Complexes of WOCl₄ and WSCl₄ with neutral N- and O- donor ligands: synthesis, spectroscopy and structures.

Victoria K. Greenacre, Andrew L. Hector, William Levason,* Gillian Reid, Danielle E. Smith, and Laura Sutcliffe

School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK

Keywords: tungsten oxide tetrachloride : tungsten sulfide tetrachloride: phosphine oxide : 2,2'-bipyridyl : X-ray structures

Abstract
The complexes [WOCl₄(L)] and [WSCl₄(L)] (L = OPPh₃, OPMe₃, pyridine, 2,2'-bipyridyl), [{WOCl₄}₂(µ-L-L)] and [{WSCl₄}₂(µ-L-L)] (L-L = Ph₂P(O)(CH₂)nP(O)Ph₂ (n = 1, 2)) have been prepared from WOCl₄ or WSCl₄ and the ligands in anhydrous CH₂Cl₂ solution, and characterised by microanalysis, IR and NMR (¹H, ³¹P{¹H}) spectroscopy. X-ray crystal structures are reported for [WOCl₄(OPPh₃)], [{WOCl₄}₂(µ-Ph₂P(O)(CH₂)₃P(O)Ph₂)] and [{WSCl₄}₂(µ-Ph₂P(O)(CH₂)₃P(O)Ph₂)]. All, except those of 2,2'-bipyridyl, are six-coordinate with the neutral donor trans to W=O or W=S. Spectroscopic data suggest that the [WOCl₄(2,2'-bipy)] and [WSCl₄(2,2'-bipy)] are seven-coordinate. Comparison of the structural and spectroscopic data for the two series of complexes indicate little difference in Lewis acidity between the two tungsten(VI) moieties. Decomposition of [WOCl₄(OPMe₃)] in solution gave the cyclic trimer [W₃O₃(µ-O)₃Cl₆(OPMe₃)₃], the structure of which revealed a six-membered W₃O₃ ring core with very asymmetric oxido-bridges. The structure of the tungsten(V) complex [WOCl₃(2,2'-bipy)] is also reported.

1. Introduction
The oxide and sulfide halides of the early d-block metals in their higher oxidation states are Lewis acidic and form complexes with a variety of neutral ligands [1]. In the solid state tungsten oxide tetrachloride contains square pyramidal WOCl₄ units linked into chains via asymmetric W=O⁻W bridges (W–O = 1.8, 2.2 Å) [2] whilst in WSCl₄ the square pyramidal

- Corresponding author . email wxl@soton.ac.uk

1
core units are weakly chloride-bridged to form dimers \([\text{SCl}_3\text{W}(\mu-\text{Cl})_2\text{WCl}_3\text{S}]\) [3]. A second polymorph of \(\text{WSCl}_4\) is a tetramer \([\text{Cl}_4\text{W}(\mu-\text{Cl})\text{SCl}_2\text{W}(\mu-\text{Cl})_2\text{WCl}_2\text{S}(\mu-\text{Cl})\text{WSCl}_4]\) in which the dimer core is linked by single chlorine bridges to two other \(\text{WSCl}_4\) units [4]. Neutral ligand complexes of \(\text{WOCl}_4\), were first reported some years ago, obtained by direct reaction of the ligand with \(\text{WOCl}_4\), by abstraction of oxygen from O-donor ligands, and for some examples by hydrolysis of \(\text{WCl}_6\) complexes [1,5,6]. Typical examples include \([\text{WOCl}_4(\text{RCN})]\) \(\text{R} = \text{Me}, \text{Et}, \text{Ph}\) [7,8], \([\text{WOCl}_4(\text{thf})]\) [7,9], \([\{\text{WOCl}_4\}_2(1,4\text{-dioxane})]\) [7,9], \([\text{WOCl}_4(\text{OMe}_2)]\) [10], \([\text{WOCl}_4(\text{Meurea})]\) [11], \([\text{WOCl}_4(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)]\) [12], \([\text{WOCl}_4(\text{PR}_3)]\) \(\text{R}_3 = \text{Ph}_3, \text{PhEt}\), \([\text{WOCl}_4(\text{PR}_3)_2]\) \(\text{R}_3 = \text{Ph}_3, \text{Et}_3\) and \([\text{WOCl}_4(\text{OPPh}_3)_n]\) \(n = 1\) or 2 [13]. Other workers have reported that phosphines abstract oxygen from \(\text{WOCl}_4\) to form phosphine oxide complexes of \(\text{W}(\text{IV})\) [14]. Detailed investigation of the reactions of \(\text{WCl}_6\) with ethers, polyethers, ketones and amides have shown that while \([\text{WOCl}_4(\text{ligand})]\) are formed in some cases, the chemistry depends upon the particular ligand and the reaction conditions, and other products include complexes of fragmented ligands and tungsten(V) complexes containing \(\text{WCl}_3\) or \(\text{WOCl}_3\) [10,11,15,16]. A few complexes of \(\text{WBr}_3\) have been described [1,5,6,7], along with the fluoro complexes, \([\text{WOBr}_4(L)]\) \(L = \text{MeCN}, \text{OPPh}_3, \text{thf}, \text{dms}, \text{py}, \text{PMe}_3\) and \([\text{WOBr}_4(\text{diphosphine})]\) \(\text{diphosphine} = \text{o-C}_6\text{H}_4(\text{PMe}_2)_2\) or \(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2\) that were reported very recently [17,18].

Some corresponding tungsten(VI) sulfide tetrachloride complexes, including \([\text{WSCl}_4(L)]\) \(L = \text{thf}, \text{py}, \text{RCN}\), \([\{\text{WSCl}_4\}_2(\mu-1,4\text{-dioxane})]\) and \([\{\text{WSCl}_4\}_2(\mu-\text{MeS(CH}_2)_2\text{SMe})]\) have been prepared, but appear to be less stable than those of \(\text{WOCl}_4\) [1,5,19,20]. Possible applications of complexes of metal sulfide halides include their use as reagents for the chemical vapour deposition of the layered metal dichalcogenide thin film materials [21,22]. We report here a comparison of the complexes of \(\text{WOCl}_4\) and \(\text{WSCl}_4\) with a series of neutral N- and O-donor ligands.

### 2. Results and Discussion

#### 2.1 Phosphine oxide complexes.

The \(\text{WOCl}_4\) and \(\text{WSCl}_4\) precursors were made by minor modifications of the literature route from \(\text{WCl}_6\) and \(\text{O(SiMe}_3)_2\) or \(\text{S(SiMe}_3)_2\), respectively, in \(\text{CH}_2\text{Cl}_2\) [23]. The complexes were subsequently synthesised by reaction of the appropriate ligand with the \(\text{WECl}_4\) \((E = \text{O or S})\) in anhydrous \(\text{CH}_2\text{Cl}_2\). Attempts to prepare the complexes by “one pot” reactions, i.e. by adding the \(\text{O(SiMe}_3)_2\) or \(\text{S(SiMe}_3)_2\) to \(\text{WCl}_6\) in \(\text{CH}_2\text{Cl}_2\), followed by addition of the ligand, were less
successful and often gave impure products or mixtures. The complexes are very readily
hydrolysed with formation of the robust [WO\textsubscript{2}Cl\textsubscript{2}(L)\textsubscript{n}] (and other products) and use of
anhydrous ligands and solvents with Schlenk and glove box techniques is essential to obtain
pure complexes. In several cases, adventitious hydrolysis led to the isolation of [WO\textsubscript{2}Cl\textsubscript{2}(L)\textsubscript{n}]
complexes, as seen in other WOX\textsubscript{4}/WO\textsubscript{2}X\textsubscript{2} systems [1,17]. The reaction of WOCl\textsubscript{4} with one
molar equivalent of OPPh\textsubscript{3} or OPMe\textsubscript{3} or 0.5 molar equivalents of Ph\textsubscript{2}P(O)(CH\textsubscript{2})\textsubscript{n}P(O)Ph\textsubscript{2} (n = 1, dppmO\textsubscript{2}; n = 2, dppeO\textsubscript{2}) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} solution gave orange or yellow complexes
[WOCl\textsubscript{4}(OPR\textsubscript{3})] (R = Me, Ph) or [WOCl\textsubscript{4}(L-L)] (L-L = dppmO\textsubscript{2}, dppeO\textsubscript{2}). X-Ray crystal
structures were determined for [WOCl\textsubscript{4}(OPPh\textsubscript{3})] and [WOCl\textsubscript{4}(dppmO\textsubscript{2})], with crystals
grown from CH\textsubscript{2}Cl\textsubscript{2} solution by slow evaporation. They show distorted octahedral tungsten
centres (Figures 1 and 2). Although they are not isomorphous, the structure of [WOCl\textsubscript{4}(OPPh\textsubscript{3})]
is very similar to that of [WOF\textsubscript{4}(OPPh\textsubscript{3})] [17] with the OPPh\textsubscript{3} trans to W=O and the tungsten
above the WCl\textsubscript{4} plane towards the oxido group, as usually found in complexes of this type. The
d(W=O) are not significantly different, 1.6841(16) Å in the present complex and 1.682(5) Å in
the fluoride, although the W-O\textsubscript{3} is shorter in the present complex. 2.1041(14) Å compared to
2.141(4) Å in the fluoride.

**Figure 1** The structure of [WOCl\textsubscript{4}(OPPh\textsubscript{3})] showing the atom numbering scheme. H atoms are omitted
for clarity. Selected bond lengths (Å) and angles (°) are: W1–C11 = 2.3457(5), W1–C12 = 2.3012(6),
W1–C13 = 2.2935(6), W1–C14 = 2.3148(6), W1–O1 = 1.6841(16), W1–O2 = 2.1041(14), C12–W1–C11 = 87.76(2), C13–W1–C12 = 92.66(2), C13–W1–C14 = 90.98(2), C14–W1–C11 = 86.61(2), O1–W1–C11 = 94.95(6), O1–W1–C12 = 94.68(7), O1–W1–C13 = 95.15(6), O1–W1–C14 = 96.60(7), O1–W1–O2 =
178.33(8), O2–W1–Cl1 = 84.62(4), O2–W1–Cl2 = 83.69(4), O2–W1–Cl3 = 85.32(4), O2–W1–Cl4 = 85.00(4). The second molecule in the asymmetric unit is very similar.

In the dimeric [{WOCl₄}₂(dppmO₂)] (Figure 2) the tungsten environments and the W=O and W–Cl bond lengths are similar to those in the OPPh₃ complex, while the W–O₁ are slightly longer, and also surprisingly disparate (W1–O2 = 2.1886(12), W2–O3 = 2.1224(13) Å).

The spectroscopic properties of the four complexes are unexceptional. The IR spectra exhibit a single strong ν(W=O) in the range 957–985 cm⁻¹, broad ν(W–Cl) ~ 337 +/- 5 cm⁻¹ and with the ν(P=O) reduced by > 60 cm⁻¹ from the values in the parent ligands. The IR spectrum of [{WOCl₄(OPPh₃)] has been reported twice, but with poor agreement [13,24]; our data are in agreement with the report of Behzadi et. al [24]. The ³¹P{¹H} NMR spectra show substantial high frequency shifts for the phosphoryl group upon coordination and for the complexes of [{WOCl₄(OPR₃)] are very similar to those observed for the corresponding [WOF₄(OPR₃)] [17]; (the [{WOF₄}₂(diphosphine dioxide)] complexes have not been reported). The report [13] that [{WOCl₄(OPPh₃)] exhibits a low frequency coordination shift of ~4 ppm is clearly in error.
Figure 2 The structure of \([\{WOCl_4\}_2(dppmO_2)\]\) showing the atom numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl1 = 2.3010(5), W1–Cl4 = 2.3092(5), W1–Cl3 = 2.3190(5), W1–Cl2 = 2.3142(5), W1–O2 = 2.1886(12), W1–O1 = 1.6861(14), W2–Cl6 = 2.3119(5), W2–Cl8 = 2.3175(5), W2–Cl5 = 2.3143(5), W2–Cl7 = 2.3198(5), W2–O3 = 2.1224(13), W2–O4 = 1.6846(14), Cl1–W–Cl(cis) 88.129(18)–90.672(19), OPr–W–Cl = 83.60(4)–87.35(4), O1–W–Cl = 93.36(5)–96.94(6), O1–W1–O2 = 176.96(6), O4–W2–O3 = 179.31(7).

The reaction of WSCl₄ with OPPh₃, OPMe₃, dppmO₂ and dppeO₂ in anhydrous CH₂Cl₂ solution, produced brown powders, \([WSCl_4(OPR_3)]\) (R = Me, Ph) and \([\{WOCl_4\}_2(L-L)\]\) (L-L = dppmO₂, dppeO₂). The X-ray crystal structure of \([WSCl_4(dppmO_2)]\) (Figure 3) shows a centrosymmetric dimer with the tungsten lying out of the WCl₄ plane towards the sulfide group. The W–Oₚ = 2.159(2) Å, is similar to the average of the corresponding links in \([\{WOCl_4\}_2(dppmO_2)\]\) (2.155 (6) Å).
Figure 3 The structure of [{WSCl4}_{2}(dppeO_2)] showing the atom numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl3 = 2.3126(8), W1–Cl4 = 2.3166(8), W1–Cl2 = 2.3484(8), W1–Cl1 = 2.3423(7), W1–S1 = 2.1059(9), W1–O1 = 2.159(2), Cl3–W1–Cl4 = 90.29(3), Cl3–W1–Cl2 = 89.06(3), Cl4–W1–Cl1 = 89.47(3), Cl1–W1–Cl2 = 87.80(3), S1–W1–Cl3 = 97.99(3), S1–W1–Cl4 = 95.99(3), S1–W1–Cl2 = 97.18(3), S1–W1–Cl1 = 96.79(3), S1–W1–O1 = 179.02(6), O1–W1–Cl3 = 82.33(6), O1–W1–Cl4 = 83.08(6), O1–W1–Cl2 = 83.74(6), O1–W1–Cl1 = 82.91(6).

2.2 Complexes of N-heterocycles

To compare the complexes of the O-donor phosphine oxides with those of N-donor ligands, the complexes with pyridine and 2,2'-bipyridyl were examined. The yellow [WOCl4(py)] and brown [WSCl4(py)] complexes [7,19] were made by reacting the constituents in a 1:1 molar ratio in dry CH2Cl2 solution. The products are diamagnetic and the spectroscopic properties are unexceptional. Under reflux or with longer reaction times, reduction to W(V) species occurs [19]. The reaction of WOCl4 with 2,2'-bipyridyl has been reported before [7,25], the green solid being variously formulated as [WOCl4(2,2'-bipy)] or the paramagnetic W(V) complex, [WOCl4(2,2'-bipy)]. By conducting the reaction in CH2Cl2 solution at room temperature and with a relatively short reaction time, we obtained a green complex [WOCl4(2,2'-bipy)], which was diamagnetic and with the 1H NMR spectrum showing equivalent pyridyl rings. Repeated attempts to obtain crystals for an X-ray study have been unsuccessful, but it is highly likely that the complex [WOCl4(2,2'-bipy)], contains seven-coordinate tungsten, probably pentagonal bipyramidal with axial O/Cl. Similar seven-coordination is established in [WOCl4(o-C6H4(AsMe2)2)] [12] and in several complexes of WOF4 [17,18,26]. The ν(W=O) of 970 cm⁻¹ is lower than the values observed in the six-coordinate complexes, but similar to those in [WOCl4(o-C6H4(AsMe2)2)] (964 cm⁻¹) [12], [WOF4(2,2'-bipy)] (968 cm⁻¹) or [WOF4(py2)] (973 cm⁻¹) [26], which supports the assignment of the higher coordination number. The new complex [WSCl4(2,2'-bipy)] was obtained as a red solid, and is spectroscopically very similar. Attempts to grow crystals of the seven-coordinate W(VI) complex from CH2Cl2 solution over several days resulted in crystals being obtained of the previously reported six-coordinate [WSCl4(2,2'-bipy)] [19] (Figure 4).
Figure 4 The structure of [WSCl(bipy)] showing the atom numbering scheme. Two crystallographically independent molecules were present in the asymmetric unit, one is shown here for clarity. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl1 = 2.284(4), W1–Cl2 = 2.356(3), W1–Cl3 = 2.363(3), W1–S1 = 2.266(4), W1–N1 = 2.268(11), W1–N2 = 2.215(11), Cl2–W1–Cl3 = 166.21(11), S1–W1–Cl2 = 96.40(13), S1–W1–N1 = 166.1(3), S1–W1–N2 = 93.3(3), S1–W1–Cl3 = 95.79(13), N1–W1–Cl2 = 83.5(3), N1–W1–Cl3 = 83.1(3), N2–W1–Cl2 = 86.2(3), N2–W1–Cl3 = 86.7(3), N2–W1–N1 = 72.8(4), N2–W1–Cl1 = 91.45(12).

A complex [WOCl(1,10-phen)] has been claimed [25], but with no reported data. Our attempts using similar reaction conditions to those used for [WOCl(2,2′-bipy)] produced a mixture of products, one of which was identified by an X-ray structure determination as [WO2Cl2(1,10-phen)]⋅CH2Cl2 by comparison of the unit cell parameters with the literature [27]. It is possible that the more rigid 1,10-phenanthroline is poorly matched to the seven-coordinate tungsten centre. It is notable that attempts to isolate [WOFe(1,10-phen)] from reaction of [WOF4(MeCN)] with 1,10-phen failed, with [WO2F2(1,10-phen)] being identified as one major product [17].

As indicated above, decomposition (probably hydrolysis) of some of the WOCl complexes to WO2Cl2 species was noted, whereas under more forcing condition (higher temperatures, excess ligand or extended reaction time) reduction to tungsten(V) species sometimes occurs [1,7,19,28]. During attempts to grow crystals from of the [WOCl(OPR3)] by slow evaporation from CH2Cl2 solutions. a few white crystals were isolated, which proved to be cyclic {Wn(µ-O)h} species. Several batches of white crystals were obtained, most with the crystal quality too poor to merit report, but a few good crystals were obtained on one occasion from the OPMe system and the structure is shown in Figure 5.
The crystals contain W(VI) with a distorted octahedral coordination environment composed of \( \text{WO}_2\text{Cl}_2(\text{OPMe}_3) \) units linked via very asymmetric oxido-bridges into a six-membered ring. Thus, the W=O group \textit{trans} to the phosphine oxide with W=O ~ 1.8 Å forms a weak bridge to a second tungsten (~2.35 Å), distances which may be compared with the terminal W=O of ~ 1.7 Å. The remaining bond lengths and angles about the tungsten centre are not significantly different to those in the other phosphine oxide complexes. Attempts to prepare a bulk sample of the complex directly by varying the conditions in the WOCl\(_4\) O(SiMe\(_3\))\(_2\), OPMe\(_3\) reaction were unsuccessful.
3. Conclusions

The synthesis of a series of phosphine oxide and pyridyl ligand complexes of WOCl₄ and WSCl₄ has been described. Under the mild synthesis conditions used, reduction to lower oxidation states of tungsten is not significant, although all complexes are hydrolytically unstable, and must be manipulated and stored under strictly anhydrous conditions. Except for the 2,2'-bipy complexes, where the small ring chelate produces seven-coordination, the other complexes are six-coordinate. Comparison of the data from various spectroscopic probes, viz the IR $\nu$(P=O) data, the coordination shift observed in the $^{31}$P{$^1$H} NMR spectra of the phosphine oxide species, and the d(W–Oₚ) bond lengths in the structures, show only small differences between the corresponding complexes of WOCl₄ and WSCl₄. The data suggest that WSCl₄ may be a marginally less strong Lewis acid than WOCl₄, but the differences in the various parameters are small. Future work will examine the corresponding complexes of these two hard W(VI) Lewis acids with much softer sulfur or phosphorus donor ligands, to establish if the trends are replicated.

4. Experimental

Syntheses were performed by using standard Schlenk and glove-box techniques under a dry N₂ atmosphere. WCl₆ (Acros organics), O(SiMe₃)₂ and S(SiMe₃)₂ (Sigma-Aldrich) were used as received. Solvents were dried by distillation from CaH₂ (CH₂Cl₂, MeCN) or Na/benzophenone ketyl (toluene, n-hexane). Ligands (2,2'-bipy, 1,10-phen, OPPh₃) were obtained from Sigma-Aldrich and dried by heating in vacuo before use. Pyridine was dried over sodium and freshly distilled. The diphosphine dioxides, dppmO₂ and dppeO₂, were made by dry air oxidation of the corresponding diphosphines in CH₂Cl₂ solution, catalysed by SnI₄ [29] and were checked for purity by $^{31}$P{$^1$H} NMR spectroscopy. They were also dried by heating in vacuo.

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 protioresonance of the solvent. $^{31}$P{$^1$H} NMR spectra were obtained from CD₂Cl₂ solutions using a Bruker AV 400 spectrometer and referenced external 85% H₃PO₄. Microanalyses on new compounds were undertaken by London Metropolitan University or Medac.

3.1 [WOCl₄]
Following the literature method [23], a solution of \((\text{Me}_3\text{Si})_2\text{O}\) (0.82 g, 5.04 mmol) in dichloromethane (5 mL) was added to a stirred solution of \(\text{WCl}_6\) (2.0 g, 5.04 mmol) in dichloromethane (5 mL). The orange solution was stirred for 1 h and the orange precipitate was filtered off and washed with cold hexane (2 x 1 mL), and dried in vacuo. IR spectrum (Nujol, \(\text{cm}^{-1}\)): 889sh W=O, 875s W=O, 381s,br W−Cl, 326s W−Cl.

3.2 [\(\text{WSCl}_4\)]

\(\text{WCl}_6\) (2.5 g, 6.3 mmol) in toluene (5 mL) was chilled to 0°C and hexamethyldisilathane (1.35 g, 6.3 mmol) in toluene (5 mL) was added dropwise over 15 min. The red/brown solution formed was stirred for 30 min. and taken to dryness in vacuo, resulting in a brown powder. The brown powder was sublimed in vacuo yielding a red powder on the cold finger. Yield: 0.950 g, 42%. IR spectrum (Nujol, \(\text{cm}^{-1}\)): 556m W=S, 372s W−Cl.

3.3 [\(\text{WOCl}_4(\text{OPPh}_3)\)]

A solution of \(\text{OPPh}_3\) (0.105 g, 0.44 mmol) in dichloromethane (5 mL) was added slowly to a suspension of \(\text{WOCl}_4\) (0.150 g, 0.44 mmol) in dichloromethane (5 mL). The clear orange solution was then stirred for 1 h, concentrated to ~ 5 mL in vacuo, filtered, and the resulting orange solid washed with hexane (2 x 1 mL), and dried in vacuo. Yield: 0.130 g, 48%. Required for \(\text{C}_{18}\text{H}_{15}\text{Cl}_4\text{O}_2\text{PW}\) (619.9): C, 34.85; H, 2.44. Found: C, 35.01; H, 2.44%. IR spectrum (Nujol, \(\text{cm}^{-1}\)): 1135s P=O, 981s W=O, 338s W−Cl. ¹H NMR (CDCl₃): \(\delta = 7.88\) (m, [6H]), 7.70 (m, [3H]), 7.58 (m, [6H]). ³¹P{¹H} NMR (CDCl₃): \(\delta = +46.6\) (s).

3.4 [\(\text{WOCl}_4(\text{OPMe}_3)\)]

\(\text{OPMe}_3\) (0.059 g, 0.44 mmol) in dichloromethane (5 mL) was slowly added to a suspension of \(\text{WOCl}_4\) (0.150 g, 0.44 mmol) in dichloromethane (5 mL). The yellow solution was then stirred for 1 h, concentrated to half the volume, filtered and the resulting yellow solid washed with hexane (2 x 1 mL), and dried in vacuo. Yield: 0.140 g, 73%. Required for \(\text{C}_3\text{H}_9\text{Cl}_4\text{O}_2\text{PW}\) (433.7): C, 8.31; H, 2.09. Found: C, 8.55; H, 2.02%. IR spectrum (Nujol, \(\text{cm}^{-1}\)): 1089s,br P=O, 957s W=O, 337s W−Cl. ¹H NMR (CDCl₃): \(\delta = 1.88\) (d, \(^2\text{J}_{\text{HP}} = 13\) Hz). ³¹P{¹H} NMR (CDCl₃): \(\delta = +64.2\) (s).

3.5 [\(\text{WOCl}_4(\text{dppmO}_2)\)]

Powdered dppmO₂ (0.120 g, 0.29 mmol) in dichloromethane (5 mL) was added slowly to an orange suspension of \(\text{WOCl}_4\) (0.200 g, 0.58 mmol) in dichloromethane (5 mL). The clear orange/brown solution formed was stirred for 1 h, then concentrated to ~ 5mL, filtered and the
orange powder washed with hexane (2 x 1 mL) and dried in vacuo. Yield: 0.264 g, 83%. Required for C_{25}H_{22}Cl_{8}O_{4}P_{2}W_{2} (1099.7): C, 27.30; H, 2.02. Found: C, 27.42; H, 2.14%. IR spectrum (Nujol, cm^{-1}): 1076 m, br P=O, 981 s, W =O, 338 s, W =Cl. 1H NMR (CDCl_{3}): \( \delta = 7.81\) (m, [8H]), 7.61 (m, [4H]), 7.43 (m, [8H]), 4.62 (t, [2H], \( ^2J_{H,P} = 15.5\) Hz). 31P{1H} NMR (CDCl_{3}): \( \delta = +44.6\) (s).

3.6 [(WOCl_{4})_{2}(dppeO_{2})]

Was made similarly to [(WOCl_{4})_{2}(dppmO_{2})] as a yellow powder. Yield 31%. Required for C_{26}H_{24}Cl_{8}O_{4}P_{2}W_{2} (1139.7): C, 28.04; H, 2.17. Found: C, 27.96; H, 2.12%. IR spectrum (Nujol, cm^{-1}): 1091 s, P=O, 985 s, W =O, 337 s, W =Cl. 1H NMR (CDCl_{3}): \( \delta = 7.86\) (m, [8H]), 7.70 (m, [4H]), 3.15 (br, s, [4H]). 31P{1H} NMR (CDCl_{3}): \( \delta = +53.2\) (s).

3.7 [(WSCl_{4})(OPPh_{3})]

OPPh_{3} (0.078 g, 0.28 mmol) in dichloromethane (2 mL) was slowly added to a red solution of WSCl_{4} (0.100 g, 0.28 mmol) in dichloromethane (5 mL). The solution was then stirred for 1 h., concentrated in vacuo to ~ 4 mL. The brown precipitate was filtered off, washed with hexane (2 x 1 mL) and dried in vacuo. Yield: 0.120 g, 69%. Required for C_{18}H_{15}Cl_{4}OPSW (636.0): C, 33.99; H, 2.38. Found: C, 34.14; H, 2.45%. IR spectrum (Nujol, cm^{-1}): 1137 m, P=O, 329 s, W =Cl. 1H NMR (CD_{2}Cl_{2}): \( \delta = 7.81\) (m, [6H]), 7.68 (t, [3H]), 7.55 (m, [6H]). 31P{1H} NMR (CD_{2}Cl_{2}): \( \delta = +45.9\) (s).

3.8 [(WSCl_{4})(OPMe_{3})]

A brown powder, made in an analogous way to [(WSCl_{4})(OPPh_{3})]. Yield: 43%. Required for C_{3}H_{9}Cl_{4}OPSW (449.8): C, 8.01; H, 2.00. Found: C, 8.14; H, 2.14%. IR spectrum (Nujol, cm^{-1}): 1075 s, br P=O, 522 m, W =S, 322 s, br W =Cl. 1H NMR (CD_{2}Cl_{2}): \( \delta = 1.81\) (d, \( ^2J_{PH} = 13\) Hz). 31P{1H} NMR (CD_{2}Cl_{2}): \( \delta = +63.8\) (s).

3.9 [(WSCl_{4})(dppmO_{2})]

Dried dppmO_{2} (0.086 g, 0.21 mmol) in dichloromethane (5 mL) was added slowly to a red suspension of WSCl_{4} (0.150 g, 0.42 mmol) in dichloromethane (5 mL). The resulting brown solution was then stirred for 1 h, concentrated in vacuo and the brown solid filtered off and rinsed with hexane (2 x 1 mL), and then dried in vacuo. Yield: 0.115 g, 48%. Required for C_{25}H_{22}Cl_{8}O_{2}P_{2}S_{2}W_{2} (1131.8): C, 26.53; H, 1.96. Found: C, 26.52; H, 2.06%. IR spectrum (Nujol, cm^{-1}): 1074 m, P=O, 530 m, W =S, 338 s, W =Cl. 1H NMR (CD_{2}Cl_{2}): \( \delta = 7.76\) (s).
3.10 [(WSCl$_4$)$_2$(dppeO$_2$)]

Dried dppeO$_2$ (0.090 g, 0.21 mmol) in dichloromethane (5 mL) was slowly added to a red
suspension of WSCl$_4$ (0.150 g, 0.42 mmol) in dichloromethane (5 mL), when a brown solution
was formed. After 1 h, the solution was concentrated in vacuo, the brown solid filtered off,
was washed with hexane (2 x 1 mL) and dried in vacuo. Yield: 0.190 g, 79%. Required for
C$_{26}$H$_{24}$Cl$_{8}$O$_2$P$_2$S$_2$W$_2$ (1145.85): C, 27.25; H, 2.11. Found: C, 27.00; H, 2.02%. IR spectrum
(Nujol, cm$^{-1}$): 1077s P=O, 536s W=S, 330s W−Cl. $^1$H NMR (CD$_2$Cl$_2$): δ = 7.93 (br, [8H]), 7.66
(br, [4H]), 7.59 (br, [8H]), 2.78 (m, [4H]). $^{31}$P{$_1$H} NMR (CD$_2$Cl$_2$): δ = +45.4
(s).

3.11 [WOCl$_4$(C$_5$H$_5$N)]

Pyridine (0.050 g, 0.58 mmol) in toluene (2 mL) was added to a red suspension of WOCl$_4$
(0.200 g, 0.58 mmol). The red solution formed was stirred for 1 h and then taken to dryness in vacuo to obtain a yellow powder. Yield: 0.120 g, 49%. Required for C$_5$H$_5$Cl$_4$NOW (420.75):
C, 14.27; H, 2.20; N, 3.33. Found: C, 14.23; H, 2.15; N, 3.31%. IR spectrum (Nujol, cm$^{-1}$):
987m W=O, 338s W−Cl. $^1$H NMR (CD$_2$Cl$_2$): δ = 9.37 (dd, [2H], J$_{HH}$ = 6.6, 1.5 Hz), 8.06 (tt,
[H], J$_{HH}$ = 7.7, 1.5 Hz), 7.65 (td, [2H], J$_{HH}$ = 6.6, 1.2 Hz).

3.12 [WSCl$_4$(C$_5$H$_5$N)]

Pyridine (0.050 g, 0.58 mmol) in toluene (2 mL) was added to a red solution of WSCl$_4$ (0.200
0.58 mmol). The brown solution formed was stirred for 1 h, and then taken to dryness in vacuo to yield a brown/grey powder. Yield: 0.160 g, 87%. Required for C$_5$H$_5$Cl$_4$NSW (436.8):
C, 13.75; H, 1.15; N, 3.21. Found: C, 14.06, H: 1.20, N: 3.29%. IR spectrum (Nujol, cm$^{-1}$):
533s W=S, 334s,br W−Cl. $^1$H NMR (CD$_2$Cl$_2$): δ = 8.78 (br, [2H]), 8.56 (br, [H]), 8.11 (br,
[2H]).

3.13 [WOCl$_4$(2,2'-bipy)]

2,2'-bipy (0.068 g, 0.44 mmol) in dichloromethane (5 mL) was added slowly to an orange
suspension of WOCl$_4$ (150 mg, 0.44 mmol) in dichloromethane (5 mL). The green solution
formed was stirred for 1 h at room temperature and then concentrated to ~ 10mL in vacuo. The
green solid was isolated by filtration, washed with hexane (2 x 1 mL) and dried in vacuo. Yield:
0.067 g, 30%. Required for C$_{10}$H$_4$Cl$_2$N$_2$OW (499.85): C, 24.11; H, 1.62; N, 5.63. Found: C,
24.33; H, 1.73; N, 5.84%. IR spectrum (Nujol, cm$^{-1}$): 970s W=O, 329s,br W−Cl. $^1$H NMR
(CDCl₃): δ = 8.99 (d, [2H], J_HH = 8.1 Hz), 8.85 (d, [2H], J_HH = 4.4 Hz), 8.22 (t, [2H], J_HH = 7.8 Hz), 7.66 (t, [2H], J_HH = 4.0 Hz).

3.14 [WSCl₄(2,2'-bipy)]

2,2'-bipy (0.065 g, 0.42 mmol) in dichloromethane (5 mL) was added slowly to a red suspension of WSCl₄ (0.150 g, 0.42 mmol) in dichloromethane (5 mL). The purple/red solution was stirred for 1 h, concentrated to ~5 mL and the red-pink powder filtered off, washed with hexane (2 x 1 mL), and dried in vacuo, yielding a red/pink powder. Yield: 0.165 g, 76%. Required for C₁₀H₈Cl₄N₂S (513.9): C, 23.37; H, 1.57; N, 5.45. Found: C, 23.36; H, 1.59; N, 5.50%. IR spectrum (Nujol, cm⁻¹): 521s W=S, 316s W−Cl. ¹H NMR (CD₂Cl₂): δ = 8.97 (d, [2H], J_HH = 8.3 Hz), 8.89 (d, [2H], J_HH = 5.1 Hz), 8.27 (t, [2H], J_HH = 7.6 Hz), 7.73 (t, [2H], J_HH = 7.6 Hz).

3.15 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 (λ = 0.71073) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K (N₂ cryostream). Crystallographic parameters are in Table 1. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2014/7 [30] and were mostly straightforward, some minor disorder within one PMe₃ group is noted in the structure of [W₃O₃(µ-O)₃Cl₆(OPMe₃)₃]⋅2CH₂Cl₂, this was modelled satisfactorily using split C atom site occupancies. H atoms were added and refined with a riding model.

Conflicts

The authors have no conflicts to declare.

Acknowledgements

We thank EPSRC for support through EP/P025137/1 and for a studentship to DLS EP/N509747/1.

Appendix A. Supplementary data

Contain the supplementary crystallographic data for this paper. CCDC numbers are 1882209: [WOCl₄(OPPh₃)], 1882210: [WOCl₄(2dppmO₂)], 882211: [WSCl₄(2dppeO2)], 1882212: [W₃O₃(µ-O)₃Cl₆(OPMe₃)₃]⋅2CH₂Cl₂, 1883854: [WSCl₃(bipy)]. 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. Supplementary data associated with this article can be found in the online version, at http://........

References

[1] R. A. Walton, Progr. Inorg. Chem. 16 (1972) 1.

[2] H. Hess, H. Hartung, Z. Anorg. Allgem Chem. 344 (1966) 157.

[3] M. G. B. Drew, R. Mandyczewsky, J. Chem. Soc. (A) (1970) 2815.

[4] F. A. Cotton, P. A. Kibala, R. B. W. Sandor, Inorg. Chem. 28 (1989) 2485.

[5] Z. Dori in Comprehensive Coordination Chemistry I, G. Wilkinson, R. D. Gillard, J. A. McCleverty (Eds), Pergamon, Oxford 1987, vol. 3, 973.

[6] T. Okamura, N. Ueyama, in Comprehensive Coordination Chemistry II., J. A. McCleverty, T. J. Meyer (Eds), Elsevier Oxford 2004, vol 4, 529.

[7] G. W. A. Fowles, J. L. Frost, J. Chem. Soc. (A) (1967) 671.

[8] P. D. W. Boyd, M. G. Glenny, C. E. F. Rickard, A. J. Neilson, Polyhedron 30 (2011) 632.

[9] S. Bianchi, M. Bortoluzzi, V. Castelvetro, F. Marchetti, G. Pampaloni, C. Pinzio, S. Zacchini, Polyhedron 117 (2016) 769.

[10] M. Bortoluzzi, F. Marchetti, G. Pampaloni, S. Zacchini, Eur. J. Inorg. Chem. (2016) 3169.

[11] M. Bortoluzzi, F. Marchetti, G. Pampaloni, S. Zacchini, New J. Chem. 40 (2016) 8271.

[12] M. G. B. Drew, R. Mandyczewsky, Chem. Commun. (1970) 292.

[13] N. Agh-Atabay, F. M. Ashwamy, C. A. McAuliffe, W. E. Hill, Inorg. Chim. Acta 104 (1985) 73.

[14] M. G. B. Drew, E. M. Page, D. A. Rice, J. Chem. Soc., Dalton Trans. (1983) 61.

[15] S. Dolci, F. Marchetti, G. Pampaloni, S. Zacchini, Dalton Trans. 42 (2013) 5635.

[16] S. Dolci, F. Marchetti, G. Pampaloni, S. Zacchini, Dalton Trans. 39 (2010) 5367.

[17] W. Levason, G. Reid, W. Zhang, J. Fluorine Chem. 184 (2016) 50.
[18] J. W. Emsley, W. Levason, F. M. Monzittu, G. Reid, W. Zhang, G. De Luca, J. Fluorine Chem. 197, (2017) 74.
[19] D. Britnell, G. W. A. Fowles, D. A. Rice, J. Chem. Soc., Dalton Trans. (1975) 213.
[20] D. Britnell, M. G. B. Drew, G. W. A. Fowles, D. A. Rice, Inorg. Nucl. Chem. Letts. 9 (1973) 501.
[21] M. Chhowalla, Z. Liu, H. Zhang, (Eds - themed issue on metal dichalcogenides) Chem. Soc. Rev. 44 (2015) 2584.
[22] Y.-P. Chang, A. L. Hector, W. Levason, G. Reid, Dalton Trans. 46 (2017) 9824.
[23] V. C. Gibson, T. P. Kee, A. Shaw, Polyhedron 9 (1990) 2293.
[24] K. Behzadi, A. O. Baghlafl, A. Thompson, J. Less Common Met. 57 (1978) 103.
[25] P. Dabas, M. K. Rastogi, Asian J. Chem. 9 (1997) 445.
[26] L. Arnaudet, R. Bougon, P. Charpin, J. Isabey, M. Lance, M. Nierlich, J. Vigner, Inorg. Chem. 28 (1989) 257.
[27] M. F. Davis, W. Levason, R. Ratnani, G. Reid, T. Rose, M. Webster, Eur. J. Inorg. Chem. (2007).
[28] M. G. B. Drew, G. F. Griffin, D. A. Rice, Inorg. Chim. Acta 34 (1979) L192.
[29] W. Levason, R. Patel, G. Reid, J. Organomet. Chem. 688 (2003) 280.
[30] G. M. Sheldrick, Acta Crystallogr., Sect. C 71 (2015) 3.
Table 1  Crystallographic data

| Compound                  | \([\text{WOCl}_4\text{(OPPh}_3\text{)}]^-\) | \([\text{([WOCl}_4\text{](dpmpO}_2\text{)])}\) | \([\text{([WSCl}_4\text{](dppeO}_2\text{)])}\) |
|---------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Formula                   | \(\text{Cs}_6\text{H}_{15}\text{Cl}_8\text{O}_4\text{P}_2\text{W}_2\) | \(\text{Cs}_6\text{H}_{22}\text{Cl}_8\text{O}_4\text{P}_2\text{W}_2\) | \(\text{Cs}_3\text{H}_2\text{Cl}_2\text{OPSW}\) |
| \(M\)                     | 1239.84                                       | 1099.66                                       | 572.91                                       |
| Crystal system            | triclinic                                      | triclinic                                      | triclinic                                      |
| Space group (no)          | \(P\ -1\) (2)                                 | \(P\ -1\) (2)                                 | \(P\ -1\) (2)                                 |
| \(a\) /Å                  | 9.36630(10)                                    | 10.3428(2)                                    | 9.1134(5)                                    |
| \(b\) /Å                  | 15.4398(2)                                     | 11.0799(2)                                    | 9.3623(3)                                    |
| \(c\) /Å                  | 16.0484(2)                                     | 15.3764(2)                                    | 11.7376(4)                                   |
| \(α\) /°                  | 109.4180(10)                                   | 81.7770(10)                                   | 97.087(3)                                    |
| \(β\) /°                  | 97.1570(10)                                    | 70.3800(10)                                   | 106.333(4)                                   |
| \(γ\) /°                  | 105.4190(10)                                   | 80.1300(10)                                   | 112.441(4)                                   |
| \(U\) /Å\(^3\)           | 2051.31(5)                                     | 1628.27(5)                                    | 857.70(7)                                    |
| \(Z\)                     | 2                                             | 2                                             | 2                                             |
| \(μ\) (Mo-K\(_α\)) /mm\(^{-1}\) | 6.241                                         | 7.846                                         | 7.565                                         |
| \(f\) (000)               | 1184                                          | 1036                                          | 542                                          |
| Total number refins       | 53470                                         | 44544                                         | 23334                                         |
| \(R_m\)                   | 0.024                                         | 0.028                                         | 0.055                                         |
| Unique refins             | 8081                                          | 9901                                          | 5298                                          |
| No. of params, restraints | 469, 0                                        | 370, 0                                        | 190, 0                                        |
| GOF                       | 1.035                                         | 1.081                                         | 1.083                                         |
| \(R_m, wR_2\) (\(I > 2σ(I)\))\(^b\) | 0.014, 0.033                                  | 0.017, 0.036                                  | 0.026, 0.063                                  |
| \(R_m, wR_2\) (all data)\(^b\) | 0.016, 0.033                                  | 0.022, 0.036                                  | 0.031, 0.064                                  |

\(^a\) common data: wavelength (Mo-K\(_α\)) = 0.71073 Å; \(θ\) (max) = 27.5°; \(^b\) \(R_1 = \Sigma|Fo| - |Fc|/Σ|Fo|; \)
\(wR_2 = (Σw(Fo^2-Fc^2)/ΣwFo^2)^{1/2}\).
| Compound | [W₃O₆Cl₆(OPMe₃)₃].2CH₂Cl₂ | [WSCl₃(2,2'-bipy)] |
|----------|-------------------------|----------------------|
| Formula  | C₁₁H³₁Cl₁₀P₃W₃        | C₁₀H₈Cl₃N₂SW        |
| M        | 1306.32                | 478.44               |
| Crystal system | monoclinic             | triclinic            |
| Space group (no.) | P2₁/c (14)             | P1 (1)               |
| a/Å      | 19.1399(5)              | 6.6843(2)            |
| b/Å      | 11.2360(2)              | 8.1998(2)            |
| c/Å      | 18.2845(5)              | 12.3744(4)           |
| α/°      | 90                     | 74.743(2)            |
| β/°      | 116.616(3)              | 89.939(2)            |
| γ/°      | 90                     | 89.988(2)            |
| U/Å³     | 3515.49(17)             | 654.34(3)            |
| Z        | 4                      | 2                    |
| μ(Mo-Kα)/mm⁻¹ | 10.724                | 9.575                |
| F(000)   | 2424                   | 446                  |
| Total number refins | 37791                  | 19122                |
| R int   | 0.030                  | 0.028                |
| Unique refins | 6842                  | 5139                 |
| No. of params, restraints | 336, 0                | 278, 3               |
| GOF      | 1.028                  | 1.131                |
| R1, wR2 [I > 2σ(I)]  | 0.016, 0.030          | 0.039, 0.070         |
| R1, wR2 (all data)   | 0.020, 0.030          | 0.030, 0.071         |

Commented [RG1]: P1 is VERY rare as space group – are you really sure??