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THE REACTION BETWEEN TUNGSTEN HEXAFLUORIDE AND PENTAFLUOROANILINE

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Abstract—Tungsten hexafluoride reacts with pentafluoroaniline to give a mixture containing the imido anions $[WF_5(NC_6F_5)]^-$ and $[W_2F_9(NC_6F_5)_2]^-$. From the solution in CF_3COOH the salt $C_6F_5NH_3^+[(C_6F_5N)WF_4(F)WF_4(NC_6F_5)]^-$ was isolated and its X-ray crystal structure determined. In the crystal there are two crystallographically distinct anions, both with fluorine bridges; in one the WFW angle is 150.8° and in the other 170.4°. The average W—N distance in the linear WNC units is 1.74 Å. A ^{19}F NMR study in MeCN suggests the anions to be linear in solution.

It has previously been shown that primary amines will react with WF_6 to produce imido–tungsten fluoride species of the type $[WF_5(NR)]^-$ [eqs (1) and (2)][1,2] and the neutral species $[WF_4(NR)\cdot MeCN]$ (R = Me;[1] R = H, Bu^t[2]).

$$WF_6+2RNH_2 \rightarrow [RNH_3]^+[WF_5(NR)]^- + HF \quad (1)$$

$$WF_6+3RNH_2 \rightarrow [RNH_3]^+[WF_5(NR)]^- + [RNH_3]^+F^-. \quad (2)$$

The combination of WF_4NMe and $[WF_5(NMe)]^-$ to form the fluorine bridged, dimeric anion $[W_2F_9(NMe)_2]^-$ has also been observed.[1] Although the structures of the chloro-derivatives $[Ph_4As]^+[WCl_5(NC_2Cl_5)]^-$[3] and $[Cl_4W{=}(NC_2Cl_5)]_2$[4] have been determined in the solid state by single crystal X-ray methods, the alkyl–imido fluoride compounds prepared to date have only been characterized in solution by NMR spectroscopy.

We report here the isolation and characterization of the salt $[C_6F_5NH_3]^+[(C_6F_5N)WF_4(F)WF_4(NC_6F_5)]^-$ from the products of the reaction between pentafluoroaniline and tungsten hexafluoride; other studies have been made of this reaction in acetonitrile and trifluoroacetic acid solutions and also of the behaviour of pentafluoroaniline towards molybdenum and rhenium hexafluorides.

EXPERIMENTAL

Standard vacuum line techniques were used with a metal manifold and FEP reaction tubes, attached to the manifold via Chemcon PTFE needle valves, to prepare all products. The air-sensitive products were manipulated in autorecirculating positive pressure dry boxes (VAC, model HE 42-2 Dri-Lab). IR spectra were recorded in the range 4000–350 cm^{-1} as dry solids ground between KBr plates using a Perkin–Elmer 580 spectrometer. Mass spectra were recorded at 70 eV using a V.G. Micromass 16B spectrometer. NMR spectra were recorded on a Bruker AM-300 spectrometer at 282.408 MHz (^{19}F) with $CFCl_3$ as external reference.

Reagents

2,3,4,5,6-Pentafluoroaniline (Aldrich) was stored in a nitrogen dry box and re-sublimed before use. Acetonitrile (BDH spectroscopic grade) was twice distilled from phosphorus pentoxide, to remove traces of moisture, and stored over molecular sieves (type 4A) activated at 390°C.

Tungsten hexafluoride (Allied Chemicals Ltd) and molybdenum hexafluoride (Ozark Mahoning Ltd) were stored over sodium fluoride before use. Rhenium hexafluoride was prepared by heating rhenium metal powder (Johnson Matthey Chemicals Ltd) with fluorine in a nickel can for 4 h at 390±10°C. The product was stored in the nickel can and used as required. Trifluoroacetic acid (Lancaster Synthesis) was twice distilled from phosphorus pentoxide and stored in a seasoned Pyrex container. Chlorine trifluoride (Ozark Mahoning Ltd) was used as supplied.

Syntheses

Reaction of $C_6F_5NH_2$ *with* WF_6. Typically $C_6F_5NH_2$ (0.59 mmol), dissolved in Genetron 113,

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was treated at $-80°C$ with an excess of WF_6 (2.15 mmol) and the mixture allowed to warm slowly to room temperature. A lemon coloured precipitate was formed immediately without gas evolution. This yellow solid and the solution above it was then gently warmed for 15 min to about 30°C and left to stand at room temperature for 2 h. The excess of WF_6 and Genetron solvent were distilled from the reaction tube and the remaining, non-volatile, lemon solid warmed to 45°C under dynamic vacuum to ensure removal of any unreacted amine. The yellow solid (m.p. 140°C), which is believed to be a mixture containing $[C_6F_5NH_3]^+[WF_5(NC_6F_5)]^-$; $[C_6F_5NH_3]^+F^-$ and $[C_6F_5NH_3]^+[W_2F_9(NC_6F_5)_2]^-$, gave a complicated IR spectrum: ν(N—H) 2800–2600 (s.br) cm^{-1}; ν(N—H) 1600(s), 1500(s) cm^{-1}; ν(C—C) 1600–1450(m) cm^{-1}; ν(C—F) 1400–1000(m) cm^{-1}; ν(W=N) 1000(s) cm^{-1}; ν(W—F) 660–600, 550(s) cm^{-1}. Mass spectrum: Assignment $[M^+/e]$ intensity (%); $^{184}WF_4NC_6F_5^+$[441]20; $^{184}WF_3NC_6F_5^+$[422]5; $^{184}WF_5^+$[279]15; $^{184}WF_4^+$[260]17; $^{184}WOF_3^+$[275]15; $^{184}WF_3^+$[241]5; $^{184}WF_2^+$[222]3; $^{184}WF^+$[203]2; $^{184}W^+$[184]40; $C_6F_5NH_3^+$[184]24; $C_6F_5NH_2^+$[183] 100. The solid was insoluble in Genetron 113 and in excess of WF_6, but dissolved readily in MeCN and TFA to give yellow solutions. ^{19}F NMR (Tables 1 and 2) showed several species to be present including $[WF_5NC_6F_5]^-$, $[W_2F_9(NC_6F_5)_2]^-$, $[C_6F_5NH_3]^+$, WOF_4 and WOF_5^-.

Solid recrystallized from TFA. An orange solid was recrystallized from a trifluoroacetic acid (TFA) solution of the original yellow material. The ^{19}F NMR spectrum (Table 2) showed the presence of the dimeric anion salt $[C_6F_5NH_3]^+[W_2F_9(NC_6F_5)_2]^-$ and the fluorinated species only. The IR spectrum possessed fewer bands than the original yellow solid ν(N—H) 1500(s) cm^{-1}; ν(C—C), ν(C—F) 1600–1000(m) cm^{-1}; ν(W=N) 1000(s) cm^{-1}; ν(W—F) 660, 600(s) cm^{-1}; ν(W—F—W) 500(m) cm^{-1}. A crystal grown from TFA proved suitable for an X-ray crystallographic study.

Reaction of $C_6F_5NH_2$ *with* MoF_6. When $C_6F_5NH_2$ (0.29 mmol) dissolved in Genetron was treated as above with an excess of MoF_6 (0.78 mmol), there formed immediately a dark, maroon solid with effervescence of the solution, and a slight staining of the reaction tube wall. After quenching with liquid nitrogen (LN) and re-warming to room temperature a maroon solid settled out from the orange Genetron solution, which did not dissolve even in warm Genetron. An IR spectrum of the volatile components showed the presence of Genetron and MoF_6 only. The reaction mixture was left to stand overnight at room temperature before distilling the volatile compounds from the reaction tube. The air-sensitive solid did not produce an X-ray powder pattern and a mass spectrum yielded fragmentation patterns of oxyfluorides only. The solid dissolved readily in MeCN, but attempts to grow crystals suitable for crystallographic study were not successful. The IR spectrum showed similar features to the product of the reaction with WF_6. IR: ν(N—H)$[C_6F_5NH_3]^+F^-$ 2640(br) cm^{-1}; 1600(s) cm^{-1}; ν(N—H)$[C_6F_5NH_3]^+$ 1500(m) cm^{-1}; ν(C—C), ν(C—F) 1650–1000(m) cm^{-1}; ν(Mo=N) 1010(m) cm^{-1}; ν(Mo—F) 750, 600(br) cm^{-1}. This solid is believed to contain $[C_6F_5NH_3]^+[MoF_5NC_6F_5]^-$.

Reaction of $C_6F_5NH_2$ *with* ReF_6 *and treatment of the product with* ClF_3. An excess of ReF_6 (1.23 mmol) was distilled at $-80°C$ onto a Genetron solution of $C_6F_5NH_2$ (0.59 mmol) and the mixture allowed to warm slowly to room temperature. A dark solid formed at the liquid–liquid junction, with purple staining of the reaction tube wall, and the solution subsequently became completely dark with effervescence. The mixture was allowed to stand at room temperature overnight. A dark solid settled out from the light red coloured Genetron solution. The non-volatile, air-sensitive solid gave an IR spectrum similar to that of the yellow WF_6 reaction product. IR: 1700(m) cm^{-1}; 1680(m) cm^{-1}; 1600(m) cm^{-1}; ν(N—H)$[C_6F_5NH_3]^+$ 1500(s) cm^{-1}; ν(C—C), ν(C—F) 1600–1000(m) cm^{-1}; ν(Re=N)? 1102(m), 1000(m) cm^{-1}; ν(Re—F) 650–600(s) cm^{-1}. The mass spectrum of the solid showed patterns associated with rhenium oxyfluorides, ReF_3N and $C_6F_5NH_2$ only. The dark solid is believed to be a mixture containing the neutral compound $ReF_4(NC_6F_5)$ and $[C_6F_5NH_3]^+F^-$.

CAUTION! Treatment with ClF_3. The dark solid (22 mg) was treated with ClF_3 in the manner described in previous work.[5] From the orange oil produced, a small amount of purple ReF_5(NCl)[5] was sublimed.

Crystallography: crystal data: $W_4C_{36}H_6F_{48}N_6$, $M = 2169.79$, Triclinic $P\bar{1}$, $a = 15.393(41)$, $b = 17.723(27)$, $c = 11.375(50)$ Å, $\alpha = 78.6(2)$, $\beta = 98.0(2)$, $\gamma = 111.3(1)°$, $U = 2827.2$ Å^3, $Z = 2$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu = 79.35$ cm^{-1}, $F(000) = 1983.6$, $d_x = 2.548$ g cm^{-3}.

The crystal used for data collection was yellow, wedge-shaped with approximate dimensions of $0.46 \times 0.12 \times 0.09$ mm. The intensities of 8730 unique reflections with $2\theta < 50°$ and ($\pm h$, $\pm K$, 0–12L) were measured on a STOE Stadi-2 Weissenberg diffractometer, with graphite monochromated Mo-K_α radiation using an omega-scan technique. The data were corrected for Lorentz and polarization effects to yield 3046 reflections with $|F_o| > 5\sigma(|F_o|)$.

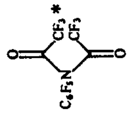
Table 1. ^{19}F NMR chemical shifts and coupling constants for the MeCN solutions of the product from ($WF_6+C_6F_5NH_2$)

Assignment	Spectral form	Chemical shift (relative to $CFCl_3$) (ppm) δF_X	δF_A	δF_o	δF_m	δF_p	Spin–spin coupling constants (Hz) $J_{F_A\text{—}F_X}$	$J_{F_X\text{—}^{183}W}$	$J_{F_o\text{—}F_m}$	$J_{F_p\text{—}F_m}$	Approx. relative molar ratio
WOF_4	X_4	67.1	—	—	—	—	—	68.9	—	—	10
$[\mathrm{WO}\mathit{F}_4\text{—}\mathrm{F_A}\text{—}\mathrm{WF_4R}]^-$	AX_4[a]	62.8	−127	—	—	—	58	70.9	—	—	51
$[\mathrm{WOF_4}\text{—}\mathrm{F_A}\text{—}\mathrm{W}\mathit{F}_4\mathrm{R}]^-$	AX_4[a]	61	−127	—	—	—	64.7	40.9	—	—	
$[\mathrm{WOF_4}\text{—}\mathrm{F_A}\text{—}\mathrm{WF_4}\mathit{R}]^-$		—	—	−144.32	−161.26	−152.34	—	—	~ 14	~ 20	
$[\mathrm{R}\mathit{W}\mathit{F}_4\text{—}\mathrm{F_A}\text{—}\mathrm{WF_4R}]^-$	AX_4	61.9	−110	—	—	—	64.7	39	—	—	126
$[\mathit{R}\mathrm{WF_4}\text{—}\mathrm{F_A}\text{—}\mathrm{WF_4}\mathit{R}]^-$		—	—	−147.1	−163.7	−153.31	—	—	~ 14	~ 20	
$[\mathrm{F_A}\text{—}\mathrm{W}\mathit{F}_4\mathrm{R}]^-$	AX_4	52.5	−63	—	—	—	64.7	41.8	—	—	250
$[\mathrm{F_A}\text{—}\mathrm{WF_4}\mathit{R}]^-$		—	—	−148.20	−163.9	−156.08	—	—	~ 14	~ 20	
$[\mathrm{WOF_4}\text{—}\mathrm{F_A}]^-$	AX_4	50.6	−94.2	—	—	—	53.6	71.3	—	—	41
$[WF_4R]$(?)[b]		—	—	−146.36	−162.63	−151.14	—	—	~ 14	~ 20	50
$[C_6F_5NH_3]^+$		—	—	−153.66	−163.4	−162.87	—	—	~ 20	~ 20	426
HF (impure)		−182.4	—	—	—	—	—	—	—	—	—

[a] Quintet broad with further unresolved coupling; R = $\text{—}NC_6F_5$.

[b] Dubious assignment, no singlet associated with W—F observed.

Table 2. ^{19}F NMR chemical shifts and coupling constants for the TFA solution of the produce from ($WF_6+C_6F_5NH_2$)

Assignment	Spectral form	Chemical shift (relative to $CFCl_3$) (ppm) δF_X	δF_A	δF_o	δF_m	δF_p	Spin–spin coupling constants (Hz) $J_{F_A-F_X}$	$J_{F_X-^{183}W}$	$J_{F_o-F_m}$	$J_{F_p-F_m}$	Approx. relative molar ratio
WOF_4	X_4	65.9	—	—	—	—	—	n.o.	—	—	21
$[RWF_4{-}F_A{-}\mathit{W}F_4R]^-$	AX_4	58.6	n.o.	—	—	—	n.o.	n.o.	—	—	39
$[\mathit{R}WF_4{-}F_A{-}WF_4\mathit{R}]^-$		—	—	−145.8	−163.3	−149.3	—	—	n.o.	n.o.	
CF_3COF_X	Quartet	13.6	—	—	—	—	6.1	—	—	—	150
$\mathit{CF_3}COF_X$	Doublet	−75	—	—	—	—	6.1	—	—	—	
$F_2C{=}O$	Singlet	−22.3	—	—	—	—	—	—	—	—	114
$[C_6F_5NH_3]^+$		—	—	−148.2	−160.3	−149.8	—	—	n.o.	n.o.	7
*		—	—	−146.1	−163.3	−154.4	—	—	n.o.	n.o.	112

n.o. = not observed; R = $—NC_6F_5$; * = Tentative assignment.

The tungsten atoms were located using the Patterson option of SHELXS 84.[6] All subsequent calculations were carried out using the computer program SHELX.[7] Cycles of least-squares refinement with the tungsten atoms included gave an R factor of 0.38 and located the carbon, fluorine and nitrogen atoms. An absorption correction was applied to the data with the maximum and minimum transmission factors of 0.533 and 0.328, respectively. Due to program restraints on the number of independent variables it was not possible to refine all atoms with anisotropic thermal parameters. All tungsten and nitrogen atoms were refined anisotropically. In addition 51 of the carbon and fluorine atoms were refined with anisotropic thermal parameters.

Final cycles of refinement employed a weighing parameter g (0.00081) $\{\omega = 1/[\sigma^2(F)+g(F)^2]\}$ and gave the final residual indices R $\{=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|\}$ 0.0879 and R_w $\{=\Sigma_w[(F_o|-|F_c|)^2/w|F_o|^2]^{1/2}\}$ 0.0878. The remaining difference Fourier map revealed $\leqslant 1.7e$ peaks (and $\geqslant -3e$ troughs) around the tungsten–fluorine region, though an analysis of the weighing scheme over $|F_o|$ and $\sin\theta/\lambda$ was satisfactory. Tables of fractional atomic coordinates; atomic thermal parameters; bond lengths and angles (Table 3) are available as supplementary material from the Editor.

RESULTS AND DISCUSSION

The aminolysis reactions of WF_6 with RNH_2 compounds are thought to proceed by first forming a 1 : 1 $WF_6:RNH_2$ complex, which then loses HF to produce an intermediate species $WF_5N(H)R$.[1] Loss of either H^+ or HF [eq. (3)] will form either $[WF_5(NR)]^-$ or the neutral $WF_4(NR)$ compound

$$WF_5N(H)R \begin{cases} \xrightarrow{-H^+} [WF_5(NR)]^- \\ \xrightarrow[-HF]{} WF_4(NR) \end{cases} . \qquad (3)$$

The identity and molar ratios of products formed in aminolysis reactions are dependent to a large extent upon solvent and stoichiometry. The reaction of $C_6F_5NH_2$ with WF_6 proceeds via aminolysis to produce a mixture of compounds.

The IR spectrum of the original yellow product showed several sharp peaks in the region 1650–1000 cm^{-1}, a region covering the range of aromatic ν(C—C) and ν(C—F) stretching frequencies. Hornig[8] assigns the ν_3 and ν_4 modes of NH_4^+ (in NH_4F) at 2815 and 1494 cm^{-1}, respectively, strong bands in the IR spectrum at 2800 and 1500 cm^{-1} are assigned to the ν(N—H) of the

Table 3. Selected bond lengths (Å) and angles (°)

Bond	Length (Å)	Atoms	Angles (°)
F(1)—W(1)	2.159(29)	W(1)—F(1)—W(2)	150.8(12)
F(1)—W(2)	2.117(25)	W(3)—F(31)—W(4)	170.4(19)
F(31)—W(3)	2.16(3)	N(2)—W(1)—F(6)	98.5(12)
F(31)—W(4)	2.06(4)	N(2)—W(1)—F(7)	101.3(13)
F(6)—W(1)	1.893(21)	N(2)—W(1)—F(8)	97.5(13)
F(7)—W(1)	1.935(22)	N(2)—W(1)—F(9)	98.5(13)
F(8)—W(1)	1.904(20)	N(1)—W(2)—F(2)	100.3(14)
F(9)—W(1)	1.867(25)	N(1)—W(2)—F(3)	94.7(15)
F(2)—W(2)	1.926(22)	N(1)—W(2)—F(4)	97.0(13)
F(3)—W(2)	1.875(24)	N(1)—W(2)—F(5)	104.3(16)
F(4)—W(2)	1.976(24)	N(4)—W(3)—F(36)	100.9(14)
F(5)—W(2)	1.840(26)	N(4)—W(3)—F(37)	101.2(14)
F(36)—W(3)	1.907(25)	N(4)—W(3)—F(38)	96.4(15)
F(37)—W(3)	1.985(26)	N(4)—W(3)—F(39)	98.8(13)
F(38)—W(3)	1.843(24)	N(3)—W(4)—F(32)	97.4(14)
F(39)—W(3)	1.998(26)	N(3)—W(4)—F(33)	102.0(14)
F(32)—W(4)	1.864(22)	N(3)—W(4)—F(34)	101.2(14)
F(33)—W(4)	2.026(21)	N(3)—W(4)—F(35)	95.8(14)
F(34)—W(4)	1.867(26)	W(1)—N(2)—C(21)	175.3(22)
F(35)—W(4)	1.968(25)	W(2)—N(1)—C(11)	170.0(30)
W(1)—N(2)	1.80(4)	W(3)—N(4)—C(51)	172.1(22)
W(2)—N(1)	1.78(4)	W(4)—N(3)—C(41)	179.6(15)
W(3)—N(4)	1.69(4)		
W(4)—N(3)	1.68(3)		
N(1)—C(11)	1.39(5)		
N(2)—C(21)	1.40(5)		
N(3)—C(41)	1.49(4)		
N(4)—C(51)	1.52(4)		

$C_6F_5NH_3^+$ cation. Similarly, Cabana and Sandorfy[9] analysed the IR spectrum of $CH_3NH_3^+F^-$ and identified (N—H) ν_7 and ν_4 modes at 2660, 2573 and 1576 cm^{-1}. Bands occurring at 2660 and 1600 cm^{-1} in the yellow solid compare well and are attributed to $[C_6F_5NH_3]^+F^-$. Assignments of ν(M═N) in several chloro anions $[MNCl_4]$[10] (M = Mo, 1055 cm^{-1}; M = W, 1030 cm^{-1}) and $[MNCl_5]^-$[11] (M = Mo, 1059, 1023; M = W 1025, 1035), chloride nitrides, $MNCl_3$ (M = Mo, 1045 cm^{-1}; M = W 1084, 1068 cm^{-1})[12] suggest that the intense band at 1000 cm^{-1} is the ν(W═N) vibration of $[WF_5(NC_6F_5)]^-$. Peaks occurring in the 600 cm^{-1} region are assigned to ν(W—F). Hence, the yellow solid was a mixture containing at least $[C_6F_5NH_3]^+F^-$ and $[C_6F_5NH_3]^+[WF_5(NC_6F_5)]^-$.

The IR spectrum of the solid recrystallized from TFA was considerably simplified and the absence of bands at 2600 and 1600 cm^{-1} suggests that the solid was free of $[C_6F_5NH_3]^+F^-$. The bands at 1500, 1000, 600 and 500 cm^{-1} are assigned to the ν(N—H), ν(W═N), ν(W—F) and ν(W—F—W) stretching frequencies of the dimeric anion salt $[C_6F_5NH_3]^+[W_2F_9(NC_6F_5)_2]^-$.

The ^{19}F NMR spectra of MeCN and TFA solutions of the yellow solid (Tables 1 and 2) show that the MeCN solution contained the expected tungsten imido–fluoride salts and oxyfluorides, as well as the mixed imido-oxyfluoride anion $[OWF_4—F—WF_4(NC_6F_5)]^-$. The TFA solution shows the presence of the dimeric $[W_2F_9(NC_6F_5)_2]^-$ ion, WOF_4 and fluorination products only. The movement to lower field of the (W—F_x) chemical shift with respect to similar imido compounds not containing C_6F_5N— e.g. $\delta F_x = 52.5$ ppm, $[WF_5(NC_6F_5)]^-$ and $\delta F_x = 28$ and 33.4 in $[WF_5(NR)]^-$ (R = Me, H)[1,2] may be attributed to the magnetic anisotropy and electron withdrawing ability of the aromatic C_6F_5N group. In MeCN both the mono- and dimeric anion species are present, each producing an AX_4 type spectrum in the ^{19}F NMR spectrum with ^{183}W satellites associated with the X_4 doublet. The monomeric ion $[WF_5(NC_6F_5)]^-$ is the major species. The dimeric ion $[W_2F_9(NC_6F_5)_2]^-$ produces a well resolved doublet associated with the eight equivalent F_x nuclei, but the expected nonet of F_a coupled to eight equivalent fluorine atoms was not clearly resolved. The ^{19}F NMR evidence indicates that in solution both $[WF_5(NC_6F_5)]^-$ and $[W_2F_9(NC_6F_5)_2]^-$ adopt the pseudo-octahedral structures proposed for $[WF_5(NR)]^-$ ions,[1,2] with linear F_a—W—N—C and C—N—W—F_a—W—N—C skeletons.

Unlike the MeCN solution, in TFA solutions the only imido species in the ^{19}F NMR is the fluorine bridged, dimeric anion $[W_2F_9(NC_6F_5)_2]^-$. The products formed as a result of fluorination were identified from ^{19}F NMR as CF_3COF and $F_2C{=}O$ and compared favourably with literature values.[13,14] A further reaction product is believed to be a diacetamido species $C_6F_5N(COCF_3)_2$ produced by the reaction of the TFA solvent with the $[C_6F_5NH_3]^+$ cation. The NMR evidence illustrates that whilst TFA can be used to isolate the dimeric anion salt $[C_6F_5NH_3]^+[W_2F_9(NC_6F_5)_2]^-$, prolonged standing will result in progressively larger amounts of fluorination products forming at the expense of the tungsten imido fluoride compound.

The dimeric salt crystallized from TFA has two formula units within the triclinic unit cell (Fig. 1, Table 3). Unlike the linear structure proposed for

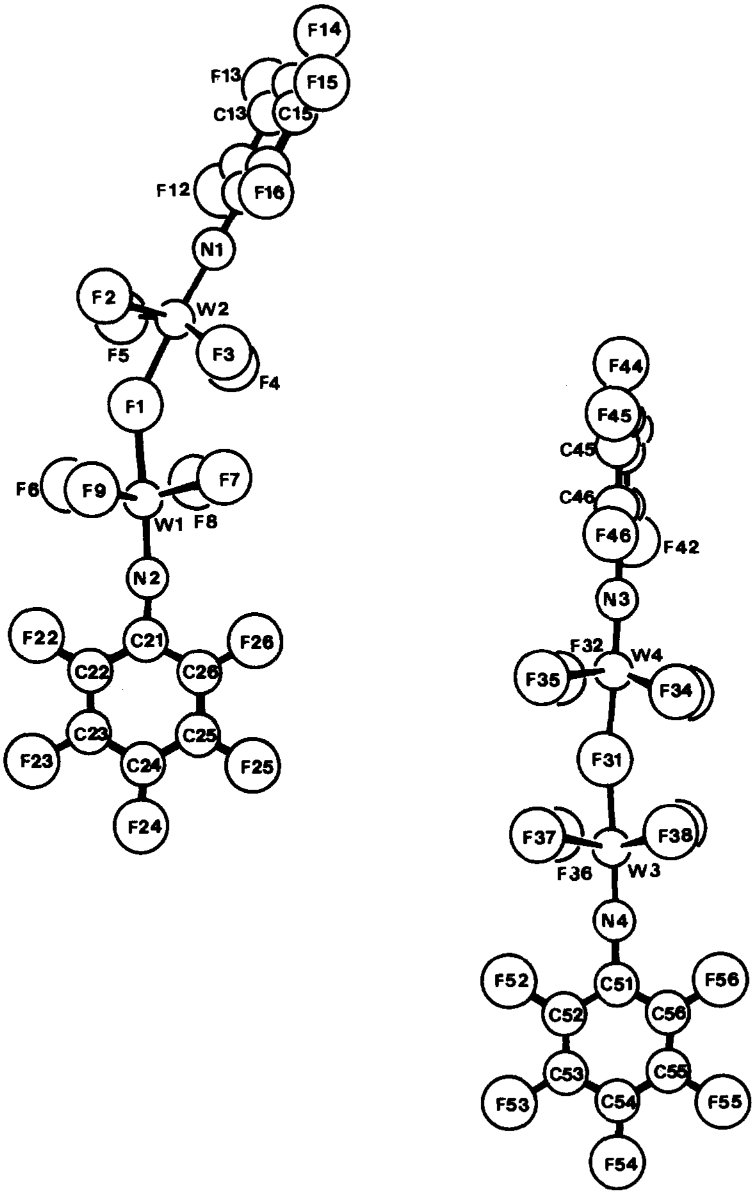


Fig. 1. A view of the two independent anions of $[C_6F_5NH_3][C_6F_5N{=}WF_4{-}F{-}WF_4{=}NC_6F_5]$ showing the atomic labelling.

Table 4. Comparison of W═N bond lengths (Å)

Compound	W—N (Å)	Ref.
$[C_6F_5NH_3]^+[W_2F_9(NC_6F_5)_2]^-$	1.74	This work
$[AsPh_4]^+[WCl_5(NC_2Cl_5)]^-$	1.648	3
$[Cl_4W{=}N{-}C_2Cl_5]_2$	1.71	4
$(ButO)_3W{\equiv}N$	1.74	21
$W(NPh)Cl_3(PPh_3)_2$	1.742	22
$W(NPh)Cl_2(PPh_3)_3$	1.755	22
$WCl_2(NSO_2Ph)_2(MeCN)_2$	1.766	23
$WCl_2(NPh)_2(bipy)$	1.789	24
$WF_4(N{=}PPh_3)_2$	1.825	20
WF_5N_3	1.85	19

the anion in solution, the anion in the solid state has near linear C—N—W fragments, but with distorted and slightly differing geometries about the two bridging fluorine atoms [F(1), F(31)]. Dehnicke and co-workers[15] have prepared a fluorine bridged nitrido–nitrene rhenium fluoride, $ReNF_4 \cdot ReF_5(NCl)$, possessing a similar bent geometry at the fluorine bridge ($Re—\hat{F}—Re = 158°$) and the tri-nuclear nitrido–nitrene complex $[Ph_3C—NWCl_4—F—WNCl_2—F—WCl_4N—CPh_3]^-$ [16] has $W—\hat{F}—W = 163°$.

The average equatorial fluorine to tungsten bond length of 1.917 Å is greater than the W—F bond lengths of WF_6\{1.832 Å\},[17] WF_5Cl\{1.836 Å\},[18] WF_5N_3\{1.836 Å\}[19] and $WF_4(N{=}PPh_3)_3$\{1.891 Å\}[20] consistent with greater withdrawal of electron density from the metal atom. The imido group exerts a noticeable *trans* influence on the *trans* W—F bonds, average $W—F_{trans} = 2.124$ Å compared with WF_5N_3\{1.89 Å\}[19] and $WF_4(N{=}PPh_3)_2$\{1.935 Å\}.[20] All equatorial W—F bonds are bent approximately 10° away from the perpendicular to the imido groups (average $N—\hat{W}—F_{eq} = 99.1°$). The same influence is observed in $ReNF_4—ReF_5(NCl)$, ($N—\widehat{Re}—F = 98°$).[15] The movement of the equatorial fluorines away from the imido group can be explained as the repulsion of the W—F bonds away from the greater electron density of the W═N bond.

The W═N bond (average length 1.74 Å), although formally assigned as a double bond, presumably possesses a bond order of greater than two (Table 4) attributed to d_π–p_π overlap to form M═N—R.

The reaction of $C_6F_5NH_2$ with MoF_6 is also believed to result in iminolysis to produce the salts $[C_6F_5NH_3]^+[MoF_5(NC_6F_5)]^-$ and $[C_6F_5NH_3]^+F^-$. The IR spectrum of the solid produced possesses the same salient features found in the tungsten product, including peaks at 2640 and 1600 cm^{-1} attributable to $[C_6F_5NH_3]^+F^-$, the ν(Mo═N) stretch is believed to be at 1000 cm^{-1}.

The reaction of $C_6F_5NH_2$ with ReF_6 produces a solid, the IR spectrum of which is slightly simpler than the molybdenum and tungsten derivatives. The absence of a band at 2600 cm^{-1} places some doubt as to the presence of $[C_6F_5NH_3]^+F^-$ in the solid. The ν(Re═N) band has been assigned at 1102 cm^{-1} [15] and 1011, 995 cm^{-1},[25] the presence of bands at both these regions means that an unambiguous assignment of ν(Re═N) is not possible due to overlap with ν(C—C) and ν(C—F) vibrational modes. The peaks in the 600 cm^{-1} region are assigned to ν(Re—F). The solid is believed to be a mixture containing the neutral species $ReF_4(NC_6F_5)$. The isolation of $ReF_5(NCl)$[5] as a product of fluorination by ClF_3 is further chemical evidence to support the present of a rhenium imido fluoride.

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