Journal of Fluorine Chemistry, 59 (1992) 141–152

Structure of the new fluoro complex of tungsten(VI): $[WF_4(bipy)_2]^{2+} \cdot 2[W_2O_2F_9]^- \cdot 0.25HF$ (bipy = 2,2′-bipyridyl)

L. Arnaudet, R. Bougon*, Buu Ban, M. Lance, A. Navaza**, M. Nierlich and J. Vigner

SCM, URA CNRS 331, CEA, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette (France)

(Received November 4, 1991; accepted January 31, 1992)

Abstract

The complex $[WF_4(bipy)_2]^{2+} \cdot 2[W_2O_2F_9]^- \cdot 0.25HF$ has been obtained by the controlled hydrolysis of a mixture of WF_6 and 2,2′-bipyridyl (bipy) in CD_2Cl_2 solution. The crystal structure of this complex has been determined from X-ray diffraction data and refined to agreement factors of $R = 0.061$ and $R_w = 0.070$ for 3484 unique reflections. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 10.995$ (3) Å, $b = 15.910$ (3) Å, $c = 21.478$ (12) Å, $\alpha = 90.11$ (3)°, $\beta = 102.12$ (3)°, $\gamma = 100.58$ (2)°, $Z = 4$. Four $[WF_4(bipy)_2]^{2+}$ cations, eight dimetallic anions $[W_2O_2F_9]^-$, formed by two WOF_4 units bridged by a fluorine atom, and one HF molecule are found in the unit cell. The coordination polyhedron of the tungsten atom in the cation is a triangular dodecahedron, and in the anion it is a distorted octahedron around each metal centre. The ranges of the observed bond distances are (in Å): W–F, 1.79 (3)–1.87 (2); W–N, 2.21 (4)–2.30 (4) for the cation, and W–F terminal, 1.74 (4)–1.88 (4); W–F bridging, 2.05 (3)–2.16 (4); W–O, 1.58 (5)–1.72 (4) for the anion.

The ^{19}F NMR spectra of the saturated solutions showed that the ion $[W_2O_2F_9]^-$ is present and that the fluorine atoms of the cation are equivalent. The ^1H NMR spectra indicated that the protons of bipy in the cation are deshielded when compared with those of the free ligand in the same solvent.

Introduction

The interaction of tungsten hexafluoride (WF_6) with the nitrogen base 2,2′-bipyridyl (bipy) has been the subject of an extensive study in this laboratory. Conditions were sometimes such that a few crystals of unexpected composition grew on standing. The structure of these crystals has been determined from single-crystal data and NMR spectra. The presence of oxygen in the compound indicated that it originated from a partial hydrolysis of the species present in solution. This hydrolysis was thought to arise from traces of H_2O brought in by the organic ligand and/or the solvent. The subsequent formation of HF, traces of which may also have been brought in with WF_6, could lead to further hydrolysis from the reaction of HF with the glass tube.

---

*Author to whom correspondence should be addressed.

**Teaching member of the Centre Pharmaceutique, Chatenay-Malabry, France.

0022-1139/92/$5.00

Experimental

The experimental procedures, materials, apparatus and instrumentation were as previously described [1, 2]. ^1H and ^{19}F NMR spectra were referenced externally with respect to $Si(CH_3)_4$ and $CFCl_3$ respectively, with positive shifts being downfield from the standards.

Crystals of the compound studied were obtained from a solution of 0.263 mmol of bipy in 10 cm^3 of CD_2Cl_2 into which 1.646 mmol of WF_6 was added by condensation at -196 °C. The pale yellow solid obtained after warming up to room temperature was decanted and washed with CD_2Cl_2. The colour of this solid turned white with washing, and its composition was found to correspond to the empirical formula $W_2F_{12}\cdot$bipy. The few orange crystals which grew in the remaining solution stored in the refrigerator were separated by decantation, followed by removal of the last traces of solvent in a dynamic vacuum. These crystals were found to be stable at room temperature under dry conditions, but to decompose quickly in air. Due to the scarcity of these crystals, their chemical identity could be established only by X-ray diffraction techniques. Crystals suitable for structure determination were selected in the dry box and sealed inside glass capillaries of 0.5 mm diameter.

A summary of the X-ray data collection parameters and structural refinement is given in Table 1. The measured intensities were corrected for background, Lorentz polarization, linear crystal decomposition (-34% during the data collection) and empirical absorption correction [6] (max./min. transmission factors: 2.9, 0.75). The position of the W atoms was determined by direct methods, using MULTAN 82 [7]. The positions of the O and F atoms were obtained from subsequent difference-Fourier maps. Due to the large number of atomic parameters, block matrix least-squares refinements were carried out keeping a common molecular fragment in consecutive cycles. Owing to high correlations, refinement was started with the distances W–F, W–N and W–O constrained to 1.85(2) Å, 2.30(2) Å and 1.65(3) Å respectively, but they were later allowed to vary. A small dumping factor was applied for the same reason. Isotropic thermal parameters were refined for all atoms except the W atoms, which were refined anisotropically. The difference maps revealed an electron density peak close to one centre of symmetry, and this peak was ascribed to a fluorine atom of an HF molecule: this atom, F(100), was assigned a fixed occupation factor of 0.5. The residual peaks on the final difference map (absolute values smaller than 1.8e/Å^3) are in the regions close to the atoms with higher thermal parameters. They might indicate some disorder. The theoretical positions (C–H = 0.95 Å) of the H atoms of the bipy ligand were calculated in order to determine the intermolecular contacts, but they were not included in the structural model. The atomic scattering factors and anomalous dispersion terms for W(VI) were taken from the *International Tables for X-Ray Crystallography* [8], and the neutral atom scattering factors [3] for F and O were those incorporated in the programs.

TABLE 1

Crystallographic data for $[WF_4(bipy)_2]^{2+} \cdot 2[W_2O_2F_9]^- \cdot 0.25HF$

Formula weight	1718.59
Crystal size (mm)	0.36×0.36×0.20
ρ_{calc} (g cm^{-3})	3.17
Space group	$P\bar{1}$
a (Å)	10.995 (3)
b (Å)	15.910 (3)
c (Å)	21.478 (12)
α (°)	90.11 (3)
β (°)	102.12 (3)
γ (°)	100.58 (2)
V (Å^3)	3607.8 (2)
Z	4
Diffractometer	CAD 4 Nonius
Monochromator	Graphite
Radiation	Mo Kα (λ=0.7107 Å)
μ (MoKα) (cm^{-1})	163.8
T (K)	293
Scan type	$\omega/2\theta$
Scan width (°)	$0.80+0.35 \tan \theta$
Intensity control reflections	3 every 60 min, variation −0.5% h^{-1}
Range of hkl	$-10 \leqslant h \leqslant 10$, $-15 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 20$
Reflections collected	7189
Unique reflections	6239
Reflections kept for refinement	($F>3\sigma$) 3484
Number of parameters varied	495
Minimized function	$\Sigma\omega(\lvert F_0\rvert-\lvert F_c\rvert)^2$
Secondary extinction	not observed
Weighting scheme	$\omega=1/(\sigma^2\lvert F_0\rvert)+0.0014\lvert F_0\rvert^2)$ for all observed reflections
$R=\Sigma\lvert\lvert F_0\rvert-\lvert F_c\rvert\rvert/\Sigma\lvert F_0\rvert$	0.061
$R_\omega=[\Sigma\omega(\lvert F_0\rvert-\lvert F_c\rvert)^2/\Sigma\omega\lvert F_0\rvert^2]^{0.5}$	0.070
$(\Delta/\sigma)_{max}$	0.03
Computer used	Microvax II
Computing programs	SHELX76 [3], SDP [4], SYBYL [5]

Results and discussion

Crystal structure

The compound contains four $[WF_4(bipy)_2]^{2+}$ cations, eight $[W_2O_2F_9]^-$ anions and one HF molecule per unit cell. Positional and thermal parameters are given in Table 2. Selected bond lengths and angles are given in Table 3, and drawings of the structures of the $[W(1)F_4(bipy)_2]^{2+}$ cation and $[W(3)W(4)O_2F_9]^-$ anion are shown in Fig. 1.

The W atoms in the two independent $[WF_4(bipy)_2]^{2+}$ cations are coordinated by the N atoms of two bipy units and by four F atoms forming a triangular dodecahedron. The choice of the coordination polyhedron was based on Lippard and Russ's criteria [9]: the two trapezoidal least-squares planes are made up of the atoms F(14), N(13), N(14), F(13) (displacements

TABLE 2

Positional parameters and their estimated standard deviations

Atom	x	y	z	B (Å^2)^a
W(1)	0.2465(2)	0.2355(1)	0.0886(1)	1.8(1)
F(11)	0.257(3)	0.153(2)	0.033(1)	2.2(4)*
F(12)	0.158(2)	0.264(2)	0.144(1)	1.9(4)*
F(13)	0.379(2)	0.210(2)	0.152(1)	2.3(5)*
F(14)	0.204(2)	0.313(2)	0.032(1)	2.0(5)*
N(11)	0.348(3)	0.363(2)	0.135(2)	2.1(6)*
C(111)	0.305(4)	0.402(3)	0.183(2)	2.9(7)*
C(112)	0.367(5)	0.486(3)	0.211(3)	3.6(7)*
C(113)	0.475(5)	0.526(3)	0.193(3)	3.9(7)*
C(114)	0.519(6)	0.485(4)	0.143(4)	8.2(8)*
C(115)	0.452(5)	0.404(3)	0.117(3)	3.7(7)*
N(12)	0.418(4)	0.281(3)	0.050(2)	4.9(7)*
C(121)	0.489(4)	0.359(3)	0.065(2)	2.0(7)*
C(122)	0.593(5)	0.398(4)	0.042(3)	4.8(7)*
C(123)	0.624(4)	0.356(3)	−0.002(3)	3.1(7)*
C(124)	0.564(5)	0.275(3)	−0.023(3)	3.7(7)*
C(125)	0.473(4)	0.236(3)	0.010(2)	2.4(7)*
N(13)	0.045(4)	0.187(2)	0.039(2)	2.6(6)*
C(131)	−0.012(4)	0.109(3)	0.053(2)	1.6(6)*
C(132)	−0.130(5)	0.069(3)	0.016(3)	4.4(8)*
C(133)	−0.197(4)	0.114(3)	−0.033(2)	2.6(7)*
C(134)	−0.148(5)	0.200(4)	−0.046(3)	5.4(7)*
C(135)	−0.028(4)	0.227(3)	−0.005(2)	2.2(7)*
N(14)	0.177(4)	0.109(2)	0.129(2)	1.9(6)*
C(141)	0.244(4)	0.079(3)	0.179(2)	1.6(6)*
C(142)	0.206(5)	−0.007(3)	0.204(3)	3.5(7)*
C(143)	0.081(4)	−0.041(3)	0.174(3)	2.6(7)*
C(144)	0.008(5)	−0.018(3)	0.122(3)	4.1(7)*
C(145)	0.060(4)	0.061(3)	0.099(2)	2.0(7)*
W(2)	0.1153(2)	0.2378(1)	0.5942(1)	2.3(1)
F(21)	−0.032(3)	0.235(2)	0.624(1)	3.7(5)*
F(22)	0.195(2)	0.172(2)	0.552(1)	2.1(5)*
F(23)	0.218(3)	0.235(2)	0.672(1)	3.4(5)*
F(24)	0.081(3)	0.309(2)	0.527(2)	3.6(5)*
N(21)	0.299(4)	0.320(3)	0.589(2)	3.2(6)*
C(211)	0.391(5)	0.288(4)	0.558(3)	4.9(8)*
C(212)	0.503(4)	0.345(3)	0.552(3)	2.6(7)*
C(213)	0.523(5)	0.426(4)	0.576(3)	4.3(7)*
C(214)	0.441(5)	0.465(3)	0.601(3)	3.5(7)*
C(215)	0.324(6)	0.408(4)	0.609(3)	6.1(8)*
N(22)	0.136(4)	0.370(3)	0.644(2)	3.7(7)*
C(221)	0.238(5)	0.431(4)	0.641(3)	5.2(8)*
C(222)	0.254(5)	0.505(4)	0.673(3)	5.2(8)*
C(223)	0.158(5)	0.528(4)	0.699(3)	4.7(7)*
C(224)	0.047(5)	0.470(4)	0.698(3)	5.2(8)*
C(225)	0.026(5)	0.384(4)	0.699(3)	5.5(8)*
N(23)	−0.039(4)	0.165(2)	0.520(2)	2.6(6)*
C(231)	−0.90(4)	0.079(3)	0.530(2)	2.6(7)*

(*continued*)

TABLE 2 (*continued*)

Atom	x	y	z	B (Å^2)^a
C(232)	−0.192(5)	0.030(3)	0.479(3)	4.2(7)*
C(233)	−0.233(5)	0.067(4)	0.426(3)	4.9(8)*
C(234)	−0.175(5)	0.148(3)	0.418(3)	3.4(7)*
C(235)	−0.086(5)	0.198(3)	0.465(3)	3.5(7)*
N(24)	0.063(3)	0.102(2)	0.626(2)	1.7(6)*
C(241)	0.119(5)	0.081(3)	0.688(3)	3.4(7)*
C(242)	0.075(4)	−0.004(3)	0.704(2)	2.5(7)*
C(243)	−0.027(5)	−0.066(3)	0.670(3)	3.6(7)*
C(244)	−0.082(4)	−0.038(3)	0.612(2)	2.1(7)*
C(245)	−0.041(4)	0.050(2)	0.587(2)	1.6(8)*
W(3)	0.2034(2)	0.2872(1)	0.8456(1)	3.1(1)
F(31)	0.241(3)	0.375(2)	0.791(2)	4.8(6)*
F(32)	0.307(3)	0.352(2)	0.911(2)	4.5(6)*
F(33)	0.134(3)	0.213(2)	0.903(2)	6.5(6)*
F(34)	0.069(3)	0.240(2)	0.784(2)	4.7(6)*
O(31)	0.299(4)	0.229(3)	0.833(2)	6.9(7)*
F(1)	0.080(3)	0.363(2)	0.866(2)	5.0(6)*
W(4)	0.0257(2)	0.4788(2)	0.8945(1)	3.2(1)
F(41)	0.160(3)	0.524(2)	0.857(1)	4.5(6)*
F(42)	−0.092(3)	0.402(2)	0.925(2)	4.7(6)*
F(43)	−0.081(3)	0.463(2)	0.815(2)	6.4(6)*
F(44)	0.147(3)	0.473(2)	0.966(2)	4.8(6)*
O(41)	−0.019(4)	0.567(3)	0.915(2)	5.7(7)*
W(5)	0.8217(2)	0.2351(1)	0.1841(1)	3.3(1)
F(51)	0.819(3)	0.247(2)	0.101(2)	6.7(6)*
F(52)	0.689(4)	0.285(2)	0.176(2)	7.5(6)*
F(53)	0.802(4)	0.199(2)	0.264(2)	8.4(7)*
F(54)	0.931(3)	0.160(2)	0.189(2)	6.3(6)*
O(51)	0.934(4)	0.326(3)	0.207(2)	6.3(7)*
F(2)	0.679(4)	0.129(2)	0.150(2)	8.6(7)*
W(6)	0.5798(3)	0.0029(2)	0.1294(1)	4.5(1)
F(61)	0.459(3)	0.062(3)	0.092(2)	10.4(7)*
F(62)	0.564(4)	0.015(3)	0.208(2)	12.1(8)*
F(63)	0.734(4)	−0.027(4)	0.151(3)	20.0(9)*
F(64)	0.617(5)	0.022(3)	0.055(2)	13.7(8)*
O(61)	0.503(4)	−0.096(2)	0.114(2)	8.0(7)*
W(7)	0.1741(2)	0.3398(2)	0.3714(1)	3.5(1)*
F(71)	0.140(3)	0.274(2)	0.298(2)	6.9(6)*
F(72)	0.168(3)	0.241(2)	0.416(2)	4.9(6)*
F(73)	0.255(3)	0.402(2)	0.444(1)	3.5(5)*
F(74)	0.223(3)	0.435(2)	0.329(2)	5.0(6)*
O(71)	0.027(3)	0.354(3)	0.375(2)	6.8(7)*
F(3)	0.355(3)	0.321(2)	0.369(1)	3.0(5)*
W(8)	0.4725(3)	0.2337(2)	0.3520(1)	4.9(1)
F(81)	0.317(4)	0.164(3)	0.320(2)	9.7(7)*
F(82)	0.468(4)	0.298(3)	0.286(2)	11.2(7)
F(83)	0.598(4)	0.319(3)	0.390(2)	10.7(7)*
F(84)	0.466(4)	0.201(3)	0.428(2)	11.4(8)*
O(81)	0.561(2)	0.163(2)	0.337(1)	9.5(8)*

(*continued*)

TABLE 2 (*continued*)

Atom	x	y	z	B (Å^2)^a
W(9)	0.3935(2)	0.9096(2)	0.3932(1)	3.5(1)
F(91)	0.233(3)	0.902(2)	0.345(2)	4.7(6)*
F(92)	0.330(3)	0.829(2)	0.443(2)	7.4(6)*
F(93)	0.549(3)	0.892(2)	0.426(2)	6.3(6)*
F(94)	0.453(3)	0.968(2)	0.329(2)	5.1(6)*
O(91)	0.397(3)	0.997(2)	0.434(2)	4.3(6)*
F(4)	0.390(3)	0.804(2)	0.338(1)	3.9(5)*
W(10)	0.3661(3)	0.7426(2)	0.2445(1)	5.0(1)
F(101)	0.290(4)	0.832(2)	0.220(3)	13.9(8)*
F(102)	0.514(3)	0.815(3)	0.249(3)	15.9(8)*
F(103)	0.468(3)	0.676(2)	0.289(2)	9.6(7)*
F(104)	0.246(4)	0.677(3)	0.276(2)	12.2(7)*
O(101)	0.350(4)	0.695(3)	0.172(2)	8.5(7)*
F(100)	−0.052(5)	0.488(4)	0.496(3)	6.0(8)*

[a] Starred atoms were refined isotropically. For anisotropically refined atoms, $B = 4/3\Sigma_i\Sigma_j a_i a_j \beta_{ij}$.

from the plane: 0.017, −0.021, 0.020, −0.016 Å) and N(12), N(11), F(12), F(11) (displacements from the plane: 0.023, −0.023, 0.018, −0.018 Å), and they form a dihedral angle of 89.1°.

The dihedral angles between the two least-squares planes of the bipy ligands coordinated to W(1) and to W(2) are 93.4° and 92.6°, respectively. Fixing both W(1) and W(2) at the same point and superimposing the corresponding coordinated N and F atoms via a least-squares process [5], the coordination polyhedra fit each other very well (0.07 Å) (see Fig. 2). However, the cations are not geometrically identical, differing slightly in the orientation of the bipy units. This is certainly due to their environment in the crystal structure and the relative rotational freedom of the bipy ligands. The best superimposed bipy units N(11)N(12)$C_{10}H_8$/N(21)N(22)$C_{10}H_8$ are the closest to some fluorine atoms [H(114)–F(32) = 2.48 Å, H(112)–F(41) = 2.54 Å, H(221)–F(93) = 2.30 Å, H(224)–F(43) = 2.38 Å, except H(142)–F(101) = 2.27 Å].

The structures of the $[W_2O_2F_9]^-$ anions are similar to that described by Hoskins *et al.* [10]; each is built up of two WOF_4 units bridged together by a fluorine atom, this bridge being *trans* to the W=O bonds. The main difference is that for the complex described here, the bridging fluorine atoms lie in a general position of the unit cell, hence the anions are not restrained by crystallographic symmetry. The intermolecular distances show that the four anions of the assymetric unit are not equivalent.

The HF molecule is held in the cavity formed by the $[W(2)F_4(bipy)_2]^{2+}$ unit, the W(7)–W(8) anion and its homologue related by the symmetry centre (0, 1/2, 1/2). The cation atom closest to this HF molecule is F(24):[F(24)–F(100) = 3.32 Å]. The distances from F(100) to the five carbon atoms of the cycle N(22) are almost all identical.

TABLE 3

Selected bond lengths (Å) and angles (°) for $[WF_4(bipy)_2]^{2+} \cdot 2[W_2O_2F_9]^- \cdot 0.25HF$

Bond	Length	Bond	Length	Bond	Length
W(1)–F(11)	1.81(3)	W(3)–F(31)	1.86(4)	W(4)–F(1)	2.16(4)
W(1)–F(12)	1.79(3)	W(3)–F(32)	1.80(3)	W(4)–F(41)	1.86(4)
W(1)–F(13)	1.87(2)	W(3)–F(33)	1.88(4)	W(4)–F(42)	1.84(4)
W(1)–F(14)	1.79(3)	W(3)–F(34)	1.81(3)	W(4)–F(43)	1.85(4)
W(1)–N(11)	2.24(3)	W(3)–O(31)	1.58(5)	W(4)–F(44)	1.83(3)
W(1)–N(12)	2.23(5)	W(3)–F(1)	2.08(4)	W(4)–O(41)	1.65(5)
W(1)–N(13)	2.24(4)				
W(1)–N(14)	2.26(4)				

Bonds	Angle	Bonds	Angle	Bonds	Angle
F(11)–W(1)–F(12)	144(1)	F(12)–W(1)–N(12)	143(1)	F(14)–W(1)–N(13)	74(1)
F(11)–W(1)–F(13)	94(1)	F(12)–W(1)–N(13)	76(1)	F(14)–W(1)–N(14)	145(1)
F(11)–W(1)–F(14)	98(1)	F(12)–W(1)–N(14)	77(1)	N(11)–W(1)–N(12)	70(0)
F(11)–W(1)–N(11)	143(1)	F(13)–W(1)–F(14)	144(1)	N(11)–W(1)–N(13)	133(1)
F(11)–W(1)–N(12)	73(1)	F(13)–W(1)–N(11)	75(1)	N(11)–W(1)–N(14)	133(1)
F(11)–W(1)–N(13)	76(1)	F(13)–W(1)–N(12)	76(1)	N(12)–W(1)–N(13)	131(2)
F(11)–W(1)–N(14)	74(1)	F(13)–W(1)–N(13)	143(1)	N(12)–W(1)–N(14)	131(2)
F(12)–W(1)–F(13)	95(1)	F(13)–W(1)–N(14)	72(1)	N(13)–W(1)–N(14)	72(1)
F(12)–W(1)–F(14)	96(1)	F(14)–W(1)–N(11)	75(1)		
F(12)–W(1)–N(11)	73(1)	F(14)–W(1)–N(12)	75(2)		
F(31)–W(3)–F(32)	90(1)	F(33)–W(3)–O(31)	95(2)	F(41)–W(4)–F(42)	162(1)
F(31)–W(3)–F(33)	166(2)	F(33)–W(3)–F(1)	83(2)	F(41)–W(4)–F(43)	90(2)
F(31)–W(3)–F(34)	89(1)	F(34)–W(3)–O(31)	98(2)	F(41)–W(4)–F(44)	86(2)
F(31)–W(3)–O(31)	99(2)	F(34)–W(3)–F(1)	84(1)	F(41)–W(4)–O(41)	101(2)
F(31)–W(3)–F(1)	83(1)	O(31)–W(3)–F(1)	177(2)	F(42)–W(4)–F(43)	89(2)
F(32)–W(3)–F(33)	90(2)	F(1)–W(4)–F(41)	79(1)	F(42)–W(4)–F(44)	91(1)
F(32)–W(3)–F(34)	164(2)	F(1)–W(4)–F(42)	82(1)	F(42)–W(4)–O(41)	97(2)
F(32)–W(3)–O(31)	98(2)	F(1)–W(4)–F(43)	83(1)	F(43)–W(4)–F(44)	166(2)
F(32)–W(3)–F(1)	80(1)	F(1)–W(4)–F(44)	83(1)	F(43)–W(4)–O(41)	96(2)
F(33)–W(3)–F(34)	88(2)	F(1)–W(4)–O(41)	179(2)	F(44)–W(4)–O(41)	99(2)
W(3)–F(1)–W(4)	156(2)				

A stereoscopic view [11] of the unit cell contents is shown in Fig. 3. Examination of the crystal packing reveals that the W(5)–W(6), W(9)–W(10) anions and HF molecule form layers parallel to the $(\bar{1}, 1, 0)$ planes and separated by layers containing the other ions. These layers are cross-linked by contacts between O, F and C atoms, giving cohesion to the structure (O···F = 2.90–3.41 Å, F···F = 2.94–3.49 Å, C···F = 2.85–3.40 Å). It can be seen from Table 2 that the thermal parameters of the moieties corresponding to the atoms W(5), W(7) and W(9) of three anions are smaller than those of the other moieties [W(6), W(8) and W(10)]: this may be explained by the weaker intra-layer and/or inter-layer contacts of the moieties corresponding to the atoms W(6), W(8) and W(10).

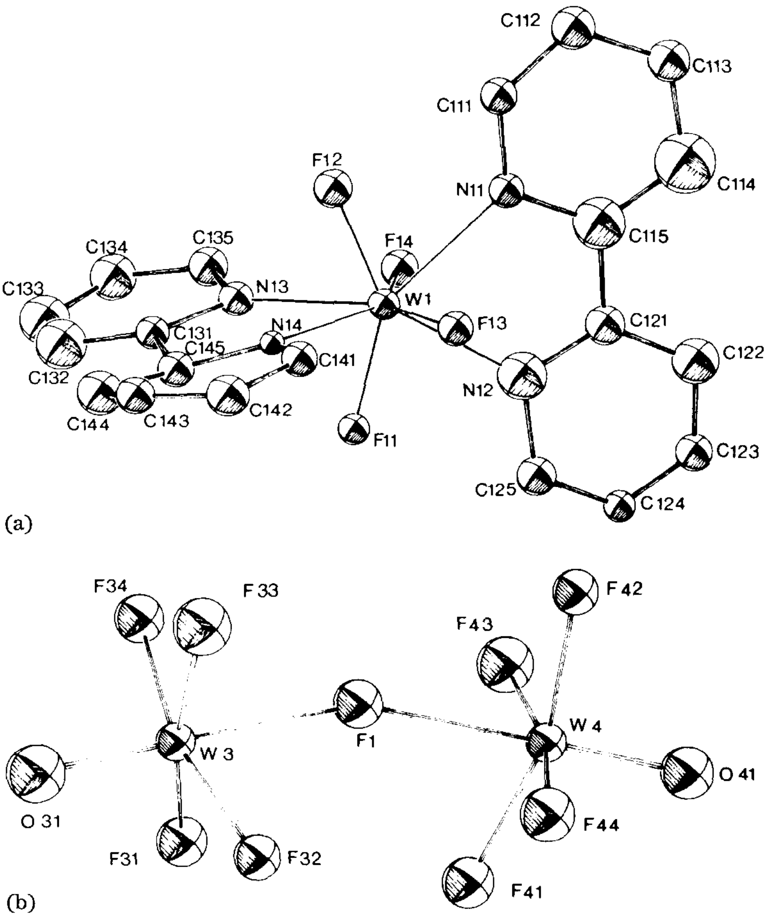

Fig. 1. ORTEP [11] drawings of (a) the $[W(1)F_4(bipy)_2]^{2+}$ cation and (b) the $[W(3)W(4)O_2F_9]^-$ anion. Vibration ellipsoids are drawn at the 30% probability level.

NMR studies

The ^{19}F NMR spectra show a single line at $\phi-162.05$ interpreted as due to HF [12] in exchange with HF_2^- [13]. In addition to the HF/HF_2^- species, the ^{19}F NMR spectra indicate the presence of the ion $[W_2O_2F_9]^-$ (doublet at ϕ 61.70 with J(W–F) = 71 Hz, J(F–F) = 55.9 Hz and an unresolved multiplet at $\phi-145.5$) [14], the excess of WF_6 (singlet at ϕ 166.68, J(W–F) = 40 Hz [15], as well as a singlet at ϕ 155.0 which was interpreted as due to the four F atoms attached to the W atom of the cation.

The intensity of some lines of the ^1H NMR spectra were found to decrease after formation of the crystals. The lines of constant intensity were assigned to the protons of the bipyridinium form of the ligand, and those of decreased intensity to the protons of $[WF_4(bipy)_2]^{2+}$. As a cross-check, the integrated areas of the ^1H and ^{19}F signals assigned to $[WF_4(bipy)_2]^{2+}$ were determined and CHF_3 was used as an internal calibration of the $^1H/^{19}F$ sensitivity ratio.

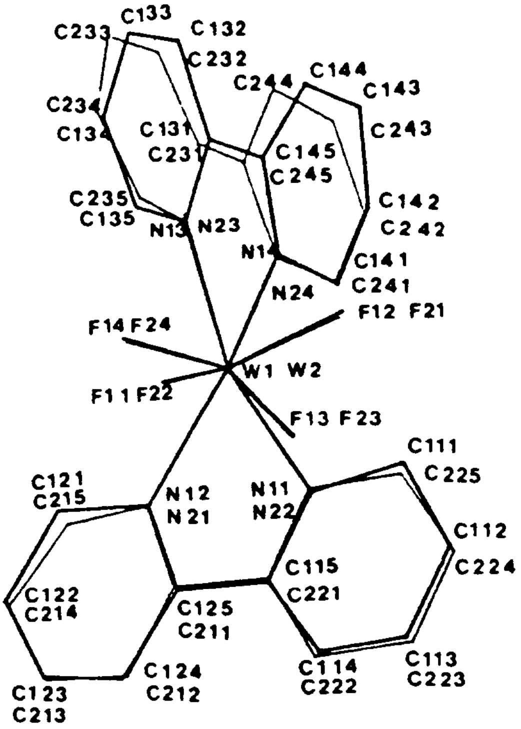

Fig. 2. SYBYL [5] drawing of the least-squares fit of the two units: $[W(1)F_4(bipy)_2]^{2+}$, ——; $[W(2)F_4(bipy)_2]^{2+}$, ——.

The H/F ratio in the cation was then determined and found to be equal to 4. The downfield shift of the protons of $[WF_4(bipy)_2]^{2+}$ when compared with those of the free ligand in the same solvent (see Table 4) indicates that they are deshielded, as may expected to be the case in the cationic part of the complex.

To conclude, this study has allowed a clear identification of the species contained in the crystal, among which the W(VI) cation $[WF_4(bipy)_2]^{2+}$ was previously unknown. The set of reactions leading to the formation of the species identified in the crystal and in solution may be assumed to be as follows:

$$WF_6 + H_2O \longrightarrow WOF_4 + 2HF \tag{1}$$

$$bipy + 2HF \longrightarrow bipyH^+ + HF_2^- \tag{2}$$

$$WF_6 + 2bipy \longrightarrow [WF_4(bipy)_2]^{2+} + 2F^- \tag{3}$$

$$F^- + 2WOF_4 \longrightarrow [W_2O_2F_9]^- \tag{4}$$

Reactions (1) and (4) are based on literature data [14, 16] and reaction (2) on the concomitant presence of the bipyridinium form of the ligand and the HF/HF_2^- species. It should be noted that owing to the high dilution of

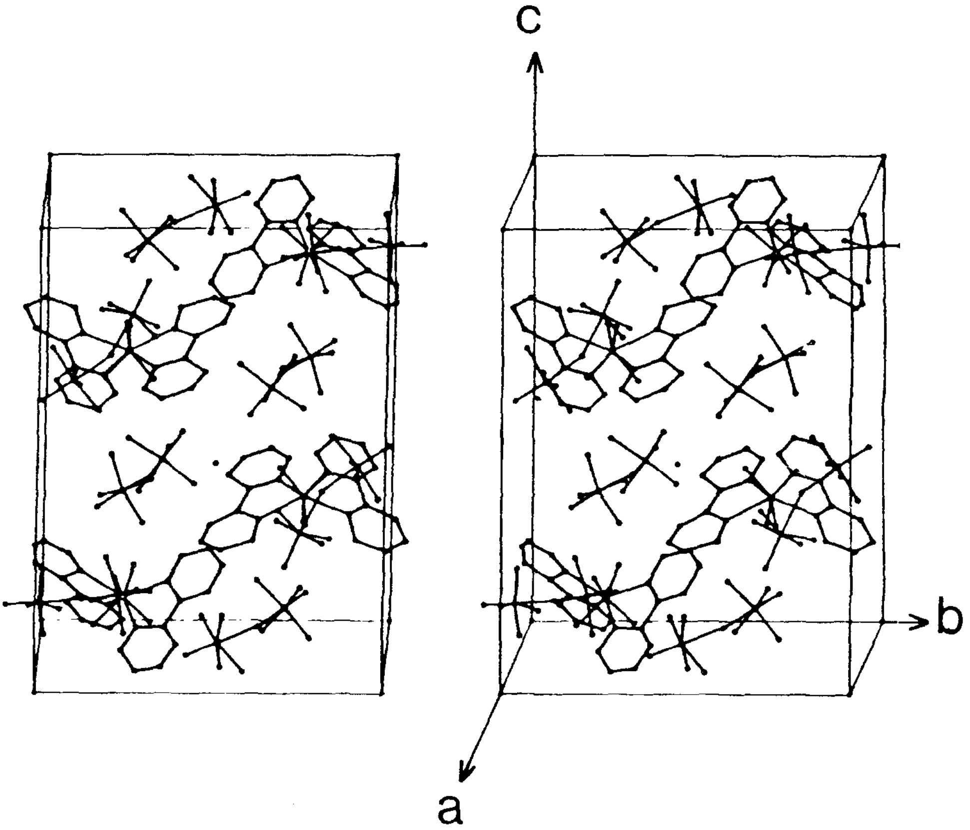

Fig. 3. Stereoscopic view of the structure in the unit cell of $[WF_4(bipy)_2]^{2+} \cdot 2[W_2O_2F_9]^- \cdot 0.25HF$.

the acid (and as attested by the chemical shifts [17]), the bipyridinium ion is present as the monoprotonated form of the ligand. Reaction (3) has to be confirmed. The only present definite observations are that the reaction of WF_6 with bipy does not take place without solvent and that reaction (3) occurs at a much lower yield than that leading to the insoluble adduct $W_2F_{12} \cdot$bipy mentioned in the experimental section.

Supplementary material

Tables of bond distances and bond angles (5 pages), anisotropic thermal parameters (1 page), calculated positional parameters of H atoms (1 page), observed and calculated structure factors (21 pages), least-squares planes, root-mean-square amplitudes of thermal vibration (3 pages), selected intermolecular distances (2 pages) and refined displacement parameters (1 page) are available from the authors on request.

TABLE 4

^1H NMR data for a saturated solution of $[WF_4(bipy)_2]^{2+} \cdot 2[W_2O_2F_9]^- \cdot 0.25HF$ in CD_2Cl_2. Comparison with those of bipy and $bipyH^+$

	Chemical shifts[a]					Coupling constants[a]						Spectrum
	δ_3	δ_4	δ_5	δ_6	δ_{NH^+}	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	
bipy	8.43	7.82	7.31	8.66		7.87	1.14	0.97	7.63	1.79	4.79	1st order
$bipyH^+$	8.39	8.45	7.91	8.87	13.95	7.9	2.40	0.90	6.43	1.43	5.36	ABXY
$[WF_4(bipy)_2]^{2+}$	8.8	8.7	8.15	9.60		7.4			5.7		5.7	ABXY

[a] Chemical shifts δ in ppm from TMS, and coupling constants in Hz; subscripts 3, 4, 5, 6 refer to hydrogen atom positions, with 3 indicating position adjacent to the C–C bond of the two pyridyl rings, and 6, 5, 4 the *ortho*, *meta* and *para* positions to the nitrogen atom, respectively. The accuracy of the data for $[WF_4(bipy)_2]^{2+}$ was poor due to the broadness of the lines (*c.* 5 Hz).

References

1 L. Arnaudet, R. Bougon, Buu Ban, P. Charpin, J. Isabey, M. Lance, M. Nierlich and J. Vigner, *Can. J. Chem.*, *68* (1990) 507.

2 L. Arnaudet, R. Bougon, Buu Ban, M. Lance and W. C. Kaska, *J. Fluorine Chem.*, *53* (1991) 171.

3 G. M. Sheldrick, *SHELX 76, Program for Crystal Structure Determination*, University of Cambridge, UK, 1976.

4 B. A. Frenz, *Enraf Nonius, Structure Determination Package, SDP-Plus, V.3.0,* Enraf Nonius, Delft, The Netherlands, 1985.

5 *SYBYL Molecular Modeling Software, V. 5.2*, Tripos Inc., MO, USA, 1989.

6 N. Walker and D. Stuart, *Acta Crystallogr.*, *A39* (1983) 158.

7 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, *MULTAN 11/82, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*, University of York, UK and Louvain, Belgium, 1982.

8 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, UK, 1974, Vol. IV, Tables 2.2B and 2.3.1.

9 S. J. Lippard and B. J. Russ, *Inorg. Chem.*, *7* (1968) 1686.

10 B. F. Hoskins, A. Linden and T. A. O'Donnell, *Inorg. Chem.*, *26* (1987) 2223.

11 C. K. Johnson, *Ortep II, Report ORNL 5138*, Oak Ridge National Laboratory, TN, USA, 1976.

12 H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, *19* (1951) 1259.

13 F. Y. Fujiwara and J. S. Martin, *J. Am. Chem. Soc.*, *96* (1974) 7625.

14 R. Bougon, T. Bui Huy and P. Charpin, *Inorg. Chem.*, *14* (1975) 1822, and refs. therein.

15 E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, *81* (1959) 1084.

16 R. T. Paine and R. S. McDowell, *Inorg. Chem.*, *13* (1974) 2367.

17 S. Castellano, H. Günther and S. Ebersole, *J. Phys. Chem.*, *69* (1965) 4166.