%. IR spectrum (Nujol / cm\(^{-1}\)): 528m W=S, 329s, br W-Cl.

**[WSCl\(_3\){iPrS(CH\(_2\)_2SiPr}]**: Made similarly using 1,2-bis(isopropylthio)ethane (0.112 g, 0.63 mmol) and WSCl\(_4\) (0.150 g, 0.42 mmol). Red/brown solid. Yield: 0.170 g, 81%. Required for C\(_8\)H\(_{18}\)Cl\(_3\)S\(_3\)W (500.62): C: 19.19, H: 3.62. Found: C: 19.50, H: 3.77%. IR spectrum (Nujol / cm\(^{-1}\)): 527s W=S, 340m, 323s W-Cl.

**X-ray experimental**

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 (\(\lambda = 0.71073\)) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K (N\(_2\) cryostream). Crystallographic parameters are presented in Table 1. Structure solution and refinement were performed using SHELX(T)-2018/2, SHELX-2018/3 through Olex2\(^{22}\) and were mostly straightforward, although some of the structures showed significant residual electron peaks near to the tungsten, which are attributed to absorption correction problems. The [WSCl\(_3\){MeS(CH\(_2\)_2SMe}] showed Cl/S disorder, which was modelled by a split atom occupancy approach, occupancies modelled as free variable and then fixed at 0.25 and 0.75. Atoms in the same site were constrained with EADP.

**LPCVD of WS\(_2\) films using [(WSCl\(_4\))\(_2\){PrS(CH\(_2\)_2SPr}]**

The precursor (20-30 mg) was loaded into the precursor bulb at the closed end of a silica tube in a N\(_2\) purged glove box, silica substrates (ca. 1 x 8 x 20 mm\(^3\)) were then positioned end-to-end lengthways along the tube outwards from the precursor. The tube was then set in a furnace so that the substrates were in the heated zone and the precursor protruded ca. 1 cm outside the furnace. The tube was evacuated to 0.1 mm Hg and the furnace heated to 700 °C and left for 10 mins. to allow the temperature to stabilise. The tube was gradually moved towards the hot zone until evaporation of the precursor began and the position was maintained until no further evaporation occurred, leaving some black solid in the precursor bulb. After ca. 20 min. the tube was cooled to room temperature and the substrates were unloaded in the glove box where they were stored for
characterisation. Brown/bronze films were observed on the substrates in the hot zone between 590-625 °C (determined by temperature profiling), i.e. 1.5-3.5 cm away from the precursor.

**Film Characterisation:** X-ray diffraction (XRD) patterns were collected in grazing incidence mode (θ1 = 1°) using a Rigaku SmartLab diffractometer (Cu-Kα, λ = 1.5418 Å) with parallel X-ray beam and a DTex Ultra 250 detector operated in 1D mode. Phase matching and lattice parameter calculations (WS2) used the PDXL2 software package and diffraction patterns from ICSD. High resolution scanning electron microscopy (SEM) measurements were carried out with a field emission SEM (Jeol JSM 7500F) at an accelerating voltage of 2 kV. X-ray photoelectron spectroscopy (XPS) data were obtained using a ThermoScientific Theta Probe system with Al-Kα radiation (photon energy= 1486.6 eV). All peak are calibrated against the adventitious C1s peak at 284.6eV. Raman spectra of the deposited films were measured at room temperature on a Renishaw InVia Micro Raman Spectrometer using 532 nm excitation. The incident laser power was adjusted to 0.1 mW for all samples.

**Results and Discussion**

**WSCl4 complexes:** The WSCl4 was made as reported from reaction of WCl6 and S(SiMe3)2 in anhydrous CH2Cl2 and purified by sublimation in vacuo. Subsequent reaction of WSCl4 with the dithioethers, RS(CH2)2SR (R = Me, Ph, hPr) and MeS(CH2)3SMe, in anhydrous CH2Cl2 in a 2:1 molar ratio and with short reaction times gave the dinuclear W(VI) products [(WSCl4)2{RS(CH2)nR}] as red-brown solids in moderate yields (Scheme 1).

![Scheme 1. Synthesis of the complexes of WSCl4.](image-url)
The complexes are easily hydrolysed, but can be prepared and handled using dry solvents via glove box and Schlenk line techniques and the solids are not degraded even over several months if stored in a dry N₂-purged glove box. If the reaction of WSCl₄ with RS(CH₂)₂SR (R = Me, iPr) is carried out with a 1:1 molar ratio, or if longer reaction times are used, reduction to W(V) occurs to give the complexes, [WSCl₃{RS(CH₂)₂SR}] (see below). Crystals of all four W(VI) dithioether complexes were obtained by slow evaporation from CH₂Cl₂ solutions in the glove box and single crystal X-ray analysis confirmed the formation of the ligand bridged dimers, as formulated above (Figs. 1a-c, S1). The structure of [[WSCl₄]₂{MeS(CH₂)₂SMe}] has been reported previously; the present structure, which is of higher precision, is included in the ESI (Fig. S1). All of the structures show the hexavalent tungsten in a distorted octahedral environment, with the W=S lying trans to the neutral sulfur donor atom and with the four equatorial chlorines bent away from the W=S unit; the corresponding W=S (~2.09 Å), W-S (~2.84 Å) and W-Cl (~2.31 Å) bond lengths are very similar across the series.

**Figure 1.** The structures with atom numbering scheme (H atoms are omitted for clarity and ellipsoids are shown at the 50% probability level) of (a) [[WSCl₄]₂{PhS(CH₂)₂SPh}]: selected bond lengths (Å) and angles (°) are W₂–Cl₆ = 2.3180(16), W₂–Cl₇ = 2.3157(18), W₂–Cl₈ = 2.2891(16), W₁–Cl₅ = 2.3143(18), W₁–Cl₂ = 2.2849(16), W₁–Cl₄ = 2.3213(16), W₁–Cl₁ = 2.3148(18), W₁–Cl₃ = 2.3041(18), W₁–S₁ = 2.1003(17), W₂–S₃ = 2.8635(16), W₂–S₄ = 2.1039(17), S₁–W₁–Cl(1–4) = 99.51(7) – 100.37(6), S₄–W₂–Cl(5–8) = 97.30(7) – 101.17(7); (b) [[WSCl₄]₂{iPrS(CH₂)₂SiPr}]: selected bond lengths (Å) and angles (°) are W₁–Cl₂ = 2.3231(17), W₁–Cl₁ = 2.3100(17), W₁–Cl₄ = 2.3155(17), W₁–Cl₃ = 2.3096(17), W₁–S₁ = 2.0967(19), W₁–S₂ = 2.8633(18), S₁–W₁–Cl(1–4) = 97.87(7) – 100.13(7), S₂–W₁–Cl(1–4) = 78.29(6) – 85.01(6); (c) [[WSCl₄]₂{MeS(CH₂)₃SMe}]: selected bond lengths (Å) and angles (°) are W₂–Cl₆ = 2.325(2), W₂–Cl₇ = 2.329(2), W₂–Cl₈ = 2.312(2), W₁–Cl₁ = 2.323(2), W₁–Cl₂ = 2.307(2), W₁–Cl₄ = 2.320(2), W₁–Cl₁ = 2.295(2), W₁–Cl₃ = 2.329(2), W₁–S₁ = 2.102(2), W₂–S₃ = 2.808(2), W₂–S₄ = 2.109(2), S₁–W₁–Cl(1–4) = 98.54(9) – 100.30(9), S₄–W₂–Cl(5–8) = 98.91(9) – 99.62(8).

The IR spectra of the [[WSCl₄]₂{dithioether}] complexes each show a strong band in the range 530-545 cm⁻¹ assigned as ν(W=S). A strong band ~ 335 cm⁻¹ and a medium intensity feature ~ 370 cm⁻¹ are assigned as the e and a₁ ν(W–Cl) modes, respectively, consistent with the solid state structures.
The diffuse reflectance UV/visible spectra show strong overlapping absorptions, which, from comparison with the spectrum of WSCl₄ itself, may be assigned as charge transfer Cl→W (~36,000, ~32,500 cm⁻¹) and S→W (~20,000 cm⁻¹) transitions; the lack of any absorptions at lower energy found in W(V) complexes confirms the oxidation state as W(VI), as formulated. The ¹H NMR spectra, obtained from rigorously anhydrous CD₂Cl₂ solutions, show the presence of symmetrically coordinated dithioethers, with the expected high frequency coordination shifts.

The red-brown mononuclear [WSCl₄(SMe₂)] was also isolated from the reaction of WSCl₄ and SMe₂ (1 : 1 molar ratio) in CH₂Cl₂ and shows very similar spectroscopic features to the dinuclear dithioether complexes, but no reaction was apparent between the less basic SPh₂ and tungsten thiochloride.

The formation of complexes of WSCl₄ with the heavier selenoether ligands was also briefly examined. Brown [WSCl₄(SeMe₂)], obtained from reacting WSCl₄ and SeMe₂ in CH₂Cl₂ solution, shows ν(W=S) at 525 cm⁻¹ and ν(W–Cl) at 331 cm⁻¹ by IR spectroscopy, while its ¹H NMR spectrum (CD₂Cl₂) is a singlet at δ = 2.23, a significant high frequency shift from SeMe₂ itself (δ = 1.93), indicative of complexation. No ⁷⁷Se{¹H} NMR resonance was seen at room temperature, presumably due to fast exchange on the NMR timescale, but at 183 K the solution showed a single resonance at δ = +81.3, a large coordination shift from ‘free’ SeMe₂ (δ = 0), also consistent with coordination to W(VI). Several attempts to isolate a WSCl₄ complex with MeSe(CH₂)₂SeMe using similar reaction conditions were unsuccessful.

WSCl₃ complexes: Two examples of the (reduced) W(V) complexes, [WSCl₃{RS(CH₂)₂SR}] (R = Me, iPr) were obtained using a WSCl₄ : ligand ratio of 1: ≥ 1 and/or heating the reaction mixture. The products are red-brown paramagnetic solids. In the IR spectra both the ν(W=S) and ν(W–Cl) are at slightly lower frequency than the values in the in the W(VI) complexes discussed above. The ν(W–Cl) will be affected by the different symmetry of the two complex types, but in both complexes the W=S is trans to a neutral thioether donor.

The crystal structure of [WSCl₃{MeS(CH₂)₂SMe}] was reported in early work, but was redetermined here to obtain higher precision data to allow comparison with the W(VI) analogues described above. The structure (Fig. 4) confirms a distorted octahedral geometry with the chelating dithioether lying trans to S/Cl. It also showed S/Cl disorder in the equatorial plane that was satisfactorily modelled using split atoms sites, which were refined to occupancies of 0.25 : 0.75; only the major component is shown in Fig. 2. Because of the disorder present, comparison of bond lengths must be made with care, but the d(W=S) appears to be little different to the values in the W(VI) analogues, whilst d(W-
Cl) is slightly longer in the W(V) complex. The d(W-S) in the latter show a marked effect of the *trans* donor, W1–S3 (**trans** to W=S) = 2.501(1) Å, W1–S2 (**trans** to W-Cl) = 2.764(1) Å.

**Figure 2** The structure of [WSCl3(MeS(CH2)2SMe)] showing the atom numbering scheme and ellipsoids are shown at the 50% probability level. Note that there is S/Cl disorder in plane, which was modelled as split atom sites 0.25 : 0.75; only the major form is shown. Selected bond lengths (Å) and angles (°) are:  W1–S3 = 2.5010(13), W1–S2 = 2.7644(13), W1–Cl2 = 2.3594(12), W1–Cl3 = 2.3494(13), W1–Cl1 = 2.315(2), W1–S1 = 2.054(5), Cl2–W1–S2 = 76.92(4), Cl2–W1–S3 = 90.01(4), Cl3–W–1S2 = 84.76(4), Cl3—W1–S3 = 82.49(5), Cl1–W1–S2 = 83.36(6), Cl1–W1–Cl2 = 90.69(6), Cl1–W1–Cl3 = 91.34(7), S1–W1–S3 = 93.48(18), S1–W1–Cl2 = 100.16(15), S1–W1–Cl3 = 97.49(16), S1–W1–Cl1 = 103.82(18), S3–W1–S2 = 79.55(4).

**WOCl4 and WOCl3 complexes:** The reaction of WOCl4 with a similar set of thioether ligands was also explored to provide some comparisons with the WSCl4 complexes described above (Scheme 2).

**Scheme 2.** Synthesis of WOCl4 complexes

Direct reaction of WOCl4 with RS(CH2)2SR (R = iPr, Ph) readily afforded the dinuclear [[WOCl42{µ-RS(CH2)2SR}]]. However, while the MeS(CH2)nSMe (n = 2, 3) appeared to form analogous complexes, these were unstable and could not be obtained as analytically pure samples, the products isolated always appearing to contain a mixture of W(VI) and W(V) complexes. A greenish-brown W(VI) monomer, [WOCl4(SMe2)], was isolated from CH2Cl2 solution using a 1:1 molar ratio of reagents. The IR spectrum of green [[WOCl42{µ-iPrS(CH2)2SPr}]] exhibits ν(W=O) at 998 cm⁻¹ and ν(W-Cl) at 325 cm⁻¹.
1, similar values to those found in the phosphine oxide or pyridine complexes. The spectrum of
\[[\text{WOCl}_4]\{\mu-\text{PhS(CH}_2)_2\text{SPh}\}\]\ is similar, except that two \(\nu(\text{W}=\text{O})\) bands at 992 and 982 cm\(^{-1}\) were observed. Neither of the bands correspond to a thioether ligand mode and the small splitting is ascribed to a solid-state effect.

The tungsten(VI) oxide tetrachloride complexes of dithiahexane and dithiaheptane could not be isolated (above), but the mixtures in CH\(_2\text{Cl}_2\) produced a few crystals of the reduced W(V) complexes, \[[\text{WOCl}_3]\{\text{MeS(CH}_2)_n\text{SMe}\}\] \((n = 2, 3)\) (Figs. 3a and b).

![Figure 3](image-url)

The structures, showing the atom numbering scheme (H atoms are omitted for clarity and ellipsoids are shown at the 50% probability level), of (a) \[[\text{WOCl}_3]\{\text{MeS(CH}_2)_3\text{SMe}\}\]: selected bond lengths (Å) and angles (°) are: W–Cl1 = 2.3602(17), W–Cl2 = 2.3316(16), W–Cl3 = 2.4639(16), W–S1 = 2.5185(17), W–O1 = 1.720(5), O1–W1–Cl1 = 100.32(17), O1–W1–Cl2 = 102.31(16), O1–W1–S1 = 89.29(16), O1–W1–S2 = 89.37(16), Cl1–W1–Cl3 = 93.29(6), Cl1–W1–S2 = 85.14(6), Cl2–W1–Cl1 = 92.19(6), Cl2–W1–S1 = 83.88(6), Cl2–W1–Cl3 = 91.63(6), S1–W1–S2 = 97.42(6), Cl3–W1–S1 = 78.06(5), Cl3–W1–S2 = 77.19(5); (b) \[[\text{WOCl}_3]\{\text{MeS(CH}_2)_2\text{SMe}\}\]: selected bond lengths (Å) and angles (°) are: W–Cl1 = 2.359(4), W–Cl2 = 2.337(3), W–Cl3 = 2.5185(17), W–O1 = 1.729(12), Cl1–W1–Cl3 = 77.13(14), Cl1–W1–S2 = 90.72(13), Cl2–W1–Cl1 = 91.68(13), Cl2–W1–S1 = 82.17(13), Cl2–W1–Cl3 = 89.99(13), S2–W1–S1 = 79.81(12), Cl3–W1–S1 = 85.91(13), Cl3–W1–S2 = 82.20(13), O1–W1–Cl1 = 98.4(4), O1–W1–Cl2 = 105.1(4), O1–W1–S2 = 93.4(4), O1–W1–Cl3 = 98.0(4).

Both structures are based upon pseudo-octahedrally coordinated tungsten with the dithioether chelating, but are different geometric isomers; \[[\text{WOCl}_3]\{\text{MeS(CH}_2)_2\text{SMe}\}\] has the neutral dithioether ligand trans O/Cl, whilst in \[[\text{WOCl}_3]\{\text{MeS(CH}_2)_3\text{SMe}\}\] the dithioether is trans Cl/Cl. The isomers found in many MEX\(_3\)L\(_2\) and MEX\(_3\)(L-L) \((E = O, S; X = \text{halide})\) have the neutral ligand(s) trans E/X and frequently show E/X disorder in plane.\(^{1,1,6,7,26}\) There is no evidence for disorder in the crystal structure of \[[\text{WOCl}_3]\{\text{MeS(CH}_2)_2\text{SMe}\}\].

**Tungsten disulfide films grown by low pressure CVD:**
The successful isolation of the series of the tungsten(VI) and (V) thiochloride complexes bearing thioether co-ligands described above raised the prospect that it may be possible to use some of these as single source CVD precursors for the growth of technologically relevant tungsten disulfide thin films. In order to test this hypothesis, the complexes selected were those containing iPr substituents in the thioether ligands, in order to provide a low energy decomposition pathway via β-hydride elimination.\(^6\) We found that low pressure CVD experiments in the temperature range 600-700 °C (0.1 mmHg) using the dinuclear W(VI) complex, [(WSCl\(_4\))\(_2\){iPrS(CH\(_2\))\(_2\)SiPr}], indeed led to deposition of bronze-coloured, reflective thin films across the substrate tiles positioned 1.5-3.5 cm from the precursor (i.e. in the temperature range 590-625 °C), the identification and characterisation of which is described below; unsurprisingly, some intractable dark residue also remained in the precursor bulb at the end of the experiments.

Notably, in contrast, the [WSCl\(_3\){iPrS(CH\(_2\))\(_2\)SiPr}] failed to produce any visible deposit on the tiles under comparable conditions, suggesting that this W(V) species is not a suitable CVD precursor under these conditions.

Characterisation of the bronze films obtained from the [(WSCl\(_4\))\(_2\){iPrS(CH\(_2\))\(_2\)SiPr}] precursor was attempted using a grazing incidence X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.
Figure 4 Grazing incidence XRD pattern (top) from a WS₂ thin film deposited by low pressure CVD using [(WSCl₄)₂{PrSi(CH₂)₂SiPr}] at 700°C / 0.1 mmHg. The broad feature at 2θ = 20-25° is from the SiO₂ substrate. XRD pattern for bulk WS₂ (bottom).²⁸

Grazing incidence XRD analysis of the films obtained from the dinuclear [(WSCl₄)₂{PrSi(CH₂)₂SiPr}] (deposited at 700°C / 0.1 mmHg) (Fig. 4) are consistent with polycrystalline 4H WS₂ in space group P6₃/mmc. Lattice parameters were refined as: \(a = 3.1523(11)\), \(c = 12.381(4)\) (Rwp = 7.67%, literature: \(a = 3.1532(4); c = 12.323(5)\) Å).²⁸ The grazing incidence diffraction patterns are dominated by the 002 reflection, suggesting a preferred orientation in the <00l> direction. This is not unusual, as these layered materials typically grow initially with the \(c\) axis normal to the substrate and suggests that the majority of the platelet crystals have grown in that orientation, with platelets flat to the substrate. The films were too thin to allow an in plane XRD measurement even over an extended period. The average crystallite size in the WS₂ film was calculated from the grazing incidence XRD data in Fig. 4 using the Williamson-Hall method, giving an estimated size of 9.1(3) nm. Scanning electron microscopy showed uniform and continuous coverage across the substrate by small hexagonal platelet crystallites (Fig. 5).
Accurate determination of the composition by energy dispersive X-ray (EDX) analysis was not possible due to overlap of the peaks due to tungsten with those from silicon in the substrate, as well as the beam penetration into the substrate, however, X-ray photoelectron spectroscopy (XPS) analysis on the as-deposited films are shown in Fig. 6. The W peaks at 32.6, 34.7, 38.2 eV can be assigned to W 4f7/2, W 4f5/2, W 5p3/2, from which it can be concluded that the films are not oxidized. The S peaks at 162.2 and 163.4eV are attributed to S 2p1/2 and S 2p3/2 and are characteristic of S²⁻ in WS₂. The W:S ratio (1 : 2.2) was estimated by integrating the W4f and S2p peaks.

Raman spectra (Fig. 7) were collected using 532 nm excitation and show the two main peaks at 352 and 419 cm⁻¹, assigned to the E₁₈ and A₁₈ vibrational modes of WS₂, respectively; the weaker features present in the Raman spectra are also consistent with literature data for WS₂.
The WS$_2$ thin film deposition, which constitutes the first successful low pressure CVD growth of WS$_2$ from a single source precursor, is very encouraging, especially given the relatively high molecular weight of the precursor and its inherently low stability (containing a soft thioether ligand bound to a hard, high oxidation state W(VI) Lewis acid). It is likely that the dinuclear precursor decomposes to a more volatile species on heating *in vacuo*, but decomposition to the W(V) analogue, [WSCl$_3$(PrS(CH$_2$)$_2$SPr)], does not appear to be involved, since the pre-formed [WSCl$_3$(PrS(CH$_2$)$_2$SPr)] complex does not afford WS$_2$ films by low pressure CVD under similar conditions. The Raman, SEM, XPS and XRD data show that the deposited WS$_2$ films are of good quality. However, we note that the temperature range for the deposition is rather limited, and coupled with the incomplete precursor evaporation during the CVD experiment, suggests that this dinuclear species may not be the ideal precursor. While the thiochloride-based single source CVD precursor development for WS$_2$ (and NbS$_2$) films incorporates rational design features, the complexes behave quite differently from the Ta(V) analogue, indicating that not all of the factors necessary for the development of effective CVD precursors are understood and so success is still a mixture of trial, error and to some extent, serendipity. Work is currently underway to further improve the WS$_2$ precursor chemistry and to optimise the deposition conditions.

**Conclusions**

A rare series of dithioether complexes of tungsten(VI), [(WSCl$_4$)$_2$(dithioether)], has been synthesised and characterised both spectroscopically and by X-ray crystallography. Complexes of WSCl$_3$ have been similarly characterised, along with some dithioether complexes of WOCl$_4$ and WOCl$_3$. This work
suggests that the thioether complexes of WOCl$_4$ are somewhat less stable than those of WSCl$_4$, possibly attributable to a greater hard/soft donor/acceptor mismatch in the oxide chloride system.

The first identification of a single source precursor for the production of thin films of the technologically-important$^{11}$ WS$_2$ by LPCVD is particularly notable, providing a potentially viable route to the growth of thin films of this important semiconducting material if satisfactory optimisation of reagents and conditions can be achieved.

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Conflicts of Interest

The authors have no conflicts to declare.

Electronic Supplementary Information (ESI) includes crystallographic parameters (Table S1), crystal structures and selected bond length and angle data for [(WSCl$_4$)$_2$(MeS(CH$_2$)$_2$SMe)] (Figs. S1). Cif files for the seven crystal structures are available from the Cambridge Crystallographic Data Centre and have been allocated CCDC numbers 1949960: [(WSCl$_4$)$_2$(MeS(CH$_2$)$_3$SMe)], 1949963: [(WSCl$_4$)$_2$(MeS(CH$_2$)$_2$SMe)], 1949961: [(WSCl$_4$)$_2$(PhS(CH$_2$)$_2$SPh)], 1949964: [(WSCl$_4$)$_2$(PrS(CH$_2$)$_3$SPr)], 1949965: [WSCl$_3$(MeS(CH$_2$)$_2$SMe)], 1949962: [WOCl$_3$(MeS(CH$_2$)$_2$SMe)], 1949966: [WOCl$_3$(MeS(CH$_2$)$_3$SMe)]. ESI also contains IR and NMR spectra for the new complexes.

References


23. ICSD: Inorganic Crystal Structure Database (ICSD), Fachinformationszentrum Karlsruhe (FIZ), accessed via the EPSRC funded National Chemical Database Service hosted by the Royal Society of Chemistry.


