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2,2′-Bipyridyl fluoro complexes of tungsten(VI): preparation, characterization and crystal structure of $[WF_4(bipy)_2]^{2+}\cdot2[WF_7]^-\cdot WF_6$ and $[WF_4(bipy)_2]^{2+}\cdot2[WF_7]^-\cdot CH_3CN$; preparation and characterization of $WF_6\cdot$bipy

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Abstract

The complex $[WF_4(bipy)_2]^{2+}\cdot2[WF_7]^-\cdot WF_6$ has been obtained by the reaction of excess WF_6 with 2,2′-bipyridyl (bipy) in acetonitrile solution, and the complex $[WF_4(bipy)_2]^{2+}\cdot2[WF_7]^-\cdot CH_3CN$ resulted from treatment of $[WF_4(bipy)_2]^{2+}\cdot2[WF_7]^-\cdot WF_6$ with CH_3CN. The adduct $WF_6\cdot$bipy, obtained from the reaction of WF_6 with bipy in a 1:1 molar ratio in CH_2Cl_2 or CH_3CN solution, is not moisture-sensitive at ambient temperature and is almost insoluble in the usual organic solvents. It was characterized by elemental analysis, X-ray powder data and infrared spectroscopy. In contrast to $WF_6\cdot$bipy, the two ionic complexes are very moisture-sensitive. They were characterized by elemental analysis, X-ray powder data, vibrational spectroscopy and ^{19}F, ^{13}C and ^1H NMR spectroscopy in CD_3CN solution.

The crystal structures of $[WF_4(bipy)_2]^{2+}\cdot2[WF_7]^-\cdot WF_6$ and $[WF_4(bipy)_2]^{2+}\cdot2[WF_7]^-\cdot CH_3CN$ have been determined from X-ray diffraction data. For both ionic complexes, the coordination polyhedron of the tungsten atom in the cation is a triangular dodecahedron and in the $[WF_7]^-$ anion is a distorted monocapped trigonal prism. The fluorine atoms of the WF_6 molecule in $[WF_4(bipy)_2]^{2+}\cdot2[WF_7]^-\cdot WF_6$ form a slightly elongated octahedron. In $[WF_4(bipy)_2]^{2+}\cdot2[WF_7]^-\cdot CH_3CN$, the WF_6 molecules are replaced by CH_3CN molecules although the crystal packing is virtually the same in the two complexes.

Introduction

The cation bis(2,2′-bipyridyl)tetrafluorotungsten(VI), $[WF_4(bipy)_2]^{2+}$, has been recently characterized [1] in the 2,2′-bipyridyl (bipy) fluoro complex of tungsten(VI): $[WF_4(bipy)_2]^{2+}\cdot2[W_2O_2F_9]^-\cdot0.25HF$ obtained by the controlled hydrolysis of a mixture of tungsten hexafluoride (WF_6) and bipy in CD_2Cl_2 solution. It was then realized that, provided any source of hydrolysis was strictly avoided, a similar salt containing the tungsten(VI) heptafluoroanion $[WF_7]^-$ instead of the dimetallic anion $[W_2O_2F_9]^-$ should be capable of preparation. As the structure of the $[WF_7]^-$ anion was still unknown, a crystal structure determination of the expected tungsten(VI) fluoro derivative was also of great interest.

Experimental

The experimental procedures, materials, apparatus and instrumentation were as previously described [2, 3]. The NMR spectra were recorded on a Bruker model AC 200 spectrometer at 200.13, 188.3 and 50.32 MHz for ^1H, ^{19}F and ^{13}C nuclei, respectively. Samples were referenced externally with respect to $Si(CH_3)_4$ or $CFCl_3$ with positive shifts being downfield from the standards. The 647.1 nm exciting line of a Kr ion model 2016 Spectra Physics laser was used to record the Raman spectra.

The complex $[WF_4(bipy)_2]^{2+}\cdot2[WF_7]^-\cdot WF_6$ (**1**) was prepared from the reaction of 1.71 mmol of bipy in 3 cm³ of CH_3CN into which 8.55 mmol of WF_6 was added by condensation at −196 °C. A deep-orange coloured solution with an orange precipitate resulted from warming the mixture to ambient temperature. More CH_3CN was then added until all the precipitate had dissolved. The glass reaction tube was then sealed under vacuum with the solution kept at −196 °C, allowed to warm up to ambient temperature and then placed in a freezer at −10 °C. After 48 h storage, a large amount of

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orange–yellow crystals had formed. These crystals were separated from the solution by decantation and dried by condensation of the volatiles in the side-arm of the reaction tube maintained at −196 °C. Analysis: Calc. for $W_2F_{12}\cdot C_{10}H_8N_2$: W, 48.90; F, 30.32; C, 15.97; H, 1.07; N, 3.72%. Found: W, 48.72; F, 30.07; C, 16.10; H, 1.15; N, 3.85%.

The complex $[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot CH_3CN$ (**2**) was prepared by slow evaporation under vacuum of an acetonitrile solution of **1**. The solution was kept at ambient temperature and the volatiles condensed at −10 °C. A red–orange crystalline residue was obtained. Analysis: Calc. for $W_3F_{18}\cdot(C_{10}H_8N_2)_2\cdot CH_3CN$: W, 44.23; F, 27.42; C, 21.19; H, 1.53; N, 5.62%. Found: W, 43.23; F, 29.21; C, 20.82; H, 1.43; N, 5.05%. The departure from ideal composition is thought to be mainly due to the retention of HF (formed through secondary reactions) by the microcrystalline part of the product.

The adduct $WF_6\cdot$bipy was prepared from the reaction of WF_6 (typically 1–2 mmol) and bipy in a 1:1 molar ratio either in CH_3CN or CH_2Cl_2. A pale yellow powder was obtained. Analysis: Calc. for $WF_6\cdot C_{10}H_8N_2$: W, 40.49; F, 25.11; C, 26.45; H, 1.78; N, 6.17%. Found: W, 40.25; F, 24.93; C, 26.61; H, 1.82; N, 6.27%. This adduct, which like $WOF_4\cdot$bipy [2] is not moisture-sensitive at ambient temperature, is also virtually insoluble in the usual compatible solvents and could not be sublimed. Consequently, single crystals for X-ray diffraction studies could not be grown. The X-ray powder data for this adduct are given in Table 1 together with those of **1** and **2**.

TABLE 1. X-Ray powder diffraction data for $[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot WF_6$(**1**), $[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot CH_3CN$ (**2**) and $WF_6\cdot$bipy

Compound **1**				Compound **2**				$WF_6\cdot$bipy	
d (Å)		Intens.[a]	*h k l*	*d* (Å)		Intens.[a]	*h k l*	d (Å)	Intens.[a]
Obs.	Calc.			Obs.	Calc.				
7.07	7.114	s	0 0 4	9.82	9.911	ms	1 0 0	6.80	ms
	7.052		1 0 3	7.52	7.487	vvw	−1 −1 1	6.10	vs
6.55	6.604	vvw	1 1 2	7.07	7.051	vs	1 0 1	5.90	s
5.24	5.272	vs	2 0 0	6.86	6.859	vs	0 −1 2	5.40	ms
4.98	5.008	m	1 0 5	6.46	6.482	w	−1 −1 2	4.44	ms
	4.943		2 0 2	5.25	5.255	s	−2 0 1	4.21	s
4.67	4.652	vvw	2 1 1	5.00	5.000	mw	−1 −1 3	3.90	vvw
4.217	4.235	s	2 0 4	4.87	4.864	mw	0 −1 3	3.782	mw
	4.222		2 1 3	4.62	4.628	mw	−2 1 0	3.616	m
3.992	4.001	m	1 1 6		4.627		−2 −1 2	3.392	ms
3.705	3.728	ms	2 2 0		4.624		1 −2 1	3.299	mw
3.601	3.631	ms	2 1 5		4.624		−2 1 1	3.184	w
	3.606		2 2 2	4.308	4.306	ms	1 2 0	3.076	vvw
3.293	3.302	m	2 2 4	4.148	4.149	ms	−1 −2 3	2.928	w, br
	3.296		3 0 3		4.149		−2 −1 3	2.692	mw, br
3.076	3.079	w	2 1 7	4.027	4.037	w	1 1 2	2.634	w
2.976	3.019	vvw	3 1 4	3.966	3.968	vvw	−1 1 3	2.576	w
	2.990		3 0 5	3.705	3.706	s	−1 0 4	2.486	mw, br
2.720	2.728	m	3 1 6		3.700	w	1 2 1		
2.653	2.659	ms	3 0 7	3.559	3.558	vw	1 −2 3		
	2.658		1 1 10	3.336	3.335	w	1 −3 1		
2.459	2.472	w	4 0 4	3.241	3.241	w	−2 −2 4		
	2.469		4 1 3	2.976		w			
	2.448		3 3 2	2.891		vvw			
2.354	2.358	w, br	2 4 0	2.820		vvw			
	2.351		3 0 9	2.753		w			
2.228	2.238	s	2 4 4	2.634		mw			
2.200	2.201	vvw	3 3 6	2.597		mw			
2.159	2.163	m	2 0 12	2.469		vw			
2.047	2.046	vw	1 5 2	2.440		vw			
1.971	1.977	w	3 4 5	2.336		mw			
1.890	1.896	vw	2 0 14	2.200		mw			
	1.895		1 5 6	2.111		mw			
1.864	1.867	m	1 0 15						

[a] Abbreviations used: br, broad; v, very; s, strong; m, medium; w, weak.

TABLE 2. Crystallographic data for $[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-$ (**1**) and $[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot CH_3CN$ (**2**)

	Compound 1		Compound 2
Crystal data			
Formula	$C_{10}H_8F_{12}N_2W_2$		$C_{22}H_{19}F_{18}N_5W_3$
Formula weight	751.87		1246.95
Crystal size (mm)	0.20×0.15×0.15		0.25×0.20×0.15
Crystal colour	orange–yellow		red–orange
Crystal system	tetragonal		triclinic
Space group	$I4_1/a$ (No. 88)		$P\bar{1}$ (No. 2)
a (Å)	10.544(5)		10.523(4)
b (Å)	10.544(5)		10.590(3)
c (Å)	28.455(16)		15.591(4)
α (°)	90		107.85(3)
β (°)	90		108.73(3)
γ (°)	90		89.38(3)
V (Å^3)	3164(2)		1559(2)
Z	4		2
d(calc.) (g cm^{-3})	3.16		2.66
μ(Mo Kα) (cm^{-1})	149.78		114.13
Data collection			
Diffractometer		CAD 4 Enraf Nonius	
Monochromator		graphite	
Radiation		Mo Kα (λ=0.71073 Å)	
T (K)		293	
θ limits (°)		1,20	
Scan type		$\omega/2\theta$	
Scan width		$0.8+0.35 \tan\theta$	
Range (abs. transm.)	0.86, 1.11		0.80, 1.24
Range h	−12, 0		0, 10
k	0, 12		−10, 10
l	0, 33		−15, 15
Reflections collected			
total	1595		3112
unique	1392		2680
kept for refinement ($I>3\sigma(I)$)	509		1213
Number of parameters varied	68		194
Minimized function		$\Sigma w[\lvert F_o\rvert-\lvert F_c\rvert]^2$	
Weighting scheme		unit weight for all reflections	
$R(F)=\Sigma\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.049		0.047
$R_w(F)=[\Sigma w[\lvert F_o\rvert-\lvert F_c\rvert]^2/\Sigma w[\lvert F_o\rvert]^2]^{1/2}$	0.056		0.054
Computer used		Microvax II	
Computing programs		SHELXS86 [6] SDP [7]	

Crystals of **1** and **2** suitable for structure determination were selected in the dry box, coated with Kel-F oil and sealed inside glass capillaries 0.5 mm in diameter.

The cell parameters were determined by least-squares refinement of the setting angles of 25 randomly selected reflections with θ between 8 and 12°. Three standard reflections were measured each hour to monitor the crystal decay (14.6% in 11.4 h for **1** and 35% in 31.6 h for **2**) with a linear correction being made. The data were corrected for Lorentz polarization effects and absorption using empirical corrections [4, 5]. A summary of the X-ray data collection parameters and structural refinement is given in Table 2. The initial position of the W atoms of both complexes was determined from the Patterson function. The position of the atoms of bipy and the F atoms was obtained from a subsequent difference Fourier map phased with the refined position and isotropic thermal parameters of the W atoms. For **1** twelve peaks were found around the W(3) atom, and these peaks were ascribed to the F atoms of a 'WF_7' entity disordered with respect to the positions of the fluorine atoms, with occupation factors of 1 for F(31), and 0.5 for F(32), F(33), F(34), F(35) and F(36). The last difference maps for **2** revealed a disordered electron density, which was interpreted as due to CH_3CN molecules. The atoms of these molecules, with positional parameters fixed to observed positions, were introduced in the calculation with an occupation factor of 0.5 and an isotropic thermal factor fixed to $B=8$ Å^2. Hydrogen atoms were not located on the difference maps. Their

TABLE 3. Positional parameters and their estimated standard deviations

Atom	x	y	z	B (Å^2)^a
$[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot WF_6$ (1)				
W(1)	0.000	0.000	0.000	2.11(3)
W(2)	0.000	0.000	0.500	6.76(8)
W(3)	0.000	0.000	0.30199(8)	3.77(5)
F(10)	0.124(2)	−0.110(2)	0.0205(6)	2.6(4)*
F(21)	−0.113(5)	0.127(5)	0.502(2)	16(1)*
F(22)	0.000	0.000	0.564(3)	21(3)*
F(31)	0.033(3)	−0.152(3)	0.331(1)	7.4(8)*
F(32)	−0.139(5)	−0.018(5)	0.343(2)	6(1)*
F(33)	−0.085(5)	−0.116(5)	0.262(2)	6(1)*
F(34)	0.036(5)	−0.106(5)	0.254(2)	6(1)*
F(35)	−0.131(9)	0.069(8)	0.265(3)	14(3)*
F(36)	0.169(7)	0.033(7)	0.306(2)	9(2)*
N(10)	0.081(3)	0.095(3)	0.0638(9)	2.1(5)*
C(11)	0.167(4)	0.200(4)	0.062(1)	3.2(8)*
C(12)	0.213(4)	0.255(4)	0.102(2)	4.6(9)*
C(13)	0.181(4)	0.205(4)	0.146(2)	5(1)*
C(14)	0.100(4)	0.101(4)	0.151(2)	4.0(8)*
C(15)	0.046(4)	0.052(4)	0.106(1)	3.5(8)*
$[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot CH_3CN$ (2)				
W(1)	0.1301(2)	0.3983(2)	0.2462(1)	2.52(3)
W(2)	0.5553(2)	0.2460(2)	0.1507(1)	5.40(6)
W(3)	0.1894(3)	0.9358(2)	0.3663(1)	5.79(6)
F(11)	−0.011(2)	0.492(2)	0.201(1)	2.4(4)*
F(12)	0.239(2)	0.268(2)	0.208(1)	3.7(5)*
F(13)	0.261(2)	0.542(2)	0.299(1)	2.6(4)*
F(14)	0.031(2)	0.288(2)	0.279(1)	3.6(5)*
F(21)	0.605(4)	0.270(4)	0.060(3)	12(1)*
F(22)	0.580(4)	0.239(4)	0.278(3)	13(1)*
F(23)	0.435(4)	0.119(4)	0.155(3)	13(1)*
F(24)	0.388(4)	0.237(4)	0.066(3)	12(1)*
F(25)	0.501(3)	0.397(3)	0.215(2)	8.9(9)*
F(26)	0.727(4)	0.352(3)	0.224(2)	11(1)*
F(27)	0.644(3)	0.095(3)	0.131(2)	9.5(9)*
F(31)	0.023(4)	0.946(4)	0.393(3)	14(1)*
F(32)	0.297(5)	0.879(4)	0.300(3)	15.0*
F(33)	0.348(5)	1.012(5)	0.451(4)	18.0*
F(34)	0.199(4)	1.103(4)	0.437(3)	14(1)*
F(35)	0.110(5)	1.018(5)	0.279(3)	16(2)*
F(36)	0.094(3)	0.790(3)	0.267(2)	8.3(8)*
F(37)	0.239(3)	0.816(3)	0.433(2)	10(1)*
N(1)	0.171(3)	0.436(3)	0.120(2)	3.0(7)*
N(2)	0.001(3)	0.254(3)	0.107(2)	4.0(8)*
N(3)	0.082(3)	0.528(3)	0.372(2)	3.0(7)*
N(4)	0.275(3)	0.372(3)	0.378(2)	3.8(7)*
C(11)	0.256(4)	0.544(4)	0.135(3)	4(1)*
C(12)	0.287(4)	0.565(4)	0.057(3)	5(1)*
C(13)	0.230(4)	0.471(4)	−0.028(3)	5(1)*
C(14)	0.146(4)	0.370(4)	−0.046(3)	5(1)*
C(15)	0.110(4)	0.359(4)	0.034(2)	3.4(9)*
C(21)	0.011(4)	0.253(4)	0.021(2)	3.6(9)*
C(22)	−0.063(4)	0.165(4)	−0.066(3)	3.8(9)*
C(23)	−0.155(4)	0.074(4)	−0.067(3)	4(1)*
C(24)	−0.170(4)	0.066(4)	0.013(3)	4(1)*
C(25)	−0.095(4)	0.156(4)	0.103(3)	5(1)*
C(31)	0.169(4)	0.541(3)	0.469(2)	2.9(8)*
C(32)	0.143(4)	0.629(4)	0.540(3)	4(1)*
C(33)	0.037(4)	0.705(4)	0.527(3)	5(1)*
C(34)	−0.048(4)	0.696(4)	0.443(3)	4(1)*
C(35)	−0.021(4)	0.607(4)	0.367(3)	5(1)*
C(41)	0.368(4)	0.289(4)	0.381(3)	6(1)*
C(42)	0.457(5)	0.276(4)	0.462(3)	6(1)*
C(43)	0.443(5)	0.355(4)	0.546(3)	6(1)*
C(44)	0.351(4)	0.442(4)	0.555(3)	4(1)*
C(45)	0.273(4)	0.453(4)	0.465(3)	5(1)*
N(100)	0.340	0.010	0.750	8.0
N(200)	0.359	0.332	0.791	8.0
C(100)	0.389	0.109	0.729	8.0
C(101)	0.473	0.195	0.730	8.0
C(200)	0.330	0.240	0.750	8.0
C(201)	0.332	0.082	0.688	8.0

(*continued*)

TABLE 3. (*continued*)

^{a}Starred atoms were refined isotropically. For anisotropically refined atoms, $B=\frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\vec{a}_i\vec{a}_j$.

theoretical positions were included for the factor structure calculation only for **2**. For both complexes, the W atoms were refined anisotropically and the other atoms isotropically. For both complexes, there was only one residual peak of 1.7 e Å^{-3} on the final difference map and the absolute value of the other was found to be smaller than 1e Å^{-3}. These residual peaks are in the regions close to the atoms with higher thermal parameters. The atomic scattering factors and anomalous dispersion terms for W^{VI} were taken from the *International Tables for X-ray Crystallography* [8].

Results and discussion

Syntheses

The reaction of WF_6 with bipy in a 1:1 molar ratio achieved either in CH_3CN or CH_2Cl_2 led solely to the insoluble adduct $WF_6\cdot$bipy. With a WF_6/bipy ratio greater than 1:1 and lower than 3:1, a mixture of $WF_6\cdot$bipy and **1** was obtained in CH_3CN solution, and with higher ratios only **1** was obtained. In CH_2Cl_2 solution, **1** could not be obtained without $WF_6\cdot$bipy. The solvent CH_3CN obviously favours the formation of the ionic derivative through F$^-$ ion exchange (see below). It is worth pointing out that no reaction was observed at ambient temperature in the absence of solvent. The properties of $WF_6\cdot$bipy closely resemble those of $WOF_4\cdot$bipy [2], and great similarities were also found between the infrared spectra of the two adducts.

The mechanism through which excess WF_6 leads to the formation of the ionic complexes **1** and **2** may be written as follows:

$$WF_6+\text{bipy}\longrightarrow WF_6\cdot\text{bipy} \qquad (1)$$

TABLE 4. Selected bond lengths (Å) and angles (°) for $[\mathrm{WF_4(bipy)_2}]^{2+}\cdot 2[\mathrm{WF_7}]^-\cdot\mathrm{WF_6}$ (**1**)

Bond	Length	Bond	Length	Bond	Length
W(1)−F(10)	1.836(4)	W(3)−F(31)	1.832(8)	N(10)−C(11)	1.41(1)
W(1)−N(10)	2.263(7)	W(3)−F(32)	1.88(1)	N(10)−C(15)	1.34(1)
W(2)−F(21)	1.77(1)	W(3)−F(33)	1.89(2)	C(11)−C(12)	1.41(1)
W(2)−F(22)	1.87(2)	W(3)−F(34)	1.80(2)	C(12)−C(13)	1.35(1)
		W(3)−F(35)	1.88(3)	C(13)−C(14)	1.43(1)
		W(3)−F(36)	1.77(2)	C(14)−C(15)	1.45(1)
				C(15)−C(15)	1.48(2)

Bonds	Angle	Bonds	Angle	Bonds	Angle
F(10)−W(1)−N(10)	75.3(2)	F(21)−W(2)−F(21)^{iv}	90.13(5)	F(31)^{i}−W(3)−F(31)	124.9(5)
F(10)−W(1)−N(10)^{i}	73.9(2)	F(21)−W(2)−F(22)	87.2(5)	F(31)−W(3)−F(32)	77.9(5)
F(10)−W(1)−N(10)^{ii}	144.3(2)	F(21)−W(2)−F(22)^{iv}	92.8(5)	F(31)^{i}−W(3)−F(32)	69.2(5)
F(10)−W(1)−N(10)^{iii}	73.7(2)	F(21)−W(2)−F(21)^{i}	174(1)	F(31)^{i}−W(3)−F(33)	138.9(5)
F(10)−W(1)−F(10)^{i}	142.1(3)			F(31)−W(3)−F(33)	79.9(5)
F(10)−W(1)−F(10)^{ii}	96.07(9)			F(31)−W(3)−F(34)	76.7(6)
F(10)−W(1)−F(10)^{iii}	96.07(9)			F(31)^{i}−W(3)−F(34)	157.8(6)
N(10)−W(1)−N(10)^{i}	70.7(3)			F(31)−W(3)−F(35)	134.9(8)
N(10)−W(1)−N(10)^{ii}	131.7(2)			F(31)^{i}−W(3)−F(35)	80.7(7)
N(10)−W(1)−N(10)^{iii}	131.7(2)			F(31)−W(3)−F(36)	89.7(7)
				F(31)^{i}−W(3)−F(36)	87.3(7)
C(11)−N(10)−C(15)	120.6(8)			F(32)−W(3)−F(34)	126.0(7)
N(10)−C(11)−C(12)	117.4(9)			F(32)−W(3)−F(35)	79.3(9)
C(11)−C(12)−C(13)	121(1)			F(32)−W(3)−F(36)	138.4(9)
C(12)−C(13)−C(14)	125(1)			F(32)−W(3)−F(33)	88.4(6)
C(13)−C(14)−C(15)	112(1)			F(32)−W(3)−F(34)	126.0(7)
N(10)−C(15)−C(14)	124.5(8)			F(32)−W(3)−F(35)	79.3(9)
N(10)−C(15)−C(15)^{i}	115.0(5)			F(32)−W(3)−F(36)	138(1)
C(14)−C(15)−C(15)^{i}	120.5(6)			F(33)−W(3)−F(34)	40.7(5)
				F(33)−W(3)−F(35)	61.0(8)
				F(33)−W(3)−F(36)	128.7(7)
				F(34)−W(3)−F(35)	86.3(8)
				F(34)−W(3)−F(36)	88.1(7)
				F(35)−W(3)−F(36)	132(1)

Symmetry codes: (i) $\bar{x}, \bar{y}, z$; (ii) $\bar{y}, x, \bar{z}$ (iii) $y, \bar{x}, \bar{z}$; (iv) $\bar{y}, x, \bar{z}+1$.

$$2\mathrm{WF_6}\cdot\mathrm{bipy}+\mathrm{WF_6}\longrightarrow [\mathrm{WF_4(bipy)_2}]^{2+}+2[\mathrm{WF_7}]^- \qquad (2)$$

$$[\mathrm{WF_4(bipy)_2}]^{2+}+2[\mathrm{WF_7}]^-+\mathrm{WF_6}\longrightarrow \mathbf{1}_{\mathrm{cryst.}}\xrightarrow[+\mathrm{CH_3CN}]{-\mathrm{WF_6}}\mathbf{2}_{\mathrm{cryst.}} \qquad (3)$$

The stoichiometry would only require a twofold excess of $\mathrm{WF_6}$ to form **1**. However, the conversion yields of reactions (2) and (3) probably depend on the relative amount of $\mathrm{WF_6}$ present.

Crystal structure

Positional and thermal parameters for **1** and **2** are listed in Table 3, and selected bond lengths and angles for **1** are presented in Table 4. Drawings of the structures of the anion and cation in **1** and **2**, and of the $\mathrm{WF_6}$ molecule in **1** are shown in Fig. 1. Stereoscopic views of the unit cell contents of **1** and **2** are shown in Fig. 2.

In **1** and **2**, the W atom of the $[\mathrm{WF_4(bipy)_2}]^{2+}$ cation is coordinated by the N atoms of two bipy units and four F atoms forming a triangular dodecahedron [see Fig. 1(a)] with the ranges of bond distances (in Å) being: W−N, 2.23(1)–2.29(1), and W−F, 1.836(4)–1.867(9). This arrangement is the same as that found for this cation in $[\mathrm{WF_4(bipy)_2}]^{2+}\cdot 2[\mathrm{W_2O_2F_9}]^-\cdot 0.25\mathrm{HF}$ [1]. The coordination polyhedron of the $[\mathrm{WF_7}]^-$ anion is a distorted monocapped trigonal prism [see Fig. 1(b)] with the range of bond distances (in Å) being: W−F, 1.75(2)–1.92(2). The determination of the structure of this anion in **2** was the key to the interpretation of its disordered structure in **1**. The F atoms of the $\mathrm{WF_6}$ molecule in **1** form a slightly elongated octahedron with one long F−W−F axis [3.74 (4) Å] and two short F−W−F axes [3.54 (2) Å]. The mean W−F distance (1.80 Å) for $\mathrm{WF_6}$ in **1** is in agreement

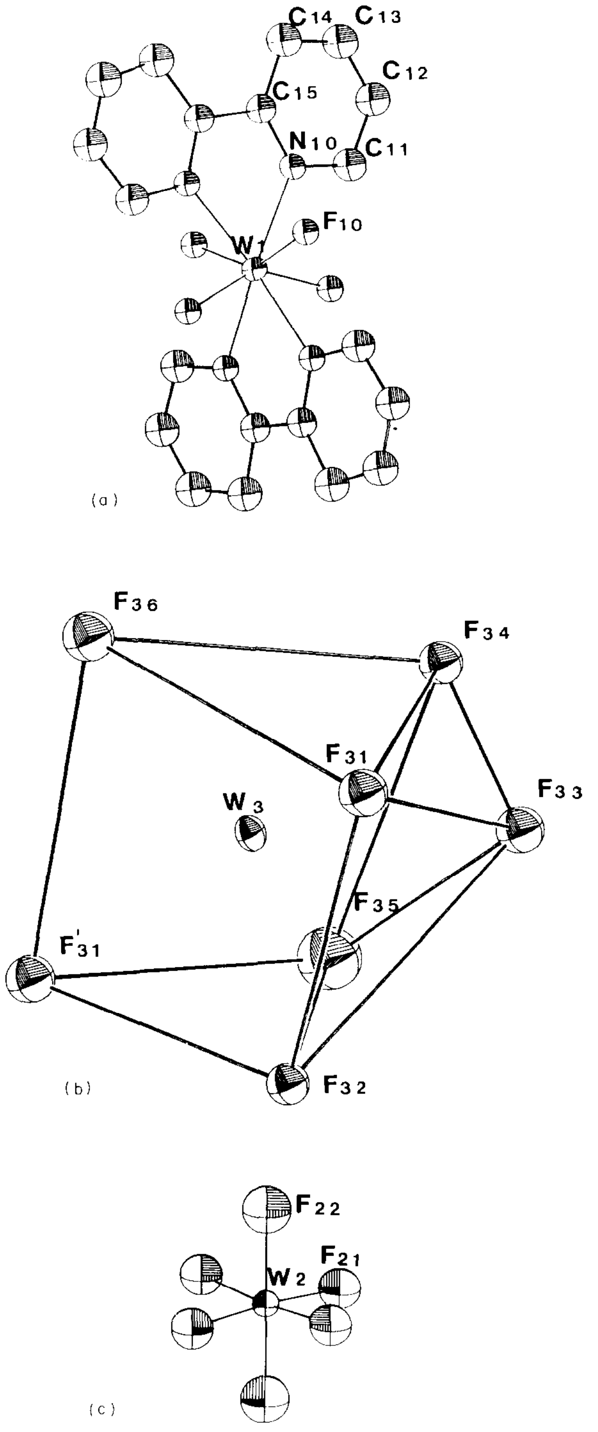

Fig. 1. ORTEP [12] drawings of (a) the $[WF_4(bipy)_2]^{2+}$ cation, (b) the coordination polyhedron of the $[WF_7]^-$ anion and (c) the WF_6 molecule. Vibration ellipsoids are drawn at the 30% probability level.

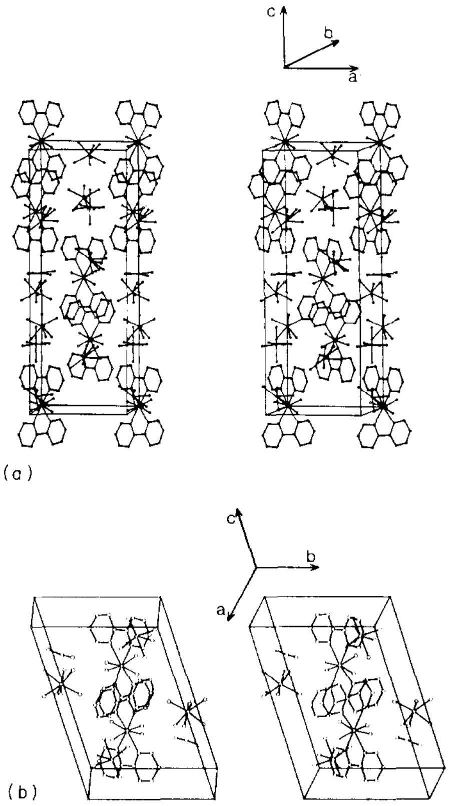

Fig. 2. Stereoscopic views of the structure in the unit cells of (a): $[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot WF_6$ (**1**); and (b): $[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot CH_3CN$ (**2**).

with that determined by neutron diffraction for its orthorhombic (1.81 Å) [9] or cubic phase (1.83 Å) [10], as well as with that measured by electron diffraction of the vapour (1.833 Å) [11]. The three different W atoms in **1** are in special positions, with W(1) and W(2) lying on the $\bar{4}$ axis and W(3) on the 2 axis. Consequently, the cation, the anion and WF_6 are packed in stacks along the *c* axis. The high-temperature factors of the F atoms suggest that WF_6 is a 'solvating molecule'. This is confirmed by the crystal packing in **2**, which is similar to that of **1** with the solvating CH_3CN molecules replacing the WF_6 molecules (see Fig. 2). The most outstanding consequence of this substitution is the loss of the tetragonal symmetry of the crystal. The similarity between the two crystal cells is better observed by comparing the parameters of **2** with those of the primitive cell of **1**: ($a = 10.54$ Å, $b = 10.54$ Å, $c = 15.18$ Å, $\alpha = 110.4°$, $\beta = 90°$, $\gamma = 90°$).

NMR studies

NMR spectra were recorded for solutions of **1** and **2** in CD_3CN. The ^1H and ^{13}C NMR data for **1** are listed in Table 5 together with those of bipy. The corresponding data for **2** were found to be identical with those of **1**. Because of the presence of 0.4 mol% of non-deuterated species in the acetonitrile-d_3 used, the protons and ^{13}C atoms of CH_3CN from **2** could not be distinguished from those of the solvent. As previously observed [1], the protons of the

TABLE 5. ^{1}H and ^{13}C NMR data[a] for solutions of $[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot WF_6$ (**1**) in CD_3CN. Comparison with those of bipy

^{1}H	Chemical shifts					Coupling constants						Spectrum
		δ_3	δ_4	δ_5	δ_6	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	
1		8.95	8.76	8.13	9.57	7.74	1.34	0	7.52	1.09	6.56	ABXY
bipy		8.41	7.87	7.37	8.65	7.96	1.20	1.00	7.62	1.83	4.38	1st order
^{13}C	δ_2	δ_3	δ_4	δ_5	δ_6	$J_{C(3)H(3)}$	$J_{C(4)H(4)}$	$J_{C(5)H(5)}$	$J_{C(6)H(6)}$			
1	152.10	127.82	146.96	130.36	147	172	172	178	172			
bipy	156.88	138.01	124.90	121.54	150.19	163	163	165	180			

[a] Chemical shifts δ in ppm from TMS and coupling constants J in Hz; subscripts 3, 4, 5 and 6 refer to hydrogen and carbon atom positions, with 3 indicating the position adjacent to the C—C bond of the two pyridyl rings, and 6, 5, 4 the *ortho*, *meta* and *para* position to the nitrogen atom, respectively; subscript 2 refers to the carbon atoms bonding the two pyridyl rings.

$[WF_4(bipy)_2]^{2+}$ cation are deshielded in comparison to those of bipy. The ^{19}F NMR spectra of solutions of **1** in CD_3CN at 263 K showed lines at ϕ 167.0, 153.2 and 144.4 ppm, which were assigned to WF_6 [13], $[WF_4(bipy)_2]^{2+}$ [1] and $[WF_7]^-$ [14, 15], respectively. Owing to the exchange of F^- anions, which takes place between WF_6 and $[WF_7]^-$ in acetonitrile [14, 15], only one broad line was observed at ϕ 144.4 ppm for these two species at ambient temperature. Apart from the absence of the WF_6 line, the ^{19}F NMR spectra of **2** were found to be identical with those of **1**.

Vibrational spectra

Infrared and Raman data for **1** are summarized in Table 6. Only infrared spectra could be obtained for **2** and $WF_6\cdot$bipy. The relevant data are also shown in Table 6. Apart from the bands due to CH_3CN, the infrared spectrum of **2** is very close to that of **1**. The positions of the bands for CH_3CN also indicate that this molecule is not coordinated in the complex, since for a coordinated molecule the bands assigned to the C—C≡N skeletal modes ν_2 (A_1) (2251 cm^{-1}) and ν_4 (A_1) (919 cm^{-1}) should appear at higher frequency than in the free molecule [16, 17]. For both complexes, several bands of the ligand bipy are shifted to higher frequencies when compared with those of its free form. These shifts are quite similar to those observed for the adducts $WOF_4\cdot$bipy and $WO_2F_2\cdot$bipy, and the relevant discussion already presented [2] is also valid here. As far as the vibrations associated with the W and F atoms are concerned, the intense Raman lines at 772 and 707 cm^{-1} are assigned to WF_6 (ν_1) [18] and $[WF_7]^-$ [14, 19], respectively. The two other intense Raman lines located in this region at 678 and 645 cm^{-1} are assigned to the symmetric W—F stretching vibrations of $[WF_4(bipy)_2]^{2+}$. The high intensity of the line at 678 cm^{-1} is explained by a contribution of the vibration (ν_2) of WF_6 [18] to this line.

Conclusions

This study has permitted a thorough characterization of the WF_6/bipy interaction. When the reaction is carried out using a 1:1 molar ratio of the reactants, the molecular adduct $WF_6\cdot$bipy is obtained, whereas with an excess of WF_6 the bis(2,2′-bipyridyl)tetrafluorotungsten(VI) cation, $[WF_4(bipy)_2]^{2+}$, and the heptafluorotungstate(VI) anion, $[WF_7]^-$, are formed. Depending on the relative concentration of WF_6 and **1** in CH_3CN, either **1** or **2** crystallizes. The molecules CH_3CN and WF_6 are present in the complexes as solvating species. The determination of the crystal structure of these complexes has shown that the coordination of the tungsten atom in the $[WF_7]^-$ ion is a distorted monocapped trigonal prism.

Taking only the electrostatic ligand repulsions into account, three most energetically favourable coordination geometries of the central atom are calculated for an AB_7-type species [20] (*i*:*j*:*k* = ligand arrangement): the pentagonal bipyramid (1:5:1), the capped octahedron (1:3:3) and the capped trigonal prism (1:4:2). Among the fluorides, only the ions $[NbF_7]^{2-}$ and $[TaF_7]^{2-}$ [21, 22] had been previously found to be close to the 1:4:2 type. By analogy between the pairs of elements Nb/Mo and Ta/W, it may be inferred that this coordination geometry of the central atom is also that of the $[MoF_7]^-$ ion.

Supplementary material

Tables of bond distances and bond angles, calculated positional parameters of H atoms for **2**, and tables of observed and calculated structure factors, root-mean square amplitudes of thermal vibration, anisotropy thermal parameters for **1** and **2** are available from the authors on request.

TABLE 6. Vibrational data[a] for $[WF_4(bipy)_2]^{2+} \cdot 2[WF_7]^- \cdot WF_6$ (**1**), $[WF_4(bipy)_2]^{2+} \cdot 2[WF_7]^- \cdot CH_3CN$ (**2**) and $WF_6 \cdot$bipy. Comparison with those of bipy

Infrared				Raman[b]		Infrared				Raman[b]	
bipy[c]	$WF_6 \cdot$bipy	**1**	**2**	bipy[c]	**1**[d]	bipy[c]	$WF_6 \cdot$bipy	**1**	**2**	bipy[c]	**1**
			3210 mw			1215 mw	1226 ms	1215 sh	1220 sh	1216 (12)	
	3147 ms	3150 ms	3148 ms	3140 (1)				1185 ms	1187 ms		
	3120 mw	3100 ms	3100 ms	3116 (1)		1170 w	1176 m	1175 ms	1175 ms		1173 (5)
3090 mw				3082 (3)		1142 m	1157 ms	1135 m	1135 m	1145 (2)	
				3073 (7)			1130 m	1120 ms	1117 ms		
3060 mw				3064 (11)		1090 ms	1112 m	1094 m	1093 m	1091 (3)	1094 (23)
		3050 sh	3048 sh	3045 (6)		1065 m	1079 m				1066 (3)
				3028 (2)		1043 ms			1048 sh	1043 (15)	1048 (7)
3010 w				3006 (3)			1037 ms	1028 s	1030 ms		1029 (81)
	2940 w		2942* mw				1024 m	1018 ms	1020 ms		
2295 w		2300 w	2290 mw			996 m	987 mw	987 m	985 ms	995 (97)	
		2270 w	2251* ms			975 sh	972 mw	975 sh			
		2253 w					927 mw		919* mw		
		2030 w	2030 mw								
1990 w	1982 w		1990 w			895 m		900 m	898 m		
1965 mw	1957 w		1960 w					793 sh	795 sh		794 (4)
1895 mw			1905 w				*777* s	*775* s	*777* s		*772* (47)
1870 mw	1872 w	1870 mw	1867 mw							813 (15)	
1803 mw						755 vs		750 w	747 w	763 (5)	
1715 mw						740 m	723 ms	720 sh	720 ms		
1695 mw								*705*	*705* w		*707* (65)
1665 mw				1673 (2)				*670* } s, br	*670* } s, br		*678* (100)
				1628 (2)		652 ms	647 s	*640*	*640*		*645* (47)
	1610 s	1610 s	1605 s	1612 (3)	1609 (75)		*637* m				
				1587 (100)		616 ms				612 (25)	
1580 s	1575 ms	1575 ms	1572 ms	1572 (80)	1574 (66)		*582* vs	*575* sh	*580* sh		
1557 ms							*547* ms				
1529 vw	1537 w	1533 mw					*527* sh	*525* mw	*523* mw		
1503 w	1512 ms	1507 ms	1507 ms		1511 (31)			*490* mw	*480* mw		*498* (4)
	1479 s	1480 s	1480 s	1480 (41)		462 w	462 mw	472 mw	470 mw		
								450 w	450 w		
1453 s	1446 s	1455 s	1445 s	1440 (72)	1440 (7.5)	422 w	425 m	415 m	415 m	437 (3)	435 (4)
1417 s						396 s		395 m	395 m		384 (11)
1397 sh							367 mw	355 m	355 mw		358 (7)
		1367 mw	1377* mw				350 mw		330 mw		347 (4)
					1337 (69)		296 mw	*325* ms, br	*320* w		*324* (11)
	1328 s	1330 s	1330 s		1330 sh				295 w		266 (3)
1306 w				1300 (43)	1310 sh			275 w	275 w		238 (45)
		1295 m	1293 m	1290 sh	1290 (1)						227 (40)
1270 w		1275 m	1277 m		1280 (3)					222 (25)	211 (58)
1253 ms	1245 ms	1245 ms	1240 ms	1235 (48)	1242 (5)						161 (63)

[a] Frequencies in cm^{-1}. Frequencies in italic are those which could be assigned to the inorganic part of the compounds, and those marked with an asterisk are due to CH_3CN. Abbreviations used: sh, shoulder; br, broad; v, very; s, strong; m, medium; w, weak.

[b] Uncorrected Raman intensities based on relative peak heights are given in parentheses.

[c] From ref. 2.

[d] The high-frequency Raman shifts are limited by the low sensitivity of the detector at wavelengths larger than 7300 Å.

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