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(E₄Me₂)₂ (E = P, As) produces [WF₆(o-C₆H₄(E₄Me₂))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 for medical imaging (PET). On the other hand, the soft, neutral Group 15 pnictines (E₄R; E = P, As, R = alkyl, aryl) have found wide utility as fluoride ligands for the first time, together with the first cationic complexes derived from WF₆ with neutral arsine complexes of WF₆ for the first time, together with the first cationic complexes derived from WF₆ with neutral arsine ligands.

Well-documented examples including [WF₄(2-F-py)] (capped trigonal prism), [WF₄(py)] (bicapped trigonal prism), [WF₄(2,2'-bipy)] (structure unknown) and the [WF₄(2,2'-bipy)]⁺ cation (distorted dodecahedron). On the other hand, reaction of WF₆ with sulfite, (RO)₂SO (R = alkyl), or phosphites, (RO)₃P, result in OR/F exchange to give, for example, [WF₅(OR)]⁻, 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 phosphine example, [WF₅(PMe₃)], was briefly described in 1968 and later work showed this compound to have a capped trigonal prismatic geometry while [WF₅(PMe₂Ph)] is a capped octahedron. We recently reported the six-coordinate oxide-fluoride species, [WOF₄(PMe₂)], 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, 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...
products are extremely moisture sensitive, turn dark blue upon trace hydrolysis, and showing varying amounts of \([\text{W}_2\text{O}_7\text{F}_6]^-\) and \([\text{WO}_7\text{F}_6]^-\) in the \(^{19}\text{F}^{{(1)}\text{H}}\) NMR spectra of such solutions. The orange-red solid, identified as \([\text{WF}_6(\text{AsMe}_3)]\) 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 AsPPh_3 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 AsPPh_3 nor the heavier SbR_3 yielded identifiable products under similar reaction conditions.

The \(^{19}\text{F}^{{(1)}\text{H}}\) NMR spectra of \([\text{WF}_6(\text{AsR}_3)]\) show singlet resonances at +130.8 (R = Me) and +134.4 ppm (R = Et). They did not exhibit \(^{19}\text{W}\) satellites, but the chemical shifts may be compared with those in \([\text{WF}_6(\text{PMe}_3)]\), \(\delta = +133.6^{17}\) and \([\text{WF}_6(\text{py})]\) (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 solid \([\text{WF}_6(\text{AsR}_3)]\) shows a very broad absorption at \(\sim 22,700 \text{ cm}^{-1}\), which accounts for the orange-red colour and may be assigned as a ligand to metal charge transfer, \(\text{As}^{(\sigma)} \rightarrow \text{W}(d)\).\(^{15,16}\) The structures of the cations are shown in Fig. 1 and 2. The cation in \([\text{WF}_6(\text{AsR}_3)]\) \([\text{WO}_7\text{F}_6]^{3-}\) is a distorted dodecahedron with \(\langle \text{cis} \rangle \text{F} - \text{W} - \text{F} \sim 94^\circ\) and \(\langle \text{P} - \text{W} - \text{P} \sim 73^\circ\), the latter reflecting the constrained bite angle of the chelating ligand. The \(d(\text{W} - \text{F})\) of 1.91(3)–1.94(3) Å are longer than those in either \([\text{WF}_6(\text{py})]\) \(1.826(2) \text{ Å}\)\(^{20}\) or in the six-coordinate \([\text{WO}_7\text{F}_6(\text{OPPh}_3)]\) 1.857(3)–1.871(3) Å,\(^{19}\) but similar to those in the seven-coordinate \([\text{WO}_7\text{F}_6(\text{PCH}_2\text{CH}_2\text{PMe}_2)]\), 1.923(9)–1.960(4) Å.\(^{20}\) The \(d(\text{W} - \text{P})\) of 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 isostructural \([\text{TaF}_6(\text{py})]^{3-}\) systems described above.\(^{15,16}\) The \([\text{WF}_6(\text{Ar}_2\text{P} - \text{P} - \text{Ar}_2)]\) \([\text{WO}_7\text{F}_6]^{3-}\) 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

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 \([\text{WF}_6(\text{Ar}_2\text{P} - \text{P} - \text{Ar}_2)]\) \([\text{WO}_7\text{F}_6]^{3-}\) cations, but contain various anions, sometimes disordered. Disordered MeCN was also present in some crystals. These results are reminiscent of the \([\text{WF}_6(2,2’\text{bipy})]^{3-}\) systems described above.\(^{15,16}\)
slowly lost over several days, but that the $^{19}$F($^{1}$H) resonance of the
[WF$_7$]$^{-}$ ion diminished rapidly over time, with new resonances
attributed to [WOF$_4$($^{19}$F)($^{1}$H)S$_2$] and possibly [WOF$_4$(MeCN)]$^{29,27,28}$
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$_4$($^{1}$H,4($^{1}$EMe$_2$)$_2$]$_2$$^{2+}$ salts
showed resonances significantly to high frequency of the values in
the parent ligands$^{29}$ and are consistent with a single environment
of the coordinated ligand. The $^{19}$F($^{1}$H) NMR spectra showed a singlet at
$\delta = +142.8$ attributed to [WF$_7$]$.^{16,28}$ The $^{19}$F($^{1}$H) NMR resonance of
the cation [WF$_4$($^{1}$C$_4$H$_4$($^{1}$AsMe$_2$)$_2$]$_2$$^{2+}$ was highly shielded, with
$\delta = -25.9$ and with $^{18}$W satellites ($J_{WF} = 88$ Hz). For the corresponding
[WF$_4$($^{1}$C$_4$H$_4$($^{1}$PMe$_2$)$_2$]$_2$$^{2+}$ cation, the $^{19}$F($^{1}$H) resonance
was a binomial quintet at $\delta = -17.5$ ($J_{PF} = 67$ Hz) (Fig. 3(b)). In this case the $^{18}$W satellites were not clearly
resolved. The significant shielding of the fluorine resonances in
[WF$_4$($^{1}$C$_4$H$_4$($^{1}$EMe$_2$)$_2$]$_2$$^{2+}$ cf [WF$_4$($^{1}$C$_4$H$_4$($^{1}$bipy)$_2$]$_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$_4$($^{1}$C$_4$H$_4$($^{1}$EMe$_2$)$_2$]$_2$ [MF$_6$]: $\delta$($^{19}$F($^{1}$H)) = +139.7 (Nb)
and +68.1 (Ta), compared to [MF$_4$($^{1}$C$_4$H$_4$($^{1}$AsMe$_2$)$_2$]$_2$ [MF$_6$]: $\delta$($^{19}$F($^{1}$H)) = +27.1
(Nb) or $\delta$ = -28.0 (Ta) and [MF$_4$($^{1}$C$_4$H$_4$($^{1}$PMe$_2$)$_2$]$_2$ [MF$_6$]: $\delta$($^{19}$F($^{1}$H)) = $\delta$($^{19}$F($^{1}$H)) =
-7.8 (Nb) or $\delta$ = -39.8 (Ta).$^{24,20}$

The diphosphine complex also exhibited a quintet $^{31}$P($^{1}$H) NMR
resonance (CD$_3$CN) at $\delta = +122.3$ ($J_{PP} = 67$ Hz). This constitutes a
remarkably large coordination shift of +177 (Fig. 3(a)) for the fivemembered chelate ring and may be compared with the coordination
shift of +131 observed in [WO$_4$($^{1}$C$_4$H$_4$($^{1}$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$_4$($^{1}$PMe$_2$CH$_2$-
CH$_2$PMe$_2$)]$_2$[WF$_7$], the second tentatively assigned as the
diphosphine-bridged [F$_4$W($^{1}$PMe$_2$CH$_2$CH$_2$PMe$_2$)WF]$_2$.

Reaction of WF$_6$ with RS(CH$_3$)$_2$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 diithioether (ESI$^{+}$).

In summary, this work has identified the first examples of eightcoordinate tetrafluorotungsten(vi) cations with chelating soft,
natural 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 triarylarasines 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
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.

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