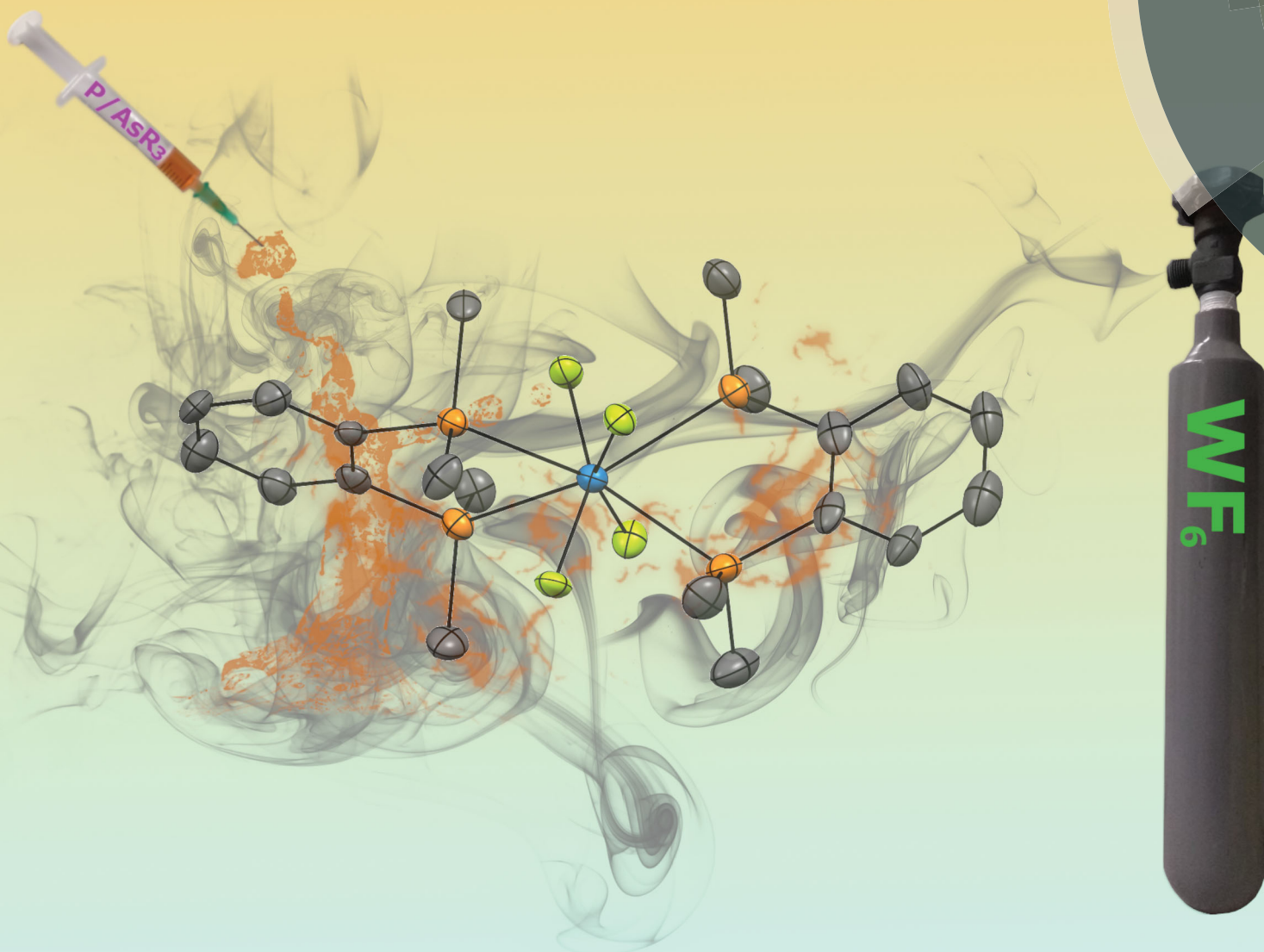


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Neutral and cationic tungsten(vi) fluoride complexes with tertiary phosphine and arsine coordination†

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Reaction of WF_6 with AsR_3 ($\text{R} = \text{Me}$ or Et) in anhydrous CH_2Cl_2 at low temperature forms the neutral seven-coordinate, $[\text{WF}_6(\text{AsR}_3)]$ ($\text{R} = \text{Me}$, Et), the first arsine complexes of WF_6 , whilst $o\text{-C}_6\text{H}_4(\text{EMe}_2)_2$ ($\text{E} = \text{P}$, As) produces $[\text{WF}_4\{o\text{-C}_6\text{H}_4(\text{EMe}_2)_2\}_2][\text{WF}_7]_2$. 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,^{2,3} while the strong affinity of Lewis acidic centres for fluoride is the basis of new F^- sensors⁴ and the development of metal chelate scaffolds for new classes of ^{18}F carriers for medical imaging (PET).^{5,6} On the other hand, the soft, neutral group 15 pnictines (ER_3 ; $\text{E} = \text{P}$, As , $\text{R} = \text{alkyl}$, aryl) have found wide utility as ligands towards many Lewis acids, most typically those from the middle and late d-block in medium or low oxidation states. The capacity to tune the electronic and steric properties of the pnictine strongly influences the resulting chemistry. Through judicious choice of the metal source and the specific pnictine, recent work has established the existence of homoleptic phosphine complexes with Group 1 cations, including the distorted octahedral $[\text{M}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_3]^+$ cations ($\text{M} = \text{Li}$, Na)⁷ and a series of seven- and eight-coordinate complexes with the hard, oxophilic $\text{Sc}(\text{III})$ and $\text{Y}(\text{III})$ ions.⁸

Tungsten hexafluoride, which contains tungsten in its highest possible oxidation state, is known to form complexes with a variety of hard Lewis bases, mostly neutral N-donor ligands.^{9–17}

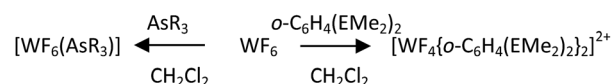
Well-documented examples including $[\text{WF}_6(2\text{-F-py})]$ (capped trigonal prism),¹³ $[\text{WF}_6(\text{py})_2]$ (bicapped trigonal prism),¹⁴ $[\text{WF}_6(2,2'\text{-bipy})]$ (structure unknown)¹⁶ and the $[\text{WF}_4(2,2'\text{-bipy})_2]^{2+}$ cation (distorted dodecahedron).^{15,16} On the other hand, reaction of WF_6 with sulfite esters, $(\text{RO})_2\text{SO}$ ($\text{R} = \text{alkyl}$), or phosphites, $(\text{RO})_3\text{P}$, result in O/F exchange to give, for example, $[\text{WF}_5(\text{OR})]$,^{12,18} while reaction of WF_6 with OMe_2 causes O/F exchange, forming $[\text{WOF}_4(\text{OMe}_2)]$.¹² Similar chemistry has been further developed and exploited to provide a useful entry into WOF_4 chemistry, by reaction of WF_6 with $(\text{Me}_3\text{Si})_2\text{O}$ in MeCN solution to form $[\text{WOF}_4(\text{MeCN})]$, from which the MeCN is easily displaced by other neutral ligands.¹⁹ In contrast, complexes of high oxidation state metal fluorides with soft donor ligands are extremely rare.¹⁰ The first phosphine example, $[\text{WF}_6(\text{PMe}_3)]$, was briefly described in 1968¹¹ and later work¹⁷ showed this compound to have a capped trigonal prismatic geometry while $[\text{WF}_6(\text{PMe}_2\text{Ph})]$ is a capped octahedron. We recently reported²⁰ the six-coordinate oxide-fluoride species, $[\text{WOF}_4(\text{PMe}_3)]$ and seven-coordinate (pentagonal bipyramidal) $[\text{WOF}_4(\text{diphosphine})]$ (diphosphine = $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ or $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$); notably, no analogues with arsenic ligands could be formed.^{19,20} Here we describe the synthesis and properties of arsine complexes of WF_6 for the first time, together with the first cationic complexes derived from WF_6 with neutral bidentate diphosphine and diarsine ligands, whose structures are confirmed crystallographically.

For the AsR_3 ($\text{R} = \text{Me}$, Et) complexes the synthesis route involved condensation of WF_6 *in vacuo* onto a frozen solution of the appropriate ligand in anhydrous CH_2Cl_2 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 WF_6 and AsMe_3 turned deep orange-red, and deposited an orange-red powder upon removal of the volatiles *in vacuo* at room temperature. The reaction solution and

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Scheme 1 Preparative method.



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 CH_2Cl_2 and the dilute solutions rapidly decompose

slowly lost over several days, but that the $^{19}\text{F}\{^1\text{H}\}$ resonance of the $[\text{WF}_7]^-$ ion diminished rapidly over time, with new resonances attributed to $[\text{WOF}_5]^-$, $[\text{W}_2\text{O}_2\text{F}_6]^-$ and possibly $[\text{WOF}_4(\text{MeCN})]^{19,27,28}$ 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 ^1H NMR spectra of the $[\text{WF}_4\{\text{o-C}_6\text{H}_4(\text{EMe}_2)_2\}_2]^{2+}$ salts showed resonances significantly to high frequency of the values in the parent ligands²⁹ and are consistent with a single environment of the coordinated ligand. The $^{19}\text{F}\{^1\text{H}\}$ NMR spectra showed a singlet at $\delta = +142.8$ attributed to $[\text{WF}_7]^-$.^{16,28} The $^{19}\text{F}\{^1\text{H}\}$ NMR resonance of the cation $[\text{WF}_4\{\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]^{2+}$ was highly shielded, with $\delta = -25.9$ and with ^{183}W satellites ($^1J_{\text{WF}} = 88$ Hz). For the corresponding $[\text{WF}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]^{2+}$ cation, the $^{19}\text{F}\{^1\text{H}\}$ resonance was a binomial quintet at $\delta = -17.5$ ($^2J_{\text{PF}} = 67$ Hz) (Fig. 3(b)). In this case the ^{183}W satellites were not clearly resolved. The significant shielding of the fluorine resonances in $[\text{WF}_4\{\text{o-C}_6\text{H}_4(\text{EMe}_2)_2\}_2]^{2+}$ cf. $[\text{WF}_4(2,2'\text{-bipy})_2]^{2+}$ ($\delta = +153$)¹⁶ is characteristic of the presence of the soft donor P and As groups. Similar trends were seen in complexes of niobium and tantalum, $[\text{MF}_4(2,2'\text{-bipy})_2][\text{MF}_6]$: $\delta(^{19}\text{F}\{^1\text{H}\}) = +139.7$ (Nb) or $+68.1$ (Ta), compared to $[\text{MF}_4\{\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2][\text{MF}_6]$: $\delta(^{19}\text{F}\{^1\text{H}\}) = +27.1$ (Nb) or -28.0 (Ta) and $[\text{MF}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2][\text{MF}_6]$: $\delta(^{19}\text{F}\{^1\text{H}\}) = -7.8$ (Nb) or -39.8 (Ta).^{24,30}

The diphosphine complex also exhibited a quintet $^{31}\text{P}\{^1\text{H}\}$ NMR resonance (CD_3CN) at $\delta = +122.3$ ($^2J_{\text{PF}} = 67$ 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 $[\text{WOF}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}]^{20}$.

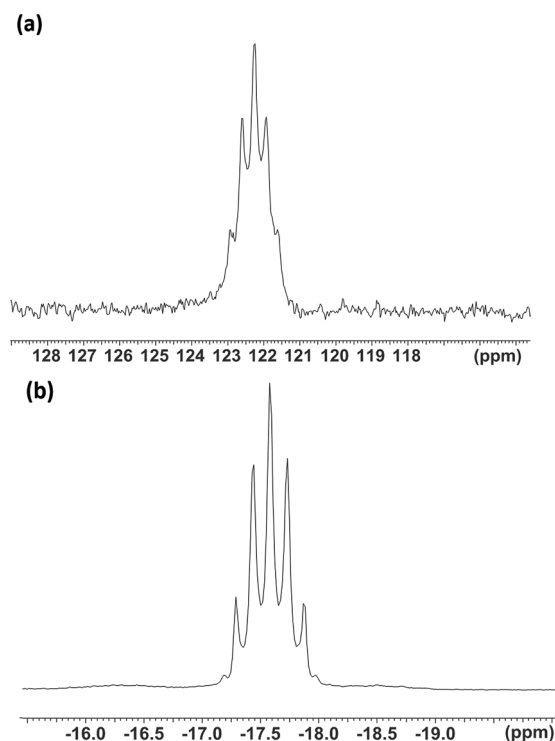


Fig. 3 The NMR spectra of $[\text{WF}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]^{2+}$: (a) $^{31}\text{P}\{^1\text{H}\}$ and (b) $^{19}\text{F}\{^1\text{H}\}$ in MeCN solution.

A similar reaction of WF_6 with the more flexible $\text{Me}_2\text{PCH}_2\text{-CH}_2\text{PMe}_2$ afforded a pale orange powder in low yield. Multinuclear NMR (^1H , $^{19}\text{F}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$) studies showed this was an inseparable mixture of two species, one identified as $[\text{WF}_4(\text{Me}_2\text{PCH}_2\text{-CH}_2\text{PMe}_2)_2][\text{WF}_7]_2$, the second tentatively assigned as the diphosphine-bridged $[\text{F}_6\text{W}(\mu\text{-Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{WF}_6]$.

Reaction of WF_6 with $\text{RS}(\text{CH}_2)_2\text{SR}$ ($\text{R} = \text{Me}$, $i\text{Pr}$) in rigorously dried CH_2Cl_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 $\text{W}(\text{vi})$ complexes with trialkylarsines 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.

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