

# ChemComm

Chemical Communications

rsc.li/chemcomm



ISSN 1359-7345



## COMMUNICATION

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Cite this: *Chem. Commun.*, 2018, 54, 11681

Received 11th July 2018,  
Accepted 3rd August 2018

DOI: 10.1039/c8cc05598j

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

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**Reaction of  $\text{WF}_6$  with  $\text{AsR}_3$  ( $\text{R} = \text{Me}$  or  $\text{Et}$ ) in anhydrous  $\text{CH}_2\text{Cl}_2$  at low temperature forms the neutral seven-coordinate,  $[\text{WF}_6(\text{AsR}_3)]$  ( $\text{R} = \text{Me}, \text{Et}$ ), the first arsine complexes of  $\text{WF}_6$ , whilst  $o\text{-C}_6\text{H}_4(\text{EMe}_2)_2$  ( $\text{E} = \text{P}, \text{As}$ ) 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,<sup>1,2</sup> can behave as specific fluorinating agents,<sup>2,3</sup> while the strong affinity of Lewis acidic centres for fluoride is the basis of new  $\text{F}^-$  sensors<sup>4</sup> and the development of metal chelate scaffolds for new classes of  $^{18}\text{F}$  carriers for medical imaging (PET).<sup>5,6</sup> On the other hand, the soft, neutral group 15 pnictines ( $\text{ER}_3$ ;  $\text{E} = \text{P}, \text{As}$ ,  $\text{R} = \text{alkyl}, \text{aryl}$ ) 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 ( $\text{M} = \text{Li}, \text{Na}$ )<sup>7</sup> and a series of seven- and eight-coordinate complexes with the hard, oxophilic  $\text{Sc}(\text{III})$  and  $\text{Y}(\text{III})$  ions.<sup>8</sup>

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.<sup>9–17</sup>

Well-documented examples including  $[\text{WF}_6(2\text{-F-py})]$  (capped trigonal prism),<sup>13</sup>  $[\text{WF}_6(\text{py})_2]$  (bicapped trigonal prism),<sup>14</sup>  $[\text{WF}_6(2,2'\text{-bipy})]$  (structure unknown)<sup>16</sup> and the  $[\text{WF}_4(2,2'\text{-bipy})_2]^{2+}$  cation (distorted dodecahedron).<sup>15,16</sup> On the other hand, reaction of  $\text{WF}_6$  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,  $[\text{WF}_5(\text{OR})]$ ,<sup>12,18</sup> while reaction of  $\text{WF}_6$  with  $\text{OMe}_2$  causes O/F exchange, forming  $[\text{WOF}_4(\text{OMe}_2)]$ .<sup>12</sup> Similar chemistry has been further developed and exploited to provide a useful entry into  $\text{WOF}_4$  chemistry, by reaction of  $\text{WF}_6$  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.<sup>19</sup> In contrast, complexes of high oxidation state metal fluorides with soft donor ligands are extremely rare.<sup>10</sup> The first phosphine example,  $[\text{WF}_6(\text{PMe}_3)]$ , was briefly described in 1968<sup>11</sup> and later work<sup>17</sup> 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 reported<sup>20</sup> 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.<sup>19,20</sup> Here we describe the synthesis and properties of arsine complexes of  $\text{WF}_6$  for the first time, together with the first cationic complexes derived from  $\text{WF}_6$  with neutral bidentate diphosphine and diarsine ligands, whose structures are confirmed crystallographically.

For the  $\text{AsR}_3$  ( $\text{R} = \text{Me}, \text{Et}$ ) complexes the synthesis route involved condensation of  $\text{WF}_6$  *in vacuo* onto a frozen solution of the appropriate ligand in anhydrous  $\text{CH}_2\text{Cl}_2$  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  $\text{WF}_6$  and  $\text{AsMe}_3$  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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† Electronic supplementary information (ESI) available: Full experimental procedures and characterisation data, original IR and NMR spectra for the compounds reported. CCDC 1854218 and 1854219. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc05598j



Scheme 1 Preparative method.



products are extremely moisture sensitive, turn dark blue upon trace hydrolysis, and showing varying amounts of  $[\text{W}_2\text{O}_2\text{F}_9]^-$  and  $[\text{WOF}_5]^{-21}$  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 ( $-18^\circ\text{C}$ ) for several weeks; the complex is decomposed by MeCN. The corresponding  $\text{AsEt}_3$  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  $\text{AsPh}_3$  nor the heavier  $\text{SbEt}_3$  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  $+130.8$  ( $\text{R} = \text{Me}$ ) and  $+134.4$  ppm ( $\text{R} = \text{Et}$ ). They did not exhibit  $^{183}\text{W}$  satellites, but the chemical shifts may be compared with those in  $[\text{WF}_6(\text{PMe}_3)]$ ,  $\delta = +133.6^{17}$  and  $\text{WF}_6$  itself,  $\delta = +167.0^{16}$ . The  $^{19}\text{F}\{^1\text{H}\}$  spectra are little changed on cooling the sample to 180 K, indicating fluxionality down to low temperatures. Fluxionality is also evident in the  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra of the pyridine complexes  $[\text{WF}_6(\text{R-py})]$  ( $\text{R} = \text{H}$  or  $\text{F}$ ) at ambient temperatures, but on cooling the solutions the separate resonances of the inequivalent fluorines of capped trigonal prismatic geometries are resolved.<sup>13,14</sup> The IR spectra have very broad strong features at 610 ( $\text{R} = \text{Me}$ ) and  $622\text{ cm}^{-1}$  ( $\text{R} = \text{Et}$ ), assigned to overlapping W-F stretches. The UV/visible spectrum of  $[\text{WF}_6(\text{AsMe}_3)]$  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,  $\text{As}(\sigma) \rightarrow \text{W}(\text{d})$ , since the  $\text{F}(\pi) \rightarrow \text{W}(\text{d})$  transitions are expected to lie in the far-UV region.<sup>22</sup>

In an attempt to increase the phosphine/arsine coordination and develop further the reaction chemistry with  $\text{WF}_6$ , the rigid *o*-phenylene ligands,  $o\text{-C}_6\text{H}_4(\text{EMe}_2)_2$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) were employed. These are amongst the strongest  $\sigma$ -donor neutral pnictines and are pre-organised for chelation. The reaction of  $\text{WF}_6$  with  $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$  or  $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$  in frozen anhydrous  $\text{CH}_2\text{Cl}_2$  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 solutions *in vacuo*. Microanalytical data and the IR spectra obtained lead to a formulation of  $[\text{WF}_4\{o\text{-C}_6\text{H}_4(\text{EMe}_2)_2\}_2][\text{WF}_7]_2$  ( $\text{E} = \text{P}$ ,  $\text{As}$ ). In particular, the IR spectra show very strong, broad features at  $\sim 615\text{ cm}^{-1}$  and a sharper, medium intensity band at  $\sim 330\text{ cm}^{-1}$ , characteristic of  $[\text{WF}_7]^-$ .<sup>23</sup> Weaker bands at  $\sim 650(\text{sh})$  and  $\sim 575\text{ cm}^{-1}$  are tentatively assigned at  $\nu(\text{WF})$  in the cations. The UV-visible spectrum of solid  $[\text{WF}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2][\text{WF}_7]_2$  shows broad features at  $20\,800$  and  $31\,500\text{ cm}^{-1}$ , the former assigned as  $\text{As}(\sigma) \rightarrow \text{W}(\text{d})$  and the latter to the  $\pi \rightarrow \pi^*$  transition of the aryl ring.<sup>24</sup> In  $[\text{WF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2][\text{WF}_7]_2$  the corresponding transitions lie at  $23\,100$ ,  $31\,650\text{ cm}^{-1}$ , the higher energy of the former compared to that in the diarsine analogue is consistent with higher electronegativity of the  $\text{P}(\sigma)$  orbital.<sup>25</sup>

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  $\text{CH}_2\text{Cl}_2$  and the dilute solutions rapidly decompose

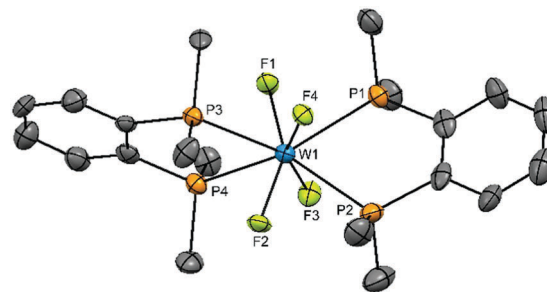


Fig. 1 The cation present in  $[\text{WF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2][\text{WOF}_5]_2\cdot\text{MeCN}$  showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{W}(1)\text{--F}(3) = 1.91(4)$ ,  $\text{W}(1)\text{--F}(2) = 1.92(4)$ ,  $\text{W}(1)\text{--F}(1) = 1.92(4)$ ,  $\text{W}(1)\text{--F}(4) = 1.93(4)$ ,  $\text{W}(1)\text{--P}(3) = 2.572(17)$ ,  $\text{W}(1)\text{--P}(1) = 2.579(18)$ ,  $\text{W}(1)\text{--P}(2) = 2.582(18)$ ,  $\text{W}(1)\text{--P}(4) = 2.592(18)$ ,  $\text{P}(3)\text{--W}(1)\text{--P}(4) = 72.6(6)$ ,  $\text{P}(1)\text{--W}(1)\text{--P}(2) = 72.8(6)$ .

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  $[\text{WF}_4\{o\text{-C}_6\text{H}_4(\text{EMe}_2)_2\}_2]^{2+}$  cations, but contain various anions, sometimes disordered. Disordered MeCN was also present in some crystals. These results are reminiscent of the  $[\text{WF}_4(2,2'\text{-bipy})_2]^{2+}$  systems described above.<sup>15,16</sup> The structures of the cations are shown in Fig. 1 and 2. The cation in  $[\text{WF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2][\text{WOF}_5]_2$  is a distorted dodecahedron with (*cis*) F-W-F angles  $\sim 94^\circ$  and  $< \text{P-W-P} \sim 73^\circ$ , the latter reflecting the constrained bite angle of the chelating ligand. The  $d(\text{W-F})$  of  $1.91(3)\text{--}1.94(3)\text{ \AA}$  are longer than those in either  $\text{WF}_6$  ( $1.826(2)\text{ \AA}$ )<sup>26</sup> or in the six-coordinate  $[\text{WOF}_4(\text{OPPh}_3)]$   $1.857(3)\text{--}1.871(3)\text{ \AA}$ ,<sup>19</sup> but similar to those in the seven-coordinate  $[\text{WOF}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)]$ ,  $1.923(9)\text{--}1.960(4)\text{ \AA}$ .<sup>20</sup> The  $d(\text{W-P}) = 2.5584(18)\text{--}2.5714(17)\text{ \AA}$ , are also similar to those in the latter complex ( $2.572(17)\text{--}2.592(18)\text{ \AA}$ ). The cation geometry is very similar to that in the isoelectronic  $[\text{TaF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]^+$ .<sup>24</sup> The  $[\text{WOF}_5]^-$  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

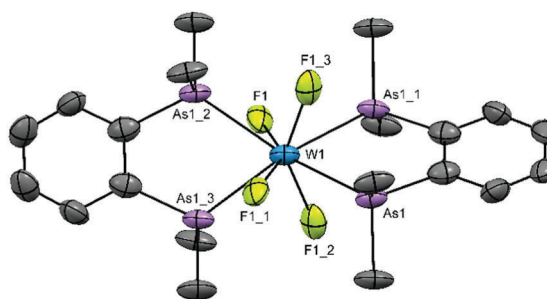


Fig. 2 The cation present in  $[\text{WF}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2][\text{WF}_8]$  showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{W}(1)\text{--F}(1) = 2.114(6)$ ,  $\text{W}(1)\text{--As}(1) = 2.6279(10)$ ,  $\text{As}(1)\text{--W}(1)\text{--As}(1) \#1 = 75.74(4)$ . 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  $^{19}\text{F}\{^1\text{H}\}$  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  $^1\text{H}$  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 ligands<sup>29</sup> 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  $[\text{WF}_7]^-$ .<sup>16,28</sup> 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  $^{183}\text{W}$  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  $^{183}\text{W}$  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.  $[\text{WF}_4(2,2'\text{-bipy})_2]^{2+}$  ( $\delta = +153$ )<sup>16</sup> 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).<sup>24,30</sup>

The diphosphine complex also exhibited a quintet  $^{31}\text{P}\{^1\text{H}\}$  NMR resonance ( $\text{CD}_3\text{CN}$ ) 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  $\text{WF}_6$  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 ( $^1\text{H}$ ,  $^{19}\text{F}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$ ) 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  $\text{WF}_6$  with  $\text{RS}(\text{CH}_2)_2\text{SR}$  ( $\text{R} = \text{Me}$ ,  $i\text{Pr}$ ) in rigorously dried  $\text{CH}_2\text{Cl}_2$  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 ( $\text{ESI}^+$ ).

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  $\text{WF}_6$  is less oxidising than the other metal hexafluorides,<sup>9</sup> 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.

We thank the EPSRC for support through EP/L505651/1, EP/N035437/1 and EP/R513325/1.

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- 1 E. F. Murphy, R. Murugavel and H. W. Roesky, *Chem. Rev.*, 1997, **97**, 3425.
- 2 B. L. Pagenkopf and E. M. Carreira, *Chem. – Eur. J.*, 1999, **5**, 3437.
- 3 H. C. S. Clark and J. H. Holloway, in *Advanced Inorganic Fluorides*, ed. T. Nakajima, B. Žemva and A. Tressaud, Elsevier, Oxford, 2000, ch. 3.
- 4 I.-S. Ke, M. Myahkostupov, F. N. Castellano and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2012, **134**, 15309.
- 5 D. Shetty, S. Y. Choi, J. M. Jeong, J. Y. Lee, L. Hoigebazar, Y.-S. Lee, D. S. Lee, J.-K. Chung, M. C. Lee and Y. K. Chung, *Chem. Commun.*, 2011, **47**, 9732; W. J. McBride, R. M. Sharkey, H. Karacay, C. A. D'Sousa, E. A. Rossi, P. Laverman, C.-H. Chang, O. C. Boerman and D. M. Goldenberg, *J. Nucl. Med.*, 2009, **50**, 991.
- 6 R. Bhalla, C. Derby, W. Levason, S. K. Luthra, G. McRobbie, G. Sanderson, W. Zhang and G. Reid, *Chem. Sci.*, 2014, **5**, 381; W. Levason, S. K. Luthra, G. McRobbie, F. M. Monzittu and G. Reid, *Dalton Trans.*, 2017, **46**, 14519; F. M. Monzittu, I. Khan, W. Levason, S. K. Luthra, G. McRobbie and G. Reid, *Angew. Chem., Int. Ed.*, 2018, **57**, 6658.
- 7 M. Carravetta, M. Concistre, W. Levason, G. Reid and W. Zhang, *Chem. Commun.*, 2015, **51**, 9555.
- 8 M. Carravetta, M. Concistre, W. Levason, G. Reid and W. Zhang, *Inorg. Chem.*, 2016, **55**, 12890.
- 9 M. J. Molski and K. Seppelt, *Dalton Trans.*, 2009, 3379.
- 10 S. L. Benjamin, W. Levason and G. Reid, *Chem. Soc. Rev.*, 2013, **42**, 1450.
- 11 F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, 1968, **7**, 172.
- 12 A. M. Noble and J. M. Winfield, *J. Chem. Soc. A*, 1970, 2574.
- 13 L. Arnaudet, R. Bougon, B. Buu, M. Lance, M. Nierlich and J. Vigner, *Inorg. Chem.*, 1993, **32**, 1142.
- 14 L. Arnaudet, R. Bougon, B. Buu, M. Lance, P. Theury, M. Nierlich and J. Vigner, *J. Fluorine Chem.*, 1995, **71**, 123.
- 15 L. Arnaudet, R. Bougon, B. Buu, M. Lance, A. Navaza, M. Nierlich and J. Vigner, *J. Fluorine Chem.*, 1992, **59**, 141.





- 16 L. Arnaudet, R. Bougon, B. Buu, M. Lance, A. Navaza, M. Nierlich and J. Vigner, *J. Fluorine Chem.*, 1994, **67**, 17.
- 17 S. El-Kurdi, A.-A. Al-Terkawi, B. M. Schmidt, A. Dimitrov and K. Seppelt, *Chem. – Eur. J.*, 2010, **16**, 595.
- 18 A. M. Noble and J. M. Winfield, *J. Chem. Soc. A*, 1970, 501.
- 19 W. Levason, G. Reid and W. Zhang, *J. Fluorine Chem.*, 2016, **194**, 50.
- 20 J. W. Emsley, W. Levason, G. Reid, W. Zhang and G. De Luca, *J. Fluorine Chem.*, 2017, **197**, 74.
- 21 L. Arnaudet, R. Bougon, B. Buu and M. Lance, *J. Fluorine Chem.*, 1991, **53**, 171.
- 22 J. H. Holloway, G. Stanger, E. G. Hope, W. Levason and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1988, 1341.
- 23 A. Beuter, W. Kuhlmann and A. Sawodny, *J. Fluorine Chem.*, 1975, **6**, 367.
- 24 W. Levason, M. E. Light, G. Reid and W. Zhang, *Dalton Trans.*, 2014, **43**, 9557.
- 25 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 2nd edn, 1984.
- 26 T. Drews, J. Supel, A. Hagenbach and K. Seppelt, *Inorg. Chem.*, 2006, **45**, 3782.
- 27 R. Bougon, T. Bui Huy and P. Charpin, *Inorg. Chem.*, 1973, **14**, 1822.
- 28 S. G. Sakharov, Y. V. Kokunov, M. P. Gustyakova and Y. A. Buslaev, *Dokl. Akad. Nauk SSSR*, 1984, **276**, 148.
- 29 W. Levason, K. G. Smith, C. A. McAuliffe, F. P. McCullough, R. D. Sedgwick and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1979, 1718.
- 30 W. Levason, G. Reid, J. Trayer and W. Zhang, *Dalton Trans.*, 2014, **43**, 3649.

