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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)][WF6]z. Crystal structures show the latter contain dodecahedral cations, and present 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,1,2 can behave as specific fluorinating agents,3,4 while the strong affinity of Lewis acidic centres for fluoride is the basis of new F- sensors5,6 and the development of metal chelate scaffolds for new classes of 18F carriers for medical imaging (PET).5,6 On the other hand, the soft, neutral group 15 pnictines (ER3; E = P, As, R = alkyl, aryl) have found wide utility as 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 [W₂O₂F₆]⁻ and [WO₅Cl]⁻ in the ¹⁹F(¹H) 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 SbEt₃ yielded identifiable products under similar reaction conditions.

The ¹⁹F(¹H) NMR spectra of [WF₆(AsR₃)] show singlet resonances at +130.8 (R = Me) and +134.4 ppm (R = Et). They did not exhibit ¹⁸¹W satellites, but the chemical shifts may be compared with those in [WF₆(PMe₃)], δ = +133.6, and WF₆ itself, δ = +167.0.¹⁶ The ¹⁹F(¹H) spectra are little changed on cooling the sample to 180 K, indicating fluxionality down to low temperatures. Fluxionality is also evident in the ¹⁹F(¹H) 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/arsine 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 pnicnites 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 similarly coloured powders precipitated on concentration of the compares solutions in anhydrous MeCN. These showed that the cations were relatively stable and their resonances were only

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 [WF₄(o-C₆H₄(EMe₂)₂)]⁺ cations, but contain various anions, sometimes disordered. Disordered MeCN was also present in some crystals. These results are reminiscent of the [WF₄(2,2′-bipy)]⁺ systems described above.¹⁵,¹⁶ The structures of the cations are shown in Fig. 1 and 2. The cation in [WF₄(o-C₆H₄(PMe₂)₂)]⁺ is a distorted dodecahedron with (cis) F-W-F angles ~94° and <P=W−P ~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)²⁶ or in the six-coordinate [WO₅(OPPh₃)] 1.857(3)–1.871(3) Å,¹⁹ but similar to those in the seven-coordinate [WO₅(MeCH₂CH₂Me₃)] 1.923(9)–1.960(4) Å.²⁰ The d(W−P) = 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 isoelectronic [TaF₄(o-C₆H₄(PMe₂)₂)]⁺.²⁴ The [WO₅]⁻ 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

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** The cation present in [WF₄(o-C₆H₄(PMe₂)₂)]⁺[WO₅Cl]−MeCN showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W(1)−F(3) = 1.91(4), W(1)−F(2) = 1.92(4), W(1)−F(1) = 1.92(4), W(1)−F(4) = 1.93(4), W(1)−P(3) = 2.572(17), W(1)−P(1) = 2.579(18), W(1)−P(2) = 2.582(18), W(1)−P(4) = 2.592(18), P(3)−W(1)−P(4) = 72.6(6), P(1)−W(1)−P(2) = 72.8(6).

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** The cation present in [WF₄(o-C₆H₄(AsMe₂)₂)]⁺[WF₆] showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W(1)−F(1) = 2.11(4), W(1)−As(1) = 2.67(5), As(1)−W(1)−As(1) #1 = 75.74(4). Symmetry operators: #1 = −x + 5/4, −y + 5/4, z; #2 = x, −y + 5/4, −z + 1/4; #3 = −x + 5/4, y, −z + 1/4.
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$_3$]$^-$, [WO$_2$F$_5$]$^-$ and possibly [WOF$_4$(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 ligand. The $^{19}$F($^1$H) NMR spectra showed a singlet at $\delta = +142.8$ 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 $\delta = -25.9$ 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 $\delta = -17.5$ ($J_{WF} = 67$ 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$_2$)$_2$)$_2$]$^{2+}$ cf. [WF$_4$(2,2’-bipy)$_2$]$^{2+}$ ($\delta = +153$)$^{16}$ is characteristic of the presence of the soft donor P and As groups. Similar trends were seen in complexes of niobium and tantalum, [MF$_4$(2,2’-bipy)$_2$][MF$_5$]: $\delta^{19}$F($^1$H) = +139.7 (Nb) or +68.1 (Ta), compared to [MF$_4$(o-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$][MF$_5$]: $\delta^{19}$F($^1$H) = +27.1 (Nb) or −28.0 (Ta) and [MF$_4$(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$][MF$_5$]: $\delta^{19}$F($^1$H) = −7.8 (Nb) or −39.8 (Ta)$^{24,20}$.

The diphosphine complex also exhibited a quintet $^{31}$P($^1$H) NMR resonance (CD$_3$CN) at $\delta = +122.3$ ($J_{P} = 67$ 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 [WOF$_4$(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$]$^{2+}$.$^{20}$

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$_7$], the second tentatively assigned as the diphosphine-bridged [F$_2$W(Me$_2$PCH$_2$CH$_2$PMe$_2$)W].

The 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 diphosphine and -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,$^9$ successful incorporation of the soft group 15 donor ligands by taking advantage of the pre-organised o-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