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Coordination complexes of the tungsten(VI) oxide fluorides WOF_4 and WO_2F_2 with neutral oxygen- and nitrogen-donor ligands

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ABSTRACT

$[WOF_4(MeCN)]$, prepared from a 1:1 ratio of WF_6 and $O(SiMe_3)_2$ in MeCN, is a convenient synthon for the preparation of complexes of WOF_4 and WO_2F_2 with neutral N- or O-donor ligands. It reacts with monodentate ligands L (L = $OPPh_3$, $OPMe_3$, dmso, py) in a 1:1 ratio to form $[WOF_4L]$, whilst reaction of $[WOF_4(MeCN)]$, $O(SiMe_3)_2$ and L′ (L′ = $OPPh_3$, py, pyNO, dmso) in 1:1:2 ratio affords $[WO_2F_2L'_2]$. The synthesis of $[WO_2F_2(L\text{-}L)]$ (L-L = $Ph_2P(O)CH_2P(O)Ph_2$ or 1,10-phenanthroline) are also described. Similar complexes with arsines, thio- or seleno-ethers are not formed by these routes. The complexes have been characterised by microanalysis, IR, ^1H and $^{19}F\{^1H\}$ NMR spectroscopy, and X-ray crystal structures are reported for $[WOF_4(OPPh_3)]$, $[WO_2F_2(OPPh_3)_2]$, $[WO_2F_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$ and $[WO_2F_2(pyNO)_2]$.

1. Introduction

The coordination chemistry of transition metal oxide chlorides and oxide bromides, has been examined in considerable detail [1], but that of the corresponding oxide fluorides has been little explored until recently and, whilst a range of related fluoroanions are known, complexes with neutral ligands are relatively rare [2–4]. In recent work we have prepared and characterised, both spectroscopically and by X-ray crystallography, complexes of VOF_3 [5], VO_2F [6] and $NbOF_3$ [7] with a range of neutral N- and O-donor ligands, although none formed complexes with softer P-donor ligands, and only VOF_3 gave (unstable) thioether complexes. Here we report similar studies of the two oxide fluorides of tungsten(VI), WOF_4 and WO_2F_2. Solid tungsten oxide tetrafluoride has a tetrameric structure with six-coordinate tungsten linked by fluoride bridges [8,9] but exists as a square pyramidal monomer in the gas phase [10]. For tungsten dioxide difluoride electron diffraction shows the expected distorted tetrahedral geometry for the gas phase molecule [11]. The structure in the solid state is unknown, spectroscopic characterisation is limited, and the purity of most samples is either doubtful or not stated [2,3].

Apart from early *in situ* solution studies using ^{19}F NMR spectroscopy [4,12], the known complexes of WOF_4 are with heterocyclic N-donor ligands, $[WOF_4(py)_n]$ ($n = 1$ or 2) [13], $[WOF_4(2\text{-F-py})]$ [14], $[WOF_4(R\text{-napy})]$ (R-napy = 1,8-naphthyridine or 2,7-dimethyl-1,8-naphthyridine) [15] and $[WOF_4(2,2'\text{-bipy})]$ [16]. Less is known about the complexes of WO_2F_2, with $[WO_2F_2(OPR_3)_2]$ formed by adding OPR_3 (R = Me or Ph) to $WO_3{\cdot}nH_2O$ in aqueous HF [17], or from $[WO_2Cl_2(OPR_3)_2]$ and Me_3SnF [18]. $[WO_2F_2(diimine)]$ (diimine = 2,2′-bipy, 1,10-phen) were obtained by prolonged refluxing of the corresponding chlorides with a suspension of Me_3SnF in CH_2Cl_2 [18]. The structure of $[WO_2F_2(2,2'\text{-bipy})]$, the only structurally characterised adduct of WO_2F_2, was determined on a crystal formed by decomposition of $[WOF_4(2,2'\text{-bipy})]$ [16]. WO_2F_2 is inert and insoluble in common solvents [2], and even the corresponding WO_2X_2 (X = Cl or Br) are strongly polymerised and very poor synthons [18]. Although a few complexes of WOF_4 have been prepared directly from the oxide fluoride [14,16], we have developed a general route to complexes of both oxide fluorides based upon F/O exchange from WF_6 using hexamethyldisiloxane, $O(SiMe_3)_2$ (HMDSO).

2. Results and discussion

2.1. Synthons

WOF_4 is not commercially available and although it is readily prepared by fluorination of WO_3 either in a flow system or an autoclave [9,10], the synthesis requires a metal vacuum line and elemental fluorine. As an alternative entry into the chemistry, we explored the reaction of commercially available WF_6 with hexamethyldisiloxane and various donor ligands in either anhydrous CH_2Cl_2 or MeCN. Although the complex of WOF_4 with, for example, $OPPh_3$, is formed in this way, obtaining pure single products and in high yield is problematic, not least due to the

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difficulties of accurately measuring small amounts of the volatile and highly reactive WF_6 (b.p. 291 K). In other systems solid (molecular) nitrile or ether (especially thf) complexes have been found to be convenient synthons, since the neutral donor is often easily displaced [4,5,19], and thus similar species were investigated for tungsten complexes.

A convenient synthon for WOF_4 adducts is $[WOF_4(MeCN)]$, which is readily made from a 1:1 molar ratio of WF_6 and HMDSO in anhydrous MeCN. The product is a colourless, very moisture sensitive powder, obtained in near quantitative yield (the reaction can be scaled up to form ~2 g at a time). The $[WOF_4(MeCN)]$ can be stored for weeks in a glove box, and is readily soluble in anhydrous MeCN or CH_2Cl_2. Hydrolysis with traces of water generates $[W_2O_2F_9]^-$, easily identified by its characteristic ^{19}F NMR spectrum {in CD_2Cl_2,$\delta(^{19}F) = +62.0$ (d, [8F]), $^2J_{FF} = 60$ Hz, −145.5 (nonet, [F])} [15]. Evaporation of a solution of $[WOF_4(MeCN)]$ in anhydrous thf, results in a colourless wax, which from its IR {$\nu(W{=}O) = 1018$ cm^{-1}}, ^1H and ^{19}F NMR spectra {$^{19}F\{^1H\}$ NMR: $\delta = +63.3$ (s, $^1J_{WF} = 64$ Hz)} is $[WOF_4(thf)]$. The waxy nature makes this complex difficult to manipulate and it darkens and decomposes in a few days. It is thus not a very convenient synthon.

WO_2F_2 is insoluble in organic solvents and unreactive towards neutral ligands [2] and reaction of WF_6 with two molar equivalents of HMDSO in MeCN gave an insoluble white powder which contained only very small amounts of C and N, and which showed only traces of MeCN in the IR spectrum. It had very broad, ill-defined absorptions <1000 cm^{-1} and is probably mostly "WO_2F_2". However, an entry into complexes of WO_2F_2 in the present study is possible via the $[WOF_4(L)]$ complex, treated with more ligand (L) and HMDSO, or from a "one pot" reaction of $[WOF_4(MeCN)]$ and appropriate amounts of L and HMDSO (Scheme 1).

2.2. WOF_4 complexes

Monitoring the reaction of a 1:1 molar ratio of $[WOF_4(MeCN)]$: $OPPh_3$ in anhydrous CD_2Cl_2 solution by ^{19}F NMR spectroscopy, shows the substitution of MeCN by $OPPh_3$ is rapid and clean, yielding $[WOF_4(OPPh_3)]$. Using a $[WOF_4(MeCN)]$: $OPPh_3$ ratio of $1{:}\geq 3$ also gave $[WOF_4(OPPh_3)]$, but after several hours the solution had developed further resonances due to $[W_2O_2F_9]^-$ [15], $[HF_2]^-$, and some unidentified products, and a white precipitate formed. However, even after one week no significant amount of $[WO_2F_2(OPPh_3)_2]$ was present, contrary to some early reports [12], although some of the latter was formed by hydrolysis of the solution, for example, by adding "wet" CH_2Cl_2.

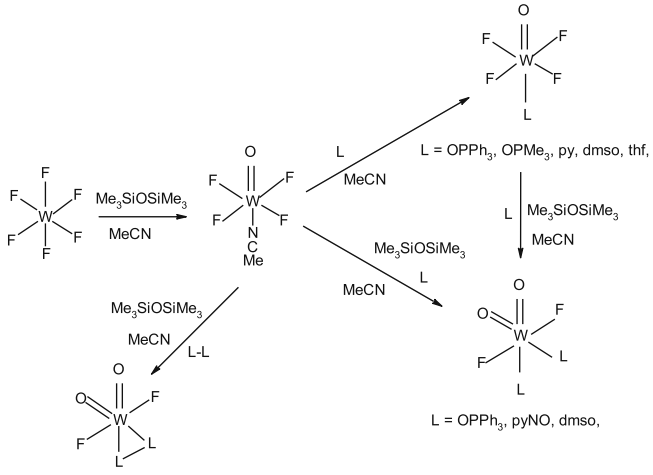
On a preparative scale, white $[WOF_4(OPPh_3)]$ was prepared in high yield from $[WOF_4(MeCN)]$ and a stoichiometric amount of $OPPh_3$ in either anhydrous MeCN or CH_2Cl_2 solution. The product is a moisture sensitive white powder, which showed a singlet ^{19}F NMR resonance (CD_2Cl_2) at $\delta = +67.4$, with ^{183}W satellites, $^1J_{WF} = 69$ Hz. The corresponding $^{31}P\{^1H\}$ NMR resonance is $\delta = +47.3$ (s), a high frequency coordination shift (Δ) of +19.3. The (Nujol mull) IR spectrum shows $\nu(PO) = 1087$ cm^{-1}, shifted from 1196 cm^{-1} in the "free" phosphine oxide, $\nu(WO) = 993$(vs), and $\nu(WF) = 628$(m), 597 (m) cm^{-1}. Theory for the C_{4v} molecule predicts one W=O (a_1) and two W—F ($a_1 + e$) IR active stretches.

Colourless, moisture sensitive crystals of $[WOF_4(OPPh_3)]$ were obtained by evaporation from a solution in $MeCN/CH_2Cl_2$, and the structure (Fig. 1) shows a distorted octahedral arrangement with the $OPPh_3$ *trans* to W=O and with the tungsten lying slightly out of the WF_4 plane towards the oxido-ligand. The geometry of the WOF_4 unit is very similar to those in $[WOF_4(R\text{-}py)]$ (Rpy=py or 2-F-py) [13,14].

The new complexes, $[WOF_4(OPMe_3)]$ and $[WOF_4(OSMe_2)]$ were made similarly, and show similar spectroscopic signatures (Table 1), but several attempts to isolate a pure sample of $[WOF_4(pyNO)]$ were unsuccessful. The initially isolated product had $\delta(^{19}F) = +58.5$ consistent with the target complex, but the cream solid initially isolated turned into a brown sticky material overnight, and the NMR spectroscopic data of this material suggested $[pyNOH]^+$ and $[W_2O_2F_9]^-$ were present as the major components, hence the study was not pursued.

The complex $[WOF_4(py)]$ was originally made from WOF_4 and neat pyridine, which produced the seven-coordinate $[WOF_4(py)_2]$, followed by vacuum sublimation, when the six-coordinate $[WOF_4(py)]$ formed [13]. The reaction of $[WOF_4(MeCN)]$ with 1 mol. equivalent of pyridine in MeCN solution, gave $[WOF_4(py)]$ directly, which was spectroscopically identical to the literature sample. Unexpectedly, addition of an MeCN solution of 1,10-phenanthroline to an MeCN solution of $[WOF_4(MeCN)]$ in a 1:1 mol. ratio gave an immediate white precipitate which proved to be $[WO_2F_2(phen)]$ (see below), and there was no evidence under these conditions for the expected $[WOF_4(phen)]$.

The $[WOF_4L]$ complexes described above are generally moisture sensitive white powders, which hydrolyse readily in solution. The spectroscopic data show characteristic features (Table 1) in the IR spectra at ~970 – 1020 cm^{-1} (W=O), and ~570–660 cm^{-1} (WF), whilst the $^{19}F\{^1H\}$ NMR resonances are singlets in the narrow range $\delta = +55$ to +70 with $^1J(^{183}W{-}^{19}F)$ satellites of 60–70 Hz.



Scheme 1. Synthesis of the tungsten oxide fluoride complexes.

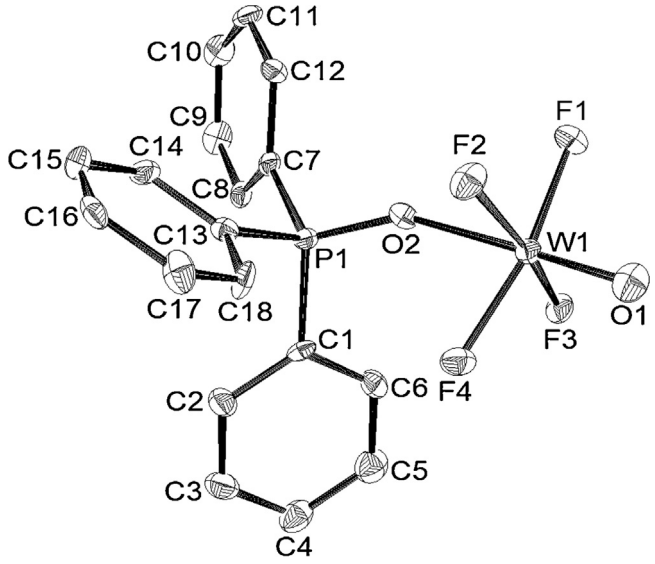


Fig. 1. Crystal structure of $[WOF_4(OPPh_3)]$ showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): W1 – O1 = 1.682(5), W1 – F1 = 1.857(3), W1 – F2 = 1.863(3), W1 – F4 = 1.870(3), W1 – F3 = 1.871(3), W1 – O2 = 2.141(4), P1 – O2 = 1.511(4), O1 – W1 – F1 = 98.0(2), O1 – W1 – F2 = 96.90(18), F1 – W1 – F2 = 89.62(17), O1 – W1 – F4 = 96.0(2), F2 – W1 – F4 = 90.95(16), O1 – W1 – F3 = 96.35(18), F1 – W1 – F3 = 88.20 (16), F1 – W1 – O2 = 83.18(16), F2 – W1 – O2 = 82.74(15), F4 – W1 – O2 = 82.81(16), F3 – W1 – O2 = 84.02(15), F4 – W1 – F3 = 88.00(16), P1 – O2 – W1 = 147.3(3).

Table 1
Selected spectroscopic data.

Complex	$\delta(^{19}F\{^1H\})$ NMR[a] ($^1J_{WF}$/Hz)	ν (W=O) cm^{-1}[b]	ν (W—F) cm^{-1}[b]	Data from this work unless indicated
$[WOF_4(MeCN)]$	+67.4 (69)	1021 (vs)	664(m), 606(s)	
$[WOF_4(OPMe_3)]$	+58.3 (66)	979 (vs)	610(m), 582(m)	
$[WOF_4(OPPh_3)]$	+60.5 (69)	993 (vs)	597 (s,br)	
$[WOF_4(OSMe_2)]$	+59.5(70)	1018(vs)	596(m), 572(s)	
$[WOF_4(py)]$	+62.9(65)	996(vs)	610(s), 580(s)	
$[WOF_4(bipy)]$	Insol.	968	638,580,527,494	Ref. [16]
$[WOF_4(thf)]$	+63.0 (64)	1018(vs)	603(s,br)	
$[WO_2F_2(OPPh_3)_2]$	−63.1 (91)	962, 919	588	
$[WO_2F_2(OPMe_3)_2]$	−65.9 (110)	956,933,896[c]	555	Ref. [18]
$[WO_2F_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$	−67.1 (108)	969, 917	571	
$[WO_2F_2(OSMe_2)_2]$	−64.6 (103)	933, 900	556	
$[WO_2F_2(pyNO)_2]$	−67.9 (~100)	959,913	568	
$[WO_2F_2(phen)]$	−69.6 (96)[d]	962, 933	578	
$[WO_2F_2(bipy)]$	−69.6 (95)	958, 918	575	Ref. [16,18]
$[WO_2F_2(py)_2]$	−69.0 (102)	961, 932	575	

[a] 293 K in CD_2Cl_2 relative to $CFCl_3$ unless indicated otherwise.
[b] Nujol mull.
[c] Assignment unclear due to ρ(PMe_3) in the same region as ν(W=O).
[d] CD_3CN.

Attempts to prepare $[WOF_4(OAsPh_3)]$ from $[WOF_4(MeCN)]$ and $OAsPh_3$ in either MeCN or CH_2Cl_2 were unsuccessful. In the former solvent, a white powder formed, which was insoluble in CD_3CN or CD_2Cl_2 and the IR spectrum showed no $OAsPh_3$, with very broad absorptions $<1000\,cm^{-1}$, assigned to polymeric WO_2F_2, indicative of O/F exchange. The supernatant solution gave a cream solid on evaporation, which was identified from its characteristic [20] ^{19}F NMR chemical shift of $\delta = -89$ as Ph_3AsF_2. The same reaction in CH_2Cl_2 solution gave the insoluble white solid, but in this case $[W_2O_2F_9]^-$ was the major soluble tungsten species formed [15]. Fluorination of $OAsPh_3$ to Ph_3AsF_2 has been observed on reaction with TeF_4 [20], AsF_3 [21], although simple adduct formation occurs with SnF_4, GeF_4, TiF_4 and ZrF_4 [22–25]. Adduct formation and fluorination both occur with NbF_5 and SbF_3 [7,21], whilst SiF_4 produced $[Ph_3AsOH]_2[SiF_6]$ [26].

2.3. WO_2F_2 complexes

Since we were unable to isolate $[WO_2F_2(MeCN)_2]$ as a possible synthon for complexes of WO_2F_2, further O/F exchange from $[WOF_4(MeCN)]$ in the presence of added ligand was explored. The reaction of $[WOF_4(OPPh_3)]$ with a further molar equivalent of $OPPh_3$ and HMDSO in MeCN solution gave a high yield of white $[WO_2F_2(OPPh_3)_2]$. The complex can also be made directly from $[WOF_4(MeCN)]$ and two molar equivalents of $OPPh_3$ in MeCN solution, followed after ~1 h by addition of one equivalent of HMDSO. If the HMDSO is added before or at the same time as the $OPPh_3$, mixtures result, including much insoluble precipitate that is assumed to be WO_2F_2. This confirms that coordination of the neutral ligand to tungsten is necessary before the second oxido-group is introduced, otherwise the "molecular WO_2F_2

intermediate" polymerises and precipitates, and is no longer available to coordinate to neutral ligands. The $[WO_2F_2(OPPh_3)_2]$ has previously been prepared from $[WO_2Cl_2(OPPh_3)_2]$ and Me_3SnF [18]. Similar syntheses using $[WOF_4(MeCN)]$, two or more equivalents of $OSMe_2$, py or pyNO in MeCN, followed by addition of HMDSO, gave the corresponding $[WO_2F_2L_2]$ (L = $OSMe_2$, pyNO, py) as white powders. The $[WO_2F_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$ was made from $[WOF_4(MeCN)]$, $Ph_2P(O)CH_2P(O)Ph_2$ and HMDSO in a 1:1:1 ratio in MeCN. The phosphine oxide complexes and $[WO_2F_2(OSMe_2)_2]$ are readily soluble in CH_2Cl_2 or MeCN, but $[WO_2F_2(pyNO)_2]$ and $[WO_2F_2(py)_2]$ are very poorly soluble in these solvents. All five complexes appear air stable in the solid state, although slowly hydrolysed on exposure of the solutions in MeCN to air.

As noted above, reaction of $[WOF_4(MeCN)]$ with 1,10-phenanthroline in a 1:1 ratio in MeCN gave a modest yield of $[WO_2F_2(phen)]$. Bougon et al. [16] reported the isolation of $[WOF_4(2,2'\text{-bipy})]$ (from WOF_4 and 2,2′-bipyridyl in MeCN, or CH_2Cl_2), and showed that in solution it disproportionated into $[WO_2F_2(bipy)]$ and $[WF_6(bipy)]$. A similar reaction, but with more rapid disproportionation, would account for the formation of $[WO_2F_2(phen)]$ in modest (37%) yield in the present case. Support for this conclusion comes from the fact that if the $[WOF_4(MeCN)]$ + 1,10-phenanthroline (1:1) mixture in MeCN is treated with a further equivalent of HMDSO the yield of $[WO_2F_2(phen)]$ increases to ~93%.

The WO_2F_2 complexes have characteristic spectroscopic fingerprints (Table 1) that are quite different from those of the WOF_4 analogues. In the IR spectra the $[WO_2F_2L_2]$ (L = py, pyNO, $OSMe_2$, $OPPh_3$, $L_2 = Ph_2P(O)CH_2P(O)Ph_2$, phen) with C_{2v} symmetry exhibit two strong $\nu(W=O)$ in the range $\sim 900-960\ cm^{-1}$ for the *cis* dioxo-group (theory $a_1 + b_1$) and a single $\nu(WF_2)$ $\sim 550-590\ cm^{-1}$ for the *trans* F–W–F unit (theory b_2). The $^{19}F\{^1H\}$ NMR resonances are singlets in the narrow range $\delta = -63$ to -70 which is ~120 ppm to low frequency of the WOF_4 analogues. The $^1J(^{183}W-^{19}F)$ satellites of 90–110 Hz in the WO_2F_2 complexes are significantly larger than those of WOF_4 complexes.

X-ray crystal structures were obtained for $[WO_2F_2(pyNO)_2]$, $[WO_2F_2(OPPh_3)_2]$ and $[WO_2F_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$.

The structure of $[WO_2F_2(pyNO)_2]$ contains distorted octahedral coordination at the tungsten (Fig. 2), with a wide O(2) – W(1) – O(1) = 102.66(14)°, with other angles involving the W=O groups greater than 90° and the remaining angles mostly <90°. The F–W–F unit also deviates significantly from linearity, at 156.62(11)°, with the unit bent away from the WO_2 group towards the neutral ligands. The greater space around the central metal occupied by the dioxo-groups is found in other early transition metal oxide halides [4–6,16,18]. The pattern of bond lengths and angles found for $[WO_2F_2(pyNO)_2]$ closely resembles those in the only literature structure, that of $[WO_2F_2(bipy)]$ [16].

The structural features found in $[WO_2F_2(pyNO)_2]$ are replicated in $[WO_2F_2(OPPh_3)_2]$ (Fig. 3). X-ray crystal structures have also been reported for $[WO_2X_2(OPPh_3)_2]$ (X = Cl or Br) [18,27], $[WO_2Cl_2(OPMe_3)_2]$ [18] and $[WO_2Cl_2(OPMePh_2)_2]$ [28]. Comparison of the geometries of these five phosphine oxide complexes shows very small changes as the halogen is changed. The W=O are essentially invariant (1.70 – 1.73 Å), as are the O–W–O angles (101–103°), whilst the X–W–X angle increases from 157.5° in $[WO_2F_2(OPPh_3)_2]$ to 163° in $[WO_2Cl_2(OPPh_3)_2]$ and 167° in $[WO_2Br_2(OPPh_3)_2]$. The W–O(P) distances in the phosphine oxides also fall in a rather narrow range (2.13–2.22 Å).

The structure of $[WO_2F_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$ (Fig. 4) is also a distorted octahedral monomer, with a chelating diphosphine dioxide ligand. The pattern of bond lengths and angles is similar to those discussed above for the OPR_3 complexes and are also similar to those reported for $[WO_2Cl_2\{Ph_2P(O)CH_2P(O)\ Ph_2\}]$ [28]. In the

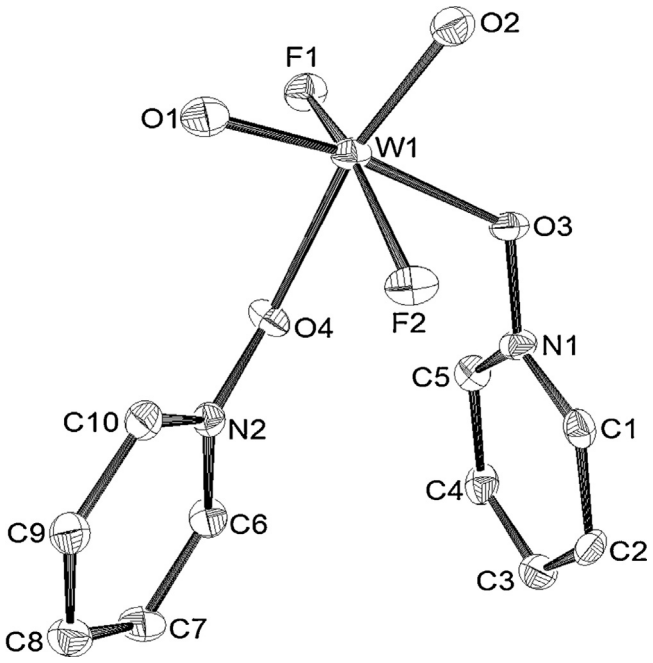


Fig. 2. Crystal structure of $[WO_2F_2(pyNO)_2]$ showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): W(1) – O(2) = 1.709(3) W(1) – O(1) = 1.722(3), W(1) – F(1) = 1.896(2), W(1) – F(2) = 1.910(3), W(1) – O(4) = 2.179(3), W(1) – O(3) = 2.190(3), O(3) – N(1) = 1.351(4), O(4) – N(2) = 1.348(4), O(2) – W(1) – O(1) = 102.66(14), O(2) – W(1) – F(1) = 97.43(13), O(1) – W(1) – F(1) = 97.60(13), O(2) – W(1) – F(2) = 98.51(13), O(1) – W(1) – F(2) = 95.46(13), F(1) – W(1) – F(2) = 156.62(11), O(1) – W(1) – O(4) = 92.20(12), F(1) – W(1) – O(4) = 78.27(11), F(2) – W(1) – O(4) = 81.95(11), O(2) – W(1) – O(3) = 86.49(13), F(1) – W(1) – O(3) = 82.43(11), F(2) – W(1) – O(3) = 81.60(11), O(4) – W(1) – O(3) = 78.73(11), N(1) – O(3) – W(1) = 122.8(2), N(2) – O(4) – W(1) = 128.2(2).

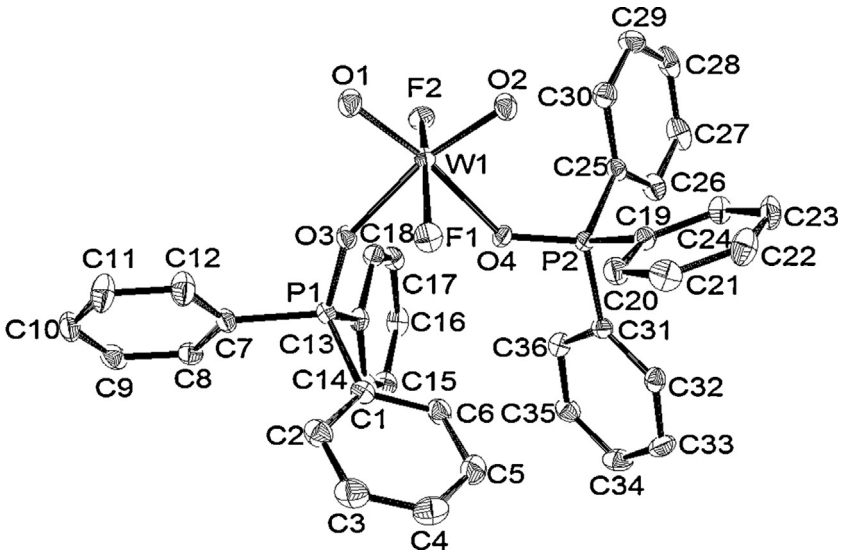


Fig. 3. Crystal sructure of $[WO_2F_2(OPPh_3)_2]$ showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): W(1) – O(1) = 1.714(2), W(1) – O(2) = 1.723(2), W(1) – F(1) = 1.906(2), W(1) – F(2) = 1.9209(19), W(1) – O(3) = 2.144(2), W(1) – O(4) = 2.223(2), P(1) – O(3) = 1.508(2), P(2) – O(4) = 1.510(2), O(1) – W(1) – O(2) = 102.07(11), O(1) – W(1) – F(1) = 98.32(11), O(2) – W(1) – F(1) = 96.86(10), O(1) – W(1) – F(2) = 96.39(10), O(2) – W(1) – F(2) = 96.65(10), F(1) – W(1) – F(2) = 157.47(9), O(1) – W(1) – O(3) = 91.25(10), F(1) – W(1) – O(3) = 81.29(9), F(2) – W(1) – O(3) = 81.41(8), O(2) – W(1) – O(4) = 88.15(10), F(1) – W(1) – O(4) = 83.91(9), F(2) – W(1) – O(4) = 88.58(8), O(3) – W(1) – O(4) = 78.54(8), P(1) – O(3) – W(1) = 152.58(15), P(2) – O(4) – W(1) = 136.97(13).

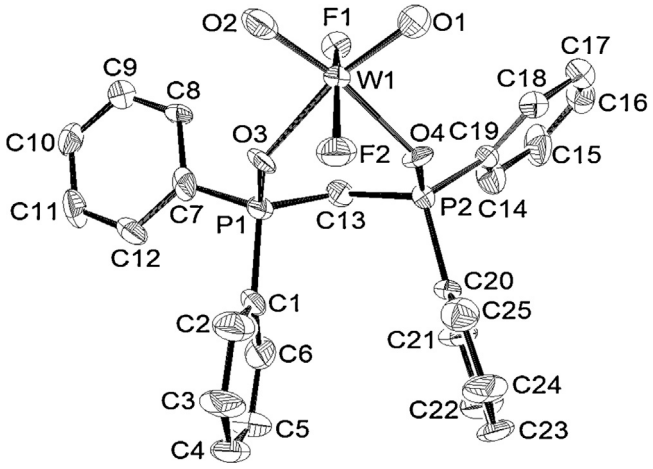


Fig. 4. Crystal structure of $[WO_2F_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$ showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): W(1) – O(2) = 1.687(9), W(1) – O(1) = 1.720(9), W(1) – F(2) = 1.899(8), W(1) – F(1) = 1.919(8), W(1) – O(3) = 2.187(8), W(1) – O(4) = 2.200(8), P(1) – O(3) = 1.500(9), P(2) – O(4) = 1.509(9), O(2) – W(1) – O(1) = 102.7(4), O(2) – W(1) – F(2) = 98.0(4), O(1) – W(1) – F(2) = 98.4(4), O(2) – W(1) – F(1) = 96.3(4), O(1) – W(1) – F(1) = 97.4(4), F(2) – W(1) – F(1) = 155.8(3), O(2) – W(1) – O(3) = 90.0(4), F(2) – W(1) – O(3) = 80.4(3), F(1) – W(1) – O(3) = 80.2(3), O(1) – W(1) – O(4) = 88.3(4), F(2) – W(1) – O(4) = 82.0(3), F(1) – W(1) – O(4) = 80.3(3), O(3) – W(1) – O(4) = 79.0(3).

latter W=O = 1.69(1)–1.73(1) Å and <O–W–O = 101–102° (there are two crystallographically independent molecules in the unit cell).

2.4. Reactions with neutral sulfur, selenium and arsenic ligands

Excess SMe_2 did not react with a solution of $[WOF_4(MeCN)]$ in MeCN or CH_2Cl_2, removal of the solvent *in vacuo* after 1 h recovered $[WOF_4(MeCN)]$. After several hours the reaction mixture in CH_2Cl_2, turned blue and a blue precipitate formed. Similar *in situ* monitoring of solutions of $[WOF_4(MeCN)]$ and $MeSCH_2CH_2SMe$ or $MeSeCH_2CH_2SeMe$ in CD_2Cl_2 by ^1H and $^{19}F\{^1H\}$ NMR spectroscopy showed no evidence for displacement of the nitrile, although the diselenoether solution decomposed, turning dark green overnight. Since the WO_2F_2 adducts of O— or N—donor ligands were more robust (see above), freshly prepared solutions of $[WOF_4(MeCN)]$ and $MeSCH_2CH_2SMe$ or $MeSeCH_2CH_2SeMe$ were treated with HMDSO in MeCN, resulting in immediate white precipitates, which appeared to be "WO_2F_2" from their IR spectra, whilst the filtrates showed only free dichalcogenoether. Hence neither WOF_4 nor WO_2F_2 seem able to form complexes with neutral sulfur or selenium ligands under these conditions. Extremely moisture sensitive yellow crystals of $[WO_2Cl_2(RSCH_2CH_2SR)]$ (R = Me or ^{i}Pr) have been prepared previously from WCl_6 or $WOCl_4$, HMDSO and the dithioether in $MeCN/CH_2Cl_2$ solution, and found by X-ray crystallography to have six-coordinate tungsten with the dithioether *trans* to the *cis* WO_2 unit [29,30]. Similar complexes with WO_2Br_2 are known [29],

The addition of $AsMe_3$ to a solution of $[WOF_4(MeCN)]$ in MeCN or CH_2Cl_2 monitored by ^1H and ^{19}F NMR spectroscopy showed no reaction occurred, with the soft arsine unable to displace the nitrile. On standing for a few hours a pale blue precipitate formed in the CH_2Cl_2 solution and the solution showed the presence of $[W_2O_2F_9]^-$ and unusually also $[WOF_5]^-$ {δ(F) = +47.6 (d, [4F]), $^2J_{FF}$ = 53 Hz, −83.0 (m, [F])}[15]. The reaction of $[WOF_4(MeCN)]$ with tertiary phosphines under similar conditions is dependent upon the R-group and the solvent (*cf.* the NbF_5-PR_3 systems [31]) and will be the subject of further study.

Complexes of type $[WF_6(EEt_2)_2]$ (E = S or Se) have been reported [31], although characterisation is very limited, but two seven coordinate $[WF_6(PR_3)]$, (R_3 = Me_3 or Me_2Ph) have been synthesised and their structures determined [32].

3. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1}. ^1H, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded using a Bruker AV-II 400 spectrometer and are referenced to the protio resonance of the solvent, external $CFCl_3$ and 85% H_3PO_4 respectively. Microanalyses were undertaken by London Metropolitan University. Solvents were dried prior to use: THF and Et_2O by distillation from sodium benzophenone ketyl, MeCN and CH_2Cl_2 from CaH_2. $OPMe_3$ and pyNO were freshly sublimed *in vacuo*, $OPPh_3$, $OAsPh_3$ and 1,10-phen were heated *in vacuo*, dmso, pyridine, SMe_2, $MeSCH_2CH_2SMe$ and $MeSeCH_2CH_2SeMe$ were dried over molecular sieves. WF_6 (Fluorochem), HMDSO (Aldrich) and $AsMe_3$ (Strem) were used as received. $Ph_2P(O)CH_2P(O)Ph_2$ was made by the literature method [33]. All preparations were undertaken using standard Schlenk techniques under a N_2 atmosphere, and samples were manipulated in a dry nitrogen filled glove box.

3.1. [WOF_4(MeCN)]

A mixture of MeCN (20 mL) and HMDSO (0.16 g, 1.0 mmol) were frozen in liquid nitrogen and then WF_6 (0.3 g, 1.0 mmol) condensed in under vacuum. The mixture was allowed to warm slowly to room temperature and stirred for 12 h. The solvent was removed *in vacuo* to leave a white powder. Yield: 0.3 g, 94%. The reaction can be scaled up readily to produce ~2 g batches. Anal: Required for $C_2H_3F_4NOW$ (316.9): C, 7.6; H, 0.9; N, 4.4. Found: C, 7.5; H, 0.9; N, 4.2%. ^1H NMR (CD_2Cl_2, 293 K): δ = 2.37 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = +67.4 (s, $^1J_{WF}$ = 69 Hz); (CD_3CN, 293 K): δ = +65.9 (s, $^1J_{WF}$ = 69 Hz). IR (Nujol)/cm^{-1}): 2319 (m, C≡N), 1021 (vs, W=O), 644 (m, WF).

3.2. [$WOF_4(OPMe_3)$]

Freshly sublimed $OPMe_3$ (0.09 g, 1.0 mmol) was added to an MeCN solution (10 mL) of $[WOF_4(MeCN)]$ (0.32 g, 1.0 mmol) and stirred for 5 h. The colourless solution was concentrated to ~2 mL resulting in precipitation of a white powder which was separated by decanting off the solvent, and drying *in vacuo*. Yield: 0.30 g, 81%. Anal: Required for $C_3H_9F_4O_2PW$ (367.92): C, 9.8; H, 2.5. Found: C, 10.0; H, 2.7%. ^1H NMR (CD_2Cl_2, 293 K): δ = 1.75 (d, $^2J_{PH}$ = 17 Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = +58.3 (s, $^1J_{WF}$ = 66 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = 66.9 (s). IR (Nujol)/cm^{-1}): 1095 (s, PO), 979 (vs, W = O), 610 (m, WF), 582 (m, br WF).

3.3. [$WOF_4(OPPh_3)$]

was made similarly, except that the $OPPh_3$ was dried by melting *in vacuo* before use. Yield: 85%. Anal: Required for $C_{18}H_{15}F_4O_2PW$ (554.12): C, 39.0; H, 2.7. Found: C, 39.1; H, 2.9%. ^1H NMR (CD_2Cl_2, 293 K): δ = 7.93 – 7.40 (m). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = +60.5 (s, $^1J_{WF}$ = 69 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): 47.3 (s). IR (Nujol/cm^{-1}): 1087 (s, PO), 993 (vs, W=O), 628 (m, WF), 597 (m, WF).

3.4. [$WOF_4(thf)$]

$[WOF_4(MeCN)]$ (0.32 g, 1.0 mmol) was dissolved in dry thf (10 mL), stirred for 3 h, and then all volatiles removed *in vacuo*, leaving a waxy colourless material which decomposed, turning black, in a few days. ^1H NMR (CD_2Cl_2, 293 K): δ = 2.09 (s, [4H]), 4.15 (m, [4H]); (200 K): δ = 2.02 (s, [4H]), 4.12 (s, [4H]. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = +63.3 (s, $^1J_{WF}$ = 64 Hz); (200 K): δ = +63.3. IR (Nujol/cm^{-1}): 1040 (COC), 1018 (vs, W=O), 877 (s, COC), 633 (s, WF) 607 (br, WF).

3.5. [$WOF_4(py)$]

$[WOF_4(MeCN)]$ (0.32 g, 1.0 mmol) was dissolved in dry MeCN (10 mL) and dry pyridine (0.08 g 1.0 mmol) added producing a very pale green solution. After 3 h, the solution was concentrated *in vacuo* to ~3 mL and the bluish-white precipitate filtered off, rinsed with dichloromethane (2 mL) and dried *in vacuo*. Yield: 0.25 g, 71%. Anal: Required for $C_5H_5F_4NOW{\cdot}CH_2Cl_2$ (439.9): C, 16.3; H, 1.6; N, 3.2. Found: C, 16.3; H, 2.0; N, 3.4%. ^1H NMR (CD_3CN, 293 K): δ = 7.6 – 8.9 (m), 5.3 (CH_2Cl_2). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): δ = +62.9 (s, $^1J_{WF}$ = 65 Hz). IR (Nujol/cm^{-1}): 995 (s, W=O), 610 (s, br, WF), 580 (br, WF).

3.6. [$WOF_4(OSMe_2)$]

$[WOF_4(MeCN)]$ (0.32 g, 1.0 mmol) was dissolved in dry MeCN (10 mL) and dry $OSMe_2$ (0.08 g, 1.0 mmol) added, producing a clear solution. After 3 h, the solution was concentrated *in vacuo* to ~3 mL, diethyl ether (5 mL) was added slowly and the cream precipitate was filtered off, rinsed with diethyl ether (2 mL) and dried *in vacuo*. Yield: 0.22 g, 62%. Anal: Required for $C_2H_6F_4O_2SW$ (354.0): C, 6.8; H, 1.8. Found: C, 7.1; H, 2.4%. ^1H NMR (CD_3CN, 293 K): δ = 2.74 (s). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): δ = +59.2 (s, $^1J_{WF}$ = 70 Hz). IR (Nujol/cm^{-1}): 1018 (s, W = O), 1000 (br s,SO), 596 (m, WF), 572 (s, WF).

3.7. [$WO_2F_2(OPPh_3)_2$]

An MeCN solution (10 mL) of $[WOF_4(MeCN)]$ (0.16 g, 0.5 mmol) was treated with $OPPh_3$ (0.28 g, 1.0 mmol) and the clear solution stirred for 1 h, followed by addition of HMDSO (0.08 g, 0.5 mmol). On stirring overnight, a quantity of white solid precipitated. This was filtered off, rinsed with MeCN (5 mL) and dried *in vacuo*. Yield: 0.13 g, 32%. Anal: Required for $C_{36}H_{30}F_2O_4P_2W$ (810.4): C, 53.4; H, 3.7. Found: C, 53.2; H, 3.6%. ^1H NMR (CD_2Cl_2, 293 K): δ = 7.46 – 7.70 (m). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = −63.1 (s, $^1J_{WF}$ = 90 Hz); (200 K): −63.8 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = 41.7 (s). IR (Nujol/cm^{-1}): 1164 (s, PO), 1081 (s, PO), 962 (vs, W=O), 919 (vs, W=O), 588(s, WF). Crystals were grown from an MeCN/CH_2Cl_2 solution by slow evaporation.

3.8. [$WO_2F_2(pyNO)_2$]

An MeCN solution (10 mL) of $[WOF_4(MeCN)]$ (0.16 g, 0.5 mmol) was treated with a solution of pyNO (0.09 g, 1.0 mmol) in CH_2Cl_2, and the clear solution stirred for 1 h, followed by addition of HMDSO (0.08 g, 0.5 mmol). On stirring overnight, a quantity of white solid precipitated. This was filtered off, rinsed with CH_2Cl_2 (2 mL) and dried *in vacuo*. Yield: 0.22 g, 85%. Anal: Required for

$C_{10}H_{10}F_2N_2O_4W{\cdot}CH_2Cl_2$ (529.0): C, 25.0; H, 2.3; N, 5.3. Found: C, 25.1; H, 2.4; N, 5.8%. ^{1}H NMR (CD_3CN, 293 K): δ = 7.73 (s, [2H]), 7.98 (s, [H]), 8.56 (s, [2H]), 5.3 (CH_2Cl_2). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): δ = −67.9 (br, s, $^1J_{WF}$ = ~100 Hz). IR (Nujol)/cm^{-1}: 1300 (m, br NO), 959 (vs, W=O), 913 (vs, W=O), 568 (vs, WF). Crystals were grown from MeCN solution.

3.9. $[WO_2F_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$

An MeCN solution (10 mL) of $[WOF_4(MeCN)]$ (0.16 g, 0.5 mmol) was treated with $Ph_2P(O)CH_2P(O)Ph_2$ (0.21 g, 0.5 mmol) dissolved in CH_2Cl_2 (10 mL) and stirred for 1 h, followed by addition of HMDSO (0.08 g, 0.5 mmol). The solution was stirred for 15 h, during which time some white solid deposited. The solution was concentrated *in vacuo* to 5 mL, the white solid filtered off, rinsed with MeCN (2 mL) and dried *in vacuo*. Yield: 0.28 g, 79%. Anal: Required for $C_{25}H_{22}F_2O_4P_2W{\cdot}1/2CH_2Cl_2$ (712.5): C, 43.0; H, 3.25. Found: C, 43.0; H, 3.1%. ^{1}H NMR (CD_2Cl_2, 293 K): δ = 3.85 (t, [2H], $^2J_{PH}$ = 13 Hz), 7.38 – 7.97 (m, [20H]), 5.3 (CH_2Cl_2). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = −67.1 (s, $^1J_{WF}$ = 108 Hz); (200 K): −63.8 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = 41.7 (s). IR (Nujol/cm^{-1}): 1156 (s, PO), 1102 (s, PO), 969 (vs, W=O), 917 (vs, W=O), 603 (sh, WF), 571 (vs, WF). Crystals were grown from MeCN solution.

3.10. $[WO_2F_2(1,10\text{-phen})]$

Method 1. An MeCN solution (10 mL) of $[WOF_4(MeCN)]$ (0.162 g, 0.5 mmol) was treated with 1,10-phen (0.095 g, 0.5 mmol) dissolved in CH_2Cl_2 (10 mL) and stirred for 1 h, producing a white precipitate. HMDSO (0.08 g, 0.5 mmol) in MeCN (25 mL) was added and the mixture stirred for 24 h. The pale blue-white powder was filtered off, washed with CH_2Cl_2 (2 mL) and dried *in vacuo*. Yield: 0.19 g, 93%. Anal: Required for $C_{10}H_8F_2N_2O_2W$ (410.0): C, 29.2; H, 2.0; N, 6.8. Found: C, 28.1; H, 2.0; N, 6.4%. ^{1}H NMR (CD_3CN, 293 K): δ = 8.24 (m, [4H]), 8.94 (m, [2H]), 9.24 (m, [2H]). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): δ = −69.6 (s, $^1J_{WF}$ = 95 Hz). IR (Nujol/cm^{-1}): 962 (s, W=O), 933 (s, W=O), 585 (s, WF).

Method 2. $[WOF_4(MeCN)]$ (0.32 g, 1.0 mmol) was dissolved in dry MeCN (10 mL) and dry 1,10-phenanthroline (0.16 g 1.0 mmol) as a solution in MeCN (5 mL) added, producing an immediate white precipitate. The solution was stirred for 3 h, and then the precipitate filtered off, rinsed with MeCN (2 mL) and dried *in vacuo*. Yield: 0.15 g, 37%. Anal. Required $C_{10}H_8F_2N_2O_2W$ (410.0): C, 29.2; H, 2.0; N, 6.8. Found: C, 29.3; H, 1.9; N, 6.4%. The spectroscopic data were identical to that from the sample from method 1.

3.11. $[WO_2F_2(OSMe_2)_2]$

An MeCN solution (10 mL) of $[WOF_4(MeCN)]$ (0.16 g, 0.5 mmol) was treated with $OSMe_2$ (0.16 g, 2.0 mmol) and the clear solution stirred for 1 h, followed by addition of HMDSO (0.08 g, 0.5 mmol). On stirring overnight, a quantity of white solid precipitated. This was filtered off, rinsed with MeCN (5 mL) and dried *in vacuo*. Refrigeration of the filtrate produced more precipitate. Yield: 0.23 g, 64%. Anal: Required for $C_4H_{12}F_2O_4S_2W$ (410.1): C, 11.7; H, 3.0. Found: C, 11.6; H, 3.2%. ^{1}H NMR (CD_2Cl_2, 293 K): δ = 2.56 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = −64.7 (s, $^1J_{WF}$ = 103 Hz). IR (Nujol/cm^{-1}): 1004 (br s,SO), 933 (vs, W=O), 900 (m, W=O), 556 (s, WF).

3.12. $[WO_2F_2(py)_2]$

An MeCN solution (15 mL) of $[WOF_4(MeCN)]$ (0.16 g, 0.5 mmol) was treated with pyridine (0.20 g, 2.5 mmol) and the solution stirred for 1 h. Some cream precipitate was filtered off and discarded, and the filtrate treated with HMDSO (0.08 g, 0.5 mmol). On stirring overnight, a quantity of white solid precipitated. This was filtered off, rinsed with MeCN (5 mL) and dried *in vacuo*. Yield: 0.20 g, 90%. The isolated complex is very poorly soluble in MeCN and insoluble in CH_2Cl_2. Anal: Required for $C_{10}H_{10}F_2N_2O_2W$ (412.1): C, 29.1; H, 2.5; N, 6.8. Found: C, 29.3; H, 2.4: N, 6.6%. ^{1}H NMR (CD_3CN, 293 K): δ = 7.5 – 8.8 (m). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): δ = −69.0 (s, $^1J_{WF}$ = 102 Hz). IR (Nujol/cm^{-1}): 961 (vs, W=O), 932 (m, W=O), 575 (br s, WF).

3.13. X-ray experimental

Details of the crystallographic data collection and refinement parameters are given in Table 2. Crystals suitable for single crystal X-ray analysis were obtained as described above. 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 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K (N_2 cryostream). Structure solution and refinements

Table 2
X-ray crystallographic data.[a]

Compound	$[WO_2F_2(pyNO)_2]$	$[WO_2F_2(OPPh_3)_2]$	$[WO_2F_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$	$[WOF_4(OPPh_3)]$
Formula	$C_{10}H_{10}F_2N_2O_4W$	$C_{36}H_{30}F_2O_4P_2W$	$C_{25}H_{22}F_2O_4P_2W$	$C_{18}H_{15}F_4O_2PW$
M	444.05	810.39	670.22	554.12
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group (no.)	P-1 (2)	P-1 (2)	$P2_1/n$ (14)	$P2_1/c$ (14)
a/Å	6.9581(10)	9.4140(10)	10.623(2)	10.282(3)
b/Å	7.1272(10)	10.3851(10)	18.628(3)	8.526(2)
c/Å	12.3851(10)	17.950(2)	12.830(3)	20.477(4)
α/°	84.866(5)	78.437(2)	90	90
β/°	80.576(3)	81.523(2)	103.535(5)	94.650(6)
γ/°	80.709(4)	64.119(3)	90	90
U/Å^3	596.71(13)	1543.2(3)	2468.3(8)	1789.0(8)
Z	2	2	4	4
μ(Mo-Kα)/mm^{-1}	9.718	3.899	4.854	6.595
F(000)	416	800	1304	1056
Total number reflns	5243	15781	41782	7805
R_{int}	0.0348	0.0280	0.2172	0.0401
Unique reflns	2351	6051	4840	3526
No. of params, restraints	172, 0	406, 0	307, 1	235, 0
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.0199, 0.0477	0.0239, 0.0632	0.0759, 0.1470	0.0367, 0.0842
R_1, wR_2 (all data)	0.0227, 0.0485	0.0275, 0.0645	0.1324, 0.1710	0.0489, 0.0901

[a] Common items: T = 100 K; wavelength (Mo-Kα) = 0.71073 Å; θ(max) = 27.5°.
[b] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma\, wF_o^4]^{1/2}$.

were performed with either SHELX(S/L) 97 or SHELX(S/L) 2013 [34] and were straightforward. H atoms bonded to C were placed in calculated positions using the default C—H distance and refined using a riding model.

Crystallographic data in cif format have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and given numbers 1443047–1443050. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366033, email: deposit@ccdc.cam.ac.uk or on the web at http://www.ccdc.cam.ac.uk.

4. Conclusions

A convenient entry into the neutral N- or O-donor ligand complexes of WOF_4 and WO_2F_2 has been developed, and several examples of each type prepared and characterised. Softer donor ligand complexes (S, Se or As donors) do not form in similar reactions. The complexes of WOF_4 are of limited stability and very readily hydrolysed, but those of WO_2F_2 are more robust. Comparison of the spectroscopic and crystallographic data on comparable complexes of WO_2X_2 (X = F, Cl or Br) shows surprisingly little differences with changing the halogen present. However, whilst for X = Cl or Br it is possible to isolate complexes with neutral thioether or arsine ligands [29,30,35], similar complexes have not been isolated with X = F. It is likely that the cause here is less the inherent lower affinity for soft donor ligands in the fluorides, but rather the formation of much stronger W–F–W bridges that compete successfully for coordination sites on the tungsten [4]. Similar differences are observed in the chemistries of $NbOF_3$ and $NbOCl_3$ [7]. The precipitation of WO_2F_2 rather than formation of $[WO_2F_2(MeCN)_2]$ from an MeCN solution of $[WOF_4(MeCN)]$ and HMDSO, contrasts with the ready isolation of $[WO_2Cl_2(MeCN)_2]$ [36] and is also explicable in terms of the greater strength of fluoride over chloride bridges. The formation of WF_6 complexes with SEt_2 and $SeEt_2$ [31,32], whereas analogues with WOF_4 were not found in the present study, shows that WF_6 is a stronger Lewis acid than WOF_4. Similar conclusions were drawn between NbF_5 and $NbOF_3$ [7], which can be rationalised by the increased π-donation from the oxido-group reducing the electron deficit at the metal centre. A recent review [37] summarises structural data on tungsten(VI) oxide halide complexes; the complexes reported in the present manuscript accord with those described.

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