Neutral and cationic tungsten(VI) fluoride complexes with tertiary phosphine and arsine coordination

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Reaction of WF₆ with AsR₃ (R = Me or Et) in anhydrous CH₂Cl₂ at low temperature forms the neutral seven-coordinate, [WF₆(AsR₃)] (R = Me, Et), the first arsine complexes of WF₆, whilst o-C₆H₄(EMe₂)₂ (E = P, As) produces [WF₆(o-C₆H₄(EMe₂)₂)]WF₇₂. Crystal structures show the latter contain dodecahedral cations, and the highest oxidation state metal fluoride complexes known (and the highest possible for tungsten) with soft neutral phosphine and arsine coordination.

Fluoride ligands bind very strongly to metal ions and often confer properties that are significantly different to those for analogous complexes bearing heavier halides, also giving rise to quite different chemistries. For example, metal fluoride complexes can exhibit different catalytic behaviour, can behave as specific fluorinating agents, while the strong affinity of Lewis acidic centres for fluoride is the basis of new F⁻ carriers, while the strong affinity of Lewis acidic centres for fluoride is the basis of new F⁻ carriers, while the strong affinity of Lewis acidic centres for fluoride is the basis of new F⁻ carriers, while the strong affinity of Lewis acidic centres for fluoride is the basis of new F⁻ carriers, while the strong affinity of Lewis acidic centres for fluoride is the basis of new F⁻ carriers, while the strong affinity of Lewis acidic centres for fluoride is the basis of new F⁻ carriers, while the strong affinity of Lewis acidic centres for fluoride is the basis of new F⁻ carriers, while the strong affinity of Lewis acidic centres for fluoride is the basis of new F⁻ carriers, while the strong affinity of Lewis acidic centres for fluoride is the basis of new F⁻ carriers.

Well-documented examples including [WF₆(2-F-py)] (capped trigonal prism), [WF₆(py)]₂ (bicapped trigonal prism), [WF₆(2,2'-bipy)] (structure unknown) and the [WF₆(2,2'-bipy)]⁺ cation (distorted dodecahedron). On the other hand, reaction of WF₆ with sulfite esters, (RO)₂SO (R = alkyl), or phosphites, (RO)₃P, result in OR/F exchange to give, for example, [WF₆(OR)]₁²⁻ while reaction of WF₆ with OMe₂ causes O/F exchange, forming [WOF₄(OMe₂)]⁻. Similar chemistry has been further developed and exploited to provide a useful entry into WOF₄ chemistry, by reaction of WF₆ with (Me₃Si)₂O in MeCN solution to form [WOF₄(MeCN)]⁻ from which the MeCN is easily displaced by other neutral ligands. In contrast, complexes of high oxidation state metal fluorides with soft donor ligands are extremely rare. The first phospine example, [WF₆(PMe₃)], was briefly described in 1968 and later work showed this compound to have a capped trigonal prismatic geometry while [WF₆(PMe₂Ph)] is a capped octahedron. We recently reported the six-coordinate oxide-fluoride species, [WOF₄(PMe₃)]⁻ and seven-coordinate (pentagonal bipyramidal) [WOF₄(diphosphine)] (diphosphine = Me₂P(CH₂)₂PMe₂ or o-C₆H₄(PMe₂)₂); notably, no analogues with arsenic ligands could be formed. Here we describe the synthesis and properties of arsine complexes of WF₆ for the first time, together with the first cationic complexes derived from WF₆ with neutral bidentate diphosphine and dianisyl ligands, whose structures are confirmed crystallographically.

For the AsR₃ (R = Me, Et) complexes the synthesis route involved condensation of WF₆ in vacuo onto a frozen solution of the appropriate ligand in anhydrous CH₂Cl₂ at 77 K, then allowing the mixture to warm slowly to room temperature (Scheme 1).

Upon melting (176 K) the reaction mixture containing a 1:1 molar ratio of WF₆ and AsMe₃ turned deep orange-red, and deposited an orange-red powder upon removal of the volatiles in vacuo at room temperature. The reaction solution and

Scheme 1 Preparative method.
products are extremely moisture sensitive, turn dark blue upon trace hydrolysis, and showing varying amounts of [WF₆O₂F₅]⁻ and [WO₅F₄]⁻² in the ¹⁹F¹H NMR spectra of such solutions. The orange-red solid, identified as [WF₆(AsMe₃)] by microanalysis, decomposes in a few days in the glove box at ambient temperature, but can be kept in a sealed tube in a freezer (−18 °C) for several weeks; the complex is decomposed by MeCN. The corresponding AsEt₃ complex is a viscous orange-red oil and even more reactive, decomposing at room temperature over a few hours and reacting more readily with trace moisture. Neither AsPH₃ nor the heavier SbR₃ yielded identifiable products under similar reaction conditions.

The ¹⁹F¹H NMR spectra of [WF₆(AsR₃)] show singlet resonances at +130.8 (R = Me) and +134.4 ppm (R = Et). They did not exhibit ¹⁸⁵W satellites, but the chemical shifts may be compared with those in [WF₆(PMe₃)] δ = +133.6¹⁷ and WF₆ itself, δ = +167.0.¹⁸ The ¹⁹F¹H spectra are little changed on cooling the sample to 180 K, indicating fluxionality down to low temperatures. Fluxionality is also evident in the ¹⁹F¹H NMR spectra of the pyridine complexes [WF₆(R-py)] (R = H or F) at ambient temperatures, but on cooling the solutions the separate resonances of the inequivalent fluorines of capped trigonal prismatic geometries are resolved.¹³,¹⁴ The IR spectra have very broad strong features at 610 (R = Me) and 622 cm⁻¹ (R = Et), assigned to overlapping W–F stretches. The UV/visible spectrum of [WF₆(AsMe₃)] shows a very broad absorption at ∼22 700 cm⁻¹, which accounts for the orange-red colour and may be assigned as a ligand to metal charge transfer, As(σ) → W(d), since the F(σ) → W(d) transitions are expected to lie in the far-UV region.²²

In an attempt to increase the phosphine/arsole coordination and develop further the reaction chemistry with WF₆, the rigid o-phenylene ligands, o-C₆H₄[(EMe₂)₂] (E = P or As) were employed. These are amongst the strongest σ-donor neutral pnictines and are pre-organised for chelation. The reaction of WF₆ with o-C₆H₄(AsMe₂)₂ or o-C₆H₄(PMe₂)₂ in frozen anhydrous CH₂Cl₂ solution in either a 1:1 or 2:1 molar ratio gave, on melting, orange-red or orange-yellow solutions, respectively, from which the orange-red solid, identified as [WF₆(AsMe₃)] by microanalysis, was isolated. Microanalytical data and the IR spectra obtained in anhydrous MeCN showed very broad features at 20 800 and 31 500 cm⁻¹, which accounts for the orange-red colour and may be assigned as a ligand to metal charge transfer, As(σ) → W(d), since the F(σ) → W(d) transitions are expected to lie in the far-UV region.²²

Obtaining solution spectroscopic data and growing crystals for X-ray analysis was very challenging as a result of the extreme moisture sensitivity of the samples. The complexes were poorly soluble in CH₂Cl₂ and the dilute solutions rapidly decompose with loss of the colour. However, they are more soluble in MeCN and decomposition is slower in this medium. Several batches of crystals were grown by evaporation of MeCN solutions in the glove box. X-ray crystal structure solution revealed that all contained well defined [WF₆(o-C₆H₄[(EMe₂)₂]₂)]⁺ cations, but contain various anions, sometimes disordered. Disordered MeCN was also present in some crystals. These results are reminiscent of the [WF₆(2,2’-bipy)]⁺ systems described above.¹⁵,¹⁶ The structures of the cations are shown in Fig. 1 and 2. The cation in [WF₆(o-C₆H₄[(EMe₂)₂]₂)][WO₅F₄] is a distorted dodecahedron with (cis) F–W–F angles ∼94° and (trans) F–W–F ∼73°, the latter reflecting the constrained bite angle of the chelating ligand. The d(W–F) of 1.91(3)–1.94(3) Å are longer than those in either WF₆ (1.826(2) Å)¹⁶ or in the six-coordinate [WO₅F₄(OPh₂)] 1.873(3)–1.971(3) Å.¹⁹ but similar to those in the seven-coordinate [WF₆(Me₆PCH₂CH₂PMe₆)] 1.923(9)–1.960(4) Å.²⁰ The d(W–P) is 2.558(18)–2.571(17) Å, are also similar to those in the latter complex (2.572(17)–2.592(18) Å). The cation geometry is very similar to that in the iso electronic [TaF₆(o-C₆H₄[(EMe₂)₂]₂)]⁺.²¹ The [WO₅F₄] anions were disordered.

Multinuclear NMR spectra were obtained from freshly prepared solutions in anhydrous MeCN. These showed that the cations were relatively stable and their resonances were only
slowly lost over several days, but that the $^{19}$F{$_1^H$} resonance of the [WF$_4$]$^-$ ion diminished rapidly over time, with new resonances attributed to [WOF$_4$], [WO$_2$F$_6$]$^-$ and possibly [WO$_4$(MeCN)]$^{19,27,28}$ appearing. The new resonances must result from trace hydrolysis and/or attack on the glass, and are consistent with the identification of these species in the X-ray structure analyses.

The $^1$H NMR spectra of the [WF$_4$(o-C$_6$H$_4$(EMe$_2$)$_2$)$_2$]$^{2+}$ salts showed resonances significantly to high frequency of the values in the parent ligands$^{29}$ and are consistent with a single environment of the coordinated donor ligands. The $^{19}$F{$_1^H$} NMR spectra showed a singlet at δ = +142.8 attributed to [WF$_4$]$^-$.$^{16,28}$ The $^{19}$F{$_1^H$} NMR resonance of the cation [WF$_4$(o-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$]$^{2+}$ was highly shielded, with δ = −25.9 and with $^{18}$W satellites ($J_{WF} = 88$ Hz). For the corresponding [WF$_4$(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$]$^{2+}$ cation, the $^{19}$F{$_1^H$} resonance was a binomial quintet at δ = −17.5 ($J_{PF} = 67$ Hz) (Fig. 3(b)). In this case the $^{18}$W satellites were not clearly resolved. The significant shielding of the fluorine resonances in [WF$_4$(o-C$_6$H$_4$(EMe$_2$)$_2$)$_2$]$^{2+}$ and [WF$_4$(2,2'-bipy)$_2$]$^{2+}$ ($J_{PF} = 67$ Hz) in this case the $^{18}$W satellites were not clearly resolved. The significant shielding of the fluorine resonances in [WF$_4$(o-C$_6$H$_4$(EMe$_2$)$_2$)$_2$]$^{2+}$ ($J_{PF} = 67$ Hz) confirmed the presence of the soft donor P and As groups. Similar trends were seen in complexes of niobium and tantalum, [MF$_6$(2,2'-bipy)$_2$][MF$_3$]: $\delta^{19}$F{$_1^H$} = +139.7 (Nb) or +68.1 (Ta), compared to [MF$_6$(o-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$][MF$_3$]: $\delta^{19}$F{$_1^H$} = +27.1 (Nb) or −28.0 (Ta) and [MF$_6$(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$][MF$_3$]: $\delta^{19}$F{$_1^H$} = −7.8 (Nb) or −39.8 (Ta)$^{24,20}$

The diphenylphosphine complex also exhibited a quintet $^{31}$P{$_1^H$} NMR resonance (CD$_3$CN) at δ = +122.3 ($J_{PP} = 67$ Hz). This constitutes a remarkably large coordination shift of +177 (Fig. 3(a)) for the five-membered chelate ring and may be compared with the coordination shift of +131 observed in [WO$_4$(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$]$^{20}$

A similar reaction of WF$_6$ with the more flexible Me$_2$PCH$_2$-CH$_2$PMe$_2$ afforded a pale orange powder in low yield. Multinuclear NMR ($^{1}$H, $^{19}$F{$_1^H$}, $^{31}$P{$_1^H$}) studies showed this was an inseparable mixture of two species, one identified as [WF$_4$(Me$_2$PCH$_2$-CH$_2$PMe$_2$)$_2$][WF$_2$], the second tentatively assigned as the diphenylphosphine-bridged [F$_2$W(Me$_2$PCH$_2$CH$_2$PMe$_2$)WF$_4$].

Reaction of WF$_6$ with RS(CH$_2$)$_2$SR (R = Me, Pr) in rigorously dried CH$_2$Cl$_2$ gave orange brown solutions at 180 K, but the colour was lost on warming, and removal of the volatiles in vacuo resulted in recovery of the dithioether (ESI$^+$).

In summary, this work has identified the first examples of eight-coordinate tetrafluorotungsten(vi) cations with chelating soft, neutral diphenylphosphine -diarsine co-ligands, whose structures are confirmed by X-ray crystallographic and spectroscopic analyses. Neutral, seven-coordinate W(vi) complexes with triarylarsines have also been established, whereas triarylarsines and trialkylstibines yield intractable materials. While WF$_6$ is less oxidising than the other metal hexafluorides, successful incorporation of the soft group 15 donor ligands by taking advantage of the pre-organised -phenylene backbone may suggest that under suitable reaction conditions coordination chemistry with neutral ligands may also exist for other members of the little studied family of very hard and more highly oxidising transition metal hexafluorides.

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Conflicts of interest
There are no conflicts to declare.

Notes and references