Tungsten(VI) and Tungsten(V) Fluoride Complexes

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Abstract: WF_6 reacts with phosphines R_3P forming 1:1 compounds. With $R = P(CH_3)_3$ the coordination around the tungsten atom is capped trigonal prismatic, with $R = P(CH_3)_2C_6H_5$ the coordination is capped octahedral, as established by single-crystal structure determinations: $[(CH_3)_3P-WF_6]$: $a = 752.5(21)$, $b = 945.7(24)$, $c = 629.8(18)$ pm. $\beta = 110.36(13)°$, space group Cm, $Z = 2$; $[(CH_3)_2(C_6H_5)P-WF_6]$: $a = 762.2(2)$, $b = 1123.5(2)$, $c = 2647.5(6)$ pm, space group $Pbca$, $Z = 8$. $[(CF_3CH_2)_2N-WF_5]$ reacts smoothly with $P(C_6H_5)_3$ forming known P-$(C_6H_5)_3(F)_2$ and $[(CF_3CH_2)_2N-WF_4-P-(C_6H_5)_3]$, a stable, green, molecular species, identified among other methods with an crystal structure determination: $a = 914.9(1)$, $b = 956.0(1)$, $c = 1449.8(2)$ pm, $\alpha = 7.642(4)$, $\beta = 81.648(3)$, $\gamma = 81.519°$, space group $P\bar{1}$, $Z = 2$.

Keywords: coordination modes · EPR spectroscopy · fluorides · tungsten · Raman spectroscopy

Introduction

The sixteen molecular hexafluorides[1] are a fascinating group of compounds because of their similar and different physical and chemical properties. This is particularly true for the five 5d hexafluorides WF_6 through PtF_6.[2] These are oxidants with moderate (WF_6) up to extreme (PtF_6) oxidation power.[3] Each hexafluoride is a stronger oxidant than the previous one. This is also reflected in their electron affinity.[3] For example, Cl_2 and ReF_6 do not react, OsF_6, dissolved in liquid chlorine forms a dark blue charge transfer complex that dissociates upon crystallisation, and IrF_6 oxidizes Cl_2 forming the rectangular Cl_4^+ cation.[4]

In the present work the transition between complex formation and redox chemistry of tungsten(VI) fluorides with phosphanes is studied. WF_6 has already been reacted with trimethyl phosphine.[5] The product was solely identified by its ^{19}F NMR spectrum, which showed a doublet assigned to coupling to ^{31}P. This spectrum, with a chemical shift of 135.5–137.4 pm, points to a tungsten(VI) fluoride compound and rules out the presence of a tungsten(V) species.

Tungsten hexafluoride has often been subjected to nucleophilic substitution reactions for which oxygen,[6–12] nitrogen[13–17] and carbon groups are predominant.[18,19] Among the nitrogen derivatives $[(CF_3CH_2)_2N-WF_5]$ is a particularly stable compound, in contrast to other nitrogen derivatives. So far a pronounced acidity of the CH_2-hydrogen atoms has been established.[13]

Among the many possible oxidation states of tungsten, the oxidation state V has certainly the smallest number of examples. Tungsten pentahalides are described, but even WF_5 tends to disproportionate at slightly elevated temperatures. Few examples are made from tungsten(VI) halide starting materials and rigorous reducing agents like Na/Hg,[20] $LiBH_4$.[21] If usual analogies hold then complex tungsten(V) fluoride compounds should be very susceptible towards disproportionation, but to the best of our knowledge are completely unknown.

Results and Discussion

The reaction between $P(CH_3)_3$ and WF_6 takes place spontaneously under formation of an orange solution and a yellow crystallite. The compound is characterized by the usual physical methods (see the Experimental Section). The ^{19}F NMR spectrum is identical to the one previously observed by Tebbe and Muetterties.[5] Owing to rapid ex-

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Table 1. Important bond lengths [pm] and angles [°] from single-crystal structure determinations.

	[(CH$_3$)$_3$P−WF$_6$]	[(C$_6$H$_5$)(CH$_3$)$_2$P−WF$_6$]	[(CF$_3$CH$_2$)$_2$N−WF$_4$ −P(C$_6$H$_5$)$_3$]
W−F	182.1(15)–189.4(13 (6×)	186.1–188.8(3) (6×)	184.5–191.2(3) (4×)
W−N	–	–	194.4(4)
W−P	259.8(9)	256.4(1)	269.9(1)
P−C	179.0–183.1(2)	179.3–180.3(4) (3×)	183.3–182.0(4) (3×)
N−C	–	–	184.0(6)
F-W-F	76.6–96.4(10)(9×), 124.7–130.9(6)(4×), 150.6(6)(2×)	79.8–86.6(1)(9×), 107.0–113.6(1)(3×), 159.2–163.3(1)(3×)	88.5–92.0(1) (4×), 160.5(1), 178.8(1)
N-W-F	–	–	89.4-101.8(2) (4×)
P-W-F	73.8–77.9(5)(4×), 134.9(9), 146.1(7)	69.96–70.95(8)(3×), 125.78–130.7(8)(3×)	77.5–90.9(1) (4×)
C-P-C	107.6–108.0(10)	107.9–109.5(2)	105.0–106.4(2) (3×)
C-N-C	–	–	113.9(4)
W-N-C	–	–	122.4, 123.6(4)

change, only one type of fluorine atom is observed in solution. The exact nature of the compound is revealed by its single-crystal structure determination, see Tables 1 and 2, and Figure 1. The complex formed, has a seven coordinated tungsten atom with a capped trigonal prism geometry, so that the overall symmetry is C_s with the phosphorous ligand taking the capping position.
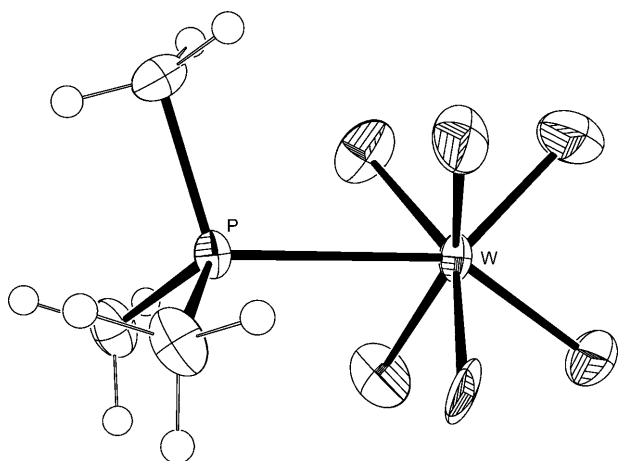

Figure 1. The structure of [(CH$_3$)$_3$P−WF$_6$] in the crystal, ORTEP representation, 50 % probability ellipsoids.

The bond between W and P must be considered weak, as the compound has a detectable dissociative vapour pressure at room temperature. Other phosphanes have been tested: Although there is little doubt that this is a general reaction, the compounds produced with P(C$_2$H$_5$)$_3$ and P(C$_6$H$_3$)$_3$ could not be identified properly. The first is an orange oil, which decomposes in attempts of distillation and does not crystallize. The product of P(C$_6$H$_5$)$_3$ with WF$_6$ is a red solid, insoluble in all polar, non polar, halogenated organic solvents, also in anhydrous HF, and decomposes above 50 °C.

Surprisingly the compound [(CH$_3$)$_2$(C$_6$H$_5$)P−WF$_6$] is formed readily. It is a dark red compound. Its single-crystal structure determination shows again a molecular adduct. Here, however, the coordinative sphere around the tungsten

atom is a capped octahedron, where the phosphorous atom takes the capping position, see Tables 1 and 2, and Figure 2. A capped octahedral structure is also observed in [Cs]$^+$ [WF$_7$]$^-$.[8] The observed isomerism is yet another proof that the different possible structures of compounds with the coordination number 7 are very close in energy.
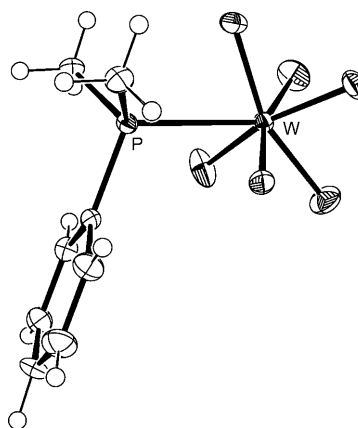

Figure 2. The structure of [(C$_6$H$_5$)(CH$_3$)$_2$P−WF$_6$] in the crystal, ORTEP representation, 50 % probability ellipsoids.

We have calculated the energy of [H$_3$P−WF$_6$] in three possible forms: capped octahedral (C_{3v}), capped trigonal prismatic (C_s), and pentagonal bipyramidal (also C_s), see Table 3, with various methods and basis sets. Shown in Table 3 are ab initio MP2 calculations with triple-ζ basis sets for the light atoms and a similar basis set for the 14 outer electrons on the tungsten atom, and describing its 60 core electrons by a relativistic corrected-core potential. Density functional methods like Becke 3 LYP fail to describe the rather weak W−P bond: In case of the capped trigonal prism the W−P bond length comes out too long by 20 pm, in the case of the capped octahedron the complex dissociates into WF$_6$ and PH$_3$. The capped trigonal prism is always the ground state, the capped octahedral state is a transition state about 7.5 kcal mol^{-1} higher in energy. Owing to the trigonal symmetry of the PH$_3$ group the pentagonal bipyra-

Table 2. Crystal data and structure refinements.

Formula	[(CH$_3$)$_3$P−WF$_6$]	[C$_6$H$_5$(CH$_3$)$_2$P−WF$_6$]	[(CF$_3$CH$_2$)$_2$N−WF$_4$−P(C$_6$H$_5$)$_3$]
formula weight [g mol^{-1}]	373.9	435.9	702.2
temperature [°C]	−140	−140	−60
space group	monoclinic, Cm	orthorhombic, Pbca	triclinic, P$\bar{1}$
a [pm]	752.5(21)	762.2(2)	914.9((1)
b [pm]	954.7(24)	1123.5(2)	956.0(1)
γ [pm]	629.8(18)	26475(6)	1449.8(2)
α [pm]	90	90	74.642(4)
b [pm]	110.36(13)	90	81.648(3)
γ [pm]	90	90	81.519(3)
V [10^6 pm^3]	424.15	2267.05	1202.04
Z	2	8	2
ρ_{calcd}[Mg m^{-3}]	2.928	2.555	1.940
μ[mm^{-1}]	13.84	10.38	4.96
reflections			
collected	3291	37471	14702
unique	1125	3461	7211
θ_{max}[°]	61.1	61.1	61.1
R_{int}	0.0758	0.0357	0.0401
parameters	65	179	392
R_1[$I \geq 2\sigma(I)$]	0.0632[a]	0.0266	0.0391
wR_2	0.1575	0.0553	0.0810
GOOF	1.080	1.095	0.924

[a] The only moderate quality of the crystal structure is owed to imperfect crystallisation. All tested crystals were imperfect owing to residual twinning. This is evident if the reduced cell is considered: $a = 606.9$, $b = 608.7$, $c = 629.8$ pm, $\alpha = 102.33$, $\beta = 102.56$, $\gamma = 103.51°$.

midal state has C_s symmetry like the capped trigonal prismatic state and therefore collapses to the ground state if the five P-W-F (equatorial) angles are not kept equal. This state is 21.0 kcal mol^{-1} higher in energy than the capped trigonal prismatic ground state, see Table 3. It is safe to assume that different packing owing to the different substitution pattern on the phosphorous atom is influential enough to overcome the small energy barrier between C_{3v} and C_s.

For comparison calculations on the three forms of WF$_7^-$ are also shown in Table 3. Capped octahedron and capped trigonal prism differ only marginally in energy, whereas the pentagonal bipyramidal form is slightly higher. This may be yet another indication of the effect that d^0 transition metal complexes avoid 90° and 180° bond angles. Even octahedral WF$_6$ has a trigonal bipyramidal transition state only 11 kcal mol^{-1} higher in energy, so that the substituted derivative [C$_6$F$_5$−OWF$_5$] shows intramolecular ex-

change of the different fluorine atoms at the high temperature limit.[22]

Variation on the tungsten side by using the fairly stable [(CF$_3$CH$_2$)$_2$N−WF$_5$] resulted in a surprise:

In contrast to the expectation of an adduct formation a very smooth redox reaction sets: [(CF$_3$CH$_2$)$_2$N−WF$_5$]+1.5 P-(C$_6$H$_5$)$_3$→[(CF$_3$CH$_2$)$_2$N−WF$_4$−P(C$_6$H$_5$)$_3$]+0.5 P(C$_6$H$_5$)$_3$(F)$_2$.

The by-product P(C$_6$H$_3$)$_3$(F)$_2$ has previously been described. It is identified by its ^{19}F, and ^{31}P NMR spectra,[23,24] and its crystallographic characteristics.[25] The novel tungsten(V) compound is a green stable material, it is obtained in high yield. Owing to its paramagnetism no NMR data can be obtained. The vibrational spectra (see the Experimental Section) show some of the characteristic bands of the -CH$_2$-, -CF$_3$, C$_6$H$_5$, and WF$_4$ groups.

In solution it has only a very intense and broad EPR signal. Upon cooling to −160 K the EPR spectrum shows some fine structure, see Figure 3. No straightforward assignment of this is possible; a multitude of hyperfine interactions can be expected, owing to the nuclear species of ^{31}P, ^{19}F, ^{1}H, and ^{14}N.

In the crystal the compound appears as a molecule with no significant intermolecular interactions. The environment around W is close to octahedral (Figure 4). The P atom occupies a position trans to N. The P−W bond distance is fairly large (269.9(1) pm). This interaction is longer than in the closest related compound [(CH$_3$)$_2$(C$_6$H$_5$)P−W(Cl)$_3$(OC$_6$H$_3$-2,4-C$_6$H$_5$)$_2$] (257.9 pm).[7] Electronegativity differences between Cl and F ligands would predict the opposite behaviour.

Table 3. Ab initio MP2 calculations of [H$_3$P−WF$_6$] and WF$_7^-$.

	[H$_3$P−WF$_6$], C_s	[H$_3$P−WF$_6$], C_{3v}	[H$_3$P−WF$_6$], "C_s"[a]	WF$_7^-$, C_s	WF$_7^-$, C_{3v}	WF$_7^-$, D_{5h}
energy [a.u.]	−1008.1353719	−1008.1234582	−1008.101861	−765.3351811	−765.3350977	765.3341626
energy, rel. [kcal mL^{-1}]	0	7.48	21.0	0	0.05	0.64
imaginary frequency [cm^{-1}]	–	30.8i	−1114i; −106.6i	–	10.7i	44.1i
bond lengths [pm]						
W−P	270.6	270.9	264.2	–	–	–
W−F	186.6(2×)	187.5(3×)	188.2(5×)	189.9	189.0	185.5(2×)
	186.0 (2×)	184.4(3×)	181.3	187.9(4×)	187.8(3×)	190.0(5×)
	184.4(2×)			188.7(2×)	188.9(3×)	
P−H	134.0(3×)	134.0(3×)	139.8(3×)	–	–	–

[a] Enforced pentagonal bipyramidal structure by fixing one angle, actual symmetry is C_s
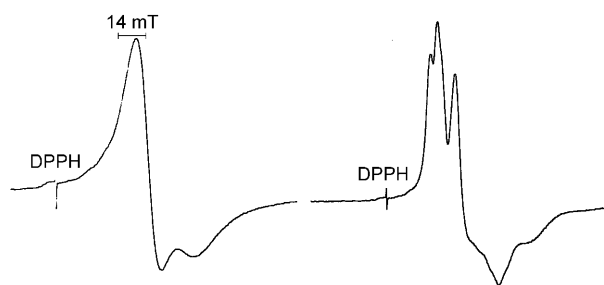
Figure 3. EPR Spectrum of $[(CF_3CH_2)_2N-WF_4-P(C_6H_5)_3]$ at room temperature (left) and at 160 K (right).
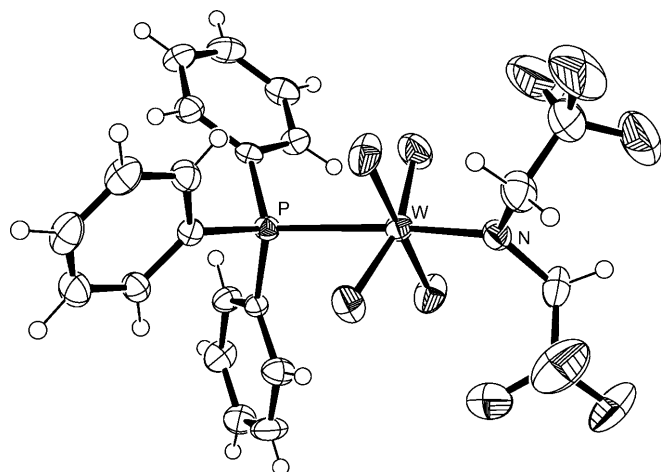
Figure 4. The structure of $[(CF_3CH_2)_2N-WF_4-P(C_6H_5)_3]$ in the crystal, ORTEP representation, 50% probability ellipsoids.

The clearly higher—even if small—oxidation capacity of $[(CF_3CH_2)_2N-WF_5]$ with respect to WF_6 may be counter intuitive, but some time ago it was shown by using electrochemical experiments that WCl_6 is a stronger oxidant than WF_6.[26] This may be the reason why WCl_6-phosphine complexes are unknown so far.

Experimental Section

Caution: Handling WF_6 and its derivatives requires eye and skin protection.

Materials: $P(CH_3)_3$, $P(C_2H_5)_3$, $P(C_6H_5)_3$ and $P(CH_3)_2(C_6H_5)$ are commercially available. WF_6 in a stainless steel container is from laboratory stock. $[(CF_3CH_2)_2N-WF_5]$ is prepared according to literature methods.[15]

Physical measurements: The IR spectra were recorded by using a Perkin–Elmer 883 instrument, the Raman spectra by using an instrument of type 1403 of Spex Industries, 1064 nm, 300 mW; and the NMR spectra by using a JEOL JNM-LA 400 instrument for ^1H, ^{19}F, and ^{13}C. Chemical shifts are given for $CFCl_3$ and tetramethylsilane as standards. Dry-boxes for the use of water-sensitive compounds were obtained from Brown GmbH (Munich, Germany). The EPR spectra were recorded by using an ER 200D-SRIC spectrometer, B-E 25 magnet (Bruker Co, Germany) with a standard diphenylpicrylhydroxyl (DPPH) $g = 2.0037$.

Single crystals are handled with cooling to $-100°C$ under nitrogen in a special device[27] and mounted on a Bruker SMART CCD 1000 TK dif-

fractometer, using MoKα radiation, a graphite monochromator, a scan width of 0.3° in ω, and a measuring time of 20 sec per frame. $2\theta_{max} = 61°$, 1800 frames, covering a full sphere. Semiempirical absorption correction is done by equalizing symmetry equivalent reflections (SADABS). The structure is solved and refined with the SHELDRICK programs.[28] Experimental details are given in Table 2.

Complex $[(CH_3)_3P-WF_6]$: $P(CH_3)_3$ (0.5 g, 6.6 mol), CH_2Cl_2 (15 mL), and WF_6 (1.96 g. 6.6 mol) are subsequently condensed into a Schlenk flask. The mixture is warmed to $-60°C$ and stirred for several minutes to produce a deeply red solution. Warming to room temperature for 30 min and cooling to $-40°C$ produces orange crystals, yield 2.2 g (90%), mp 144–146°C. The product is recrystallized from CH_3CN at $-15°C$. ^1H NMR (400 MHz, CD_3CN): $\delta = 2.26$ ppm ($^2J_{PH} = 13.6$ Hz); ^{19}F NMR (376.3 MHz, CD_3CN): $\delta = 133.6$ pm, ($^2J_{PF} = 74$ Hz); ^{31}P NMR (161.9 MHz, CD_3CN): $\delta = 115.5$ ppm (m); Raman (solid): $\tilde{\nu} = 2997(m)$, 2925(s), 1423(m), 1304(w), 951(m), 849(w), 688(s), 673 sn,sh), 609(w), 533(w), 417(m), 345(vs), 307(m), 272(s), 195(vs), 118 cm^{-1} (w); IR (nujol): $\tilde{\nu} = $ 1424(m), 1415(m), 1290(s), 959(s), 851(s), 763(s), 620–500 cm^{-1} (s,br); Owing to a low vapour pressure no elemental analysis could be performed.

$[(C_6H_5)(CH_3)_2P-WF_6]$: WF_6 (2.3 g, 7.6 mol) is condensed in vacuum into a 50 mL Schlenk flask containing a frozen solution of $P(CH_3)_2(C_6H_5)$ (1 mL, 7.6 mmol), dissolved in CH_2Cl_2 (15 mL). The mixture is warmed to $-60°C$, stirred for several minutes to form a deeply red solution, then warmed to room temperature for one hour and cooled to $-40°C$ to produce a red, crystalline solid, yield 3.1 g (94%), mp 71–75°C. The product is recrystallized from CH_2Cl_2 for the growth of single crystals. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.5–7.8$ (C_6H_5), 2.31 ppm ($^2J_{HP} = 14.5$ Hz; CH_3); ^{19}F NMR (376.3 MHz, CD_2Cl_2): $\delta = 136.54$ ppm; ^{31}P NMR (161.9 MHz, CD_2Cl_2): $\delta = 96.6$ ppm; Raman (solid): $\tilde{\nu} = 3077(w)$, 3060(m), 3007(m), 2927(m), 1584(m), 1435(w), 1415(w), 1195(w), 1166(w), 1116(m), 1031(m), 999(s), 954(w), 918(w), 773(w), 751(w), 735(w), 684(s), 641(w), 616(w), 569(vw), 551(vw), 480(w) 420(s), 359(w), 324(s), 280(w), 270(w), 206(w,sh), 179(s), 98 cm^{-1} (vs); IR (Nujol): $\tilde{\nu} = 1435$ (s9, 1419(s), 1343(m), 1316 (m), 1307(m), 1293(m), 1115(s), 987(m) 961(s), 925(m), 916(m), 877(s), 734(s), 620–541(s,br), 469(s), 419 cm^{-1} (s); elemental analysis (%) calcd $C_8H_{11}F_6PW$: C 22.04, H 2.54; found: C 21.68, 21.93, H 2.61, 2.79.

Attempts to obtain $[(C_2H_5)_3P-WF_6]$ and $[(C_6H_5)_3P-WF_6]$: The reaction between $P(C_2H_5)_3$ and $P(C_6H_5)_3$ with WF_6 is done in a similar fashion as with $P(CH_3)_3$ and $P(CH_3)_2(C_6H_5)$. $[(C_2H_5)_3P-WF_6]$ is possibly also formed as a red oil. Recrystallizations from various solvents remained unsuccessful. The NMR data indicated a similar composition as $[(CH_3)_3P-WF_6]$.

The reaction between $P(C_6H_5)_3$ and WF_6 produces a brick red solid, insoluble in all possible solvents. Heating above $+60°C$ decomposed the material. Purification and characterisation of both adducts remained unsuccessful.

In all of the four reactions of phosphanes, $WF_6 \cdot PF_2(R)_3$ has been formed only in trace amounts, as detected by NMR spectroscopy.

$[(CF_3CH_2)_2N-WF_4-P(C_6H_5)_3]$: In a glove box $[(CF_3CH_2)_2N-WF_5]$ (305 mg, 0.65 mmol) and $P(C_6H_5)_3$ (262 mg, 1.0 mol) are filled into a PFA (Polyperfluorovinylether-tetrafluoroethylene-copolymerisate) reaction tube of 1 cm inner diameter. 4 mL dry CH_2Cl_2 are condensed on it with a vacuum line. Upon warming to room temperature the colour changes from red to green within few minutes. The resulting solution is cooled slowly within 14 hr to $-80°C$, and colourless needles of $(C_6H_5)_3PF_2$ crystallizes out. The supervalent solution is transferred with a teflon capillary into a second PFA tube. The solvent is pumped off, then the green solid is washed with very little resulting in 0.4 g (0.56 mmol, 87% yield) mp 99.1–101.5°C. IR(KBr): $\tilde{\nu} = 3065(w)$, 3960(w), 1333(m), 1310(m), 1259(s), 1209(m), 1171(s), 1155(s), 1115(w), 1100(m), 1082(m), 1024(s), 999(m,sh), 930(w), 837(m), 746(m), 729(m), 692(m,sh), 662(m), 627(w), 602(w), 573(w), 557(w), 524(w), 496(w), 419 cm^{-1} (m); Raman (solid): $\tilde{\nu} = $ 3063(m), 2965(w), 1586(m), 1576(w), 1198(w), 1160(w), 1096(m), 1027(m), 1001(vs), 928(w), 823(w), 686(m), 675(w), 656(w), 616(m), 572(vw), 546(w), 523(vw), 416(vw), 388(vw), 364(vw), 290(m), 247(s), 227(m), 215(m), 194(s), 163 cm^{-1} (s); Raman (CH_2Cl_2): $\tilde{\nu} = 1587(w)$,

1574(vw), 1114(vw), 1096(vw), 1028(w), 998(m), 930(w), 822(w), 731(s), 658(w), 616(w), 523(vw), 248 cm^{-1} (m); EPR Spectrum, band: $g = 1.9365$, 14 mT half width, see Figure 3.

Ab initio MP2 calculations: Gaussian 03, Revision D.01 program package,[29] basis sets for C,H,F,P,N: cc-pVTZ, as implemented in the program. W: 8s7p6d2f1g/6s5p3d2f1g basis set and relativistically corrected core potential for 60 electrons.[30]

CCDC-744037, 744036, and 744035 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

[1] SF$_6$, SeF$_6$, TeF$_6$, XeF$_6$, MoF$_6$, TcF$_6$, RuF$_6$, RhF$_6$, WF$_6$, ReF$_6$, OsF$_6$, IrF$_6$, PtF$_6$, UF$_6$, NpF$_6$, PuF$_6$.

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