reflect the small amount of structural reorganization required for this conversion as well as the existence of a facile mechanism for the elimination of RH as a stable byproduct (Figure 3). A detailed study of the mechanism of this thermal decomposition process in the case of the trimethylaluminum–ammonia system is in progress.

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Supplementary Material Available: Full listings of crystal data and summary of data collection and refinement, anisotropic thermal parameters, hydrogen coordinates, and bond distances and angles (Tables S1–S6) for $[(CH_3)_2AlNH_2]_3$ (**1**) and $[(t\text{-}C_4H_9)_2AlNH_2]_3$ (**2**) (8 pages); listings of observed and calculated structure factors (Tables S7 and S8) (7 pages). Ordering information is given on any current masthead page.

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Preparation, Characterization, and Crystal Structure of the Adducts $WOF_4 \cdot nC_5H_5N$ (n = 1, 2)

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$WOF_4 \cdot 2C_5H_5N$ was prepared from the reaction of WOF_4 with an excess of pyridine, and $WOF_4 \cdot C_5H_5N$ resulted from pumping of $WOF_4 \cdot 2C_5H_5N$ at room temperature or the reaction of stoichiometric amounts of WOF_4 and C_5H_5N in dichloromethane. The two adducts were characterized by elemental analyses, X-ray powder data, and vibrational spectroscopy. Solutions of the adducts in dichloromethane were studied by ^{19}F and ^{1}H NMR spectroscopy. The crystal structures of $WOF_4 \cdot 2C_5H_5N$ and $WOF_4 \cdot C_5H_5N$ have been determined by X-ray diffraction methods. Both adducts are of molecular type. In $WOF_4 \cdot 2C_5H_5N$ two nitrogen atoms of the pyridine ligands, one oxygen, and two fluorine atoms form a regular pentagon around the tungsten atom. Two other fluorine atoms, located at the apical positions, complete the pentagonal bipyramid of ligands. In $WOF_4 \cdot C_5H_5N$, the tungsten atom is surrounded by a distorted octahedron of ligands with the nitrogen of the pyridine ligand being trans to the oxygen atom and the equatorial plane made up of four fluorine atoms located at the corners of a regular rectangle. The space groups, unit cell parameters, and R factors are as follows: $WOF_4 \cdot 2C_5H_5N$, monoclinic, $C2/c$, a = 8.248 (3) Å, b = 11.465 (3) Å, c = 13.507 (3) Å, β = 108.10 (2)°, V = 1296 Å^3, Z = 4, and R = 0.031; $WOF_4 \cdot C_5H_5N$, monoclinic, $P2_1/c$, a = 7.757 (2) Å, b = 14.442 (3) Å, c = 7.859 (7) Å, β = 105.79 (4)°, V = 847 Å^3, Z = 4, and R = 0.059.

Introduction

Oxide tetrafluorides of transition elements such as tungsten or molybdenum are known to be good electron acceptors,[1-17] and for instance their acid character has been demonstrated by their reactions with strong bases such as CsF[8] or NOF or $ClOF_3$.[7] All the adducts, except those obtained with XeF_2 or KrF_2,[9,10,12,14,15] have been found to be ionic and to contain the species $M_2O_2F_9^-$, MOF_5^-, or MOF_6^{2-} (M = W, Mo). As far as organic bases are concerned, their interaction with $MoOF_4$ or WOF_4, used as reactants or formed in situ, has been found[18-32] to yield either molecular or ionic species depending on the reaction conditions and/or bases. The data regarding the species of these organic base derivatives have been obtained mainly by ^{19}F NMR spectroscopy, and no crystal data have been published so far.

Considering that the chemical properties of WF_6 and WOF_4 are closely related and also that Tebbe and Mutterties[18] had shown

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that pyridine and WF_6 reacted to yield stable adducts, this organic base was selected for a thorough study of the interaction taking place between an oxide tetrafluoride of a 5d transition element and a strong organic base.

Experimental Section

Apparatus. Volatile fluorides were manipulated in an all-metal vacuum line equipped with Teflon or metal valves. Other volatile materials were purified and transferred in a glass vacuum line designed to handle highly moisture-sensitive materials.[33] Solid products were handled in gloveboxes flushed with dry nitrogen. Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using small crystals pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.).

A standard cell, equipped with KBr windows, was also used for liquids. Raman spectra of the solutions contained in 5 mm o.d. NMR tubes or of crystals in 0.5 mm o.d. glass capillaries were recorded on a Coderg Model T 800 spectrophotometer using the 514.5-nm exciting line of an Ar ion Spectra-Physics laser filtered with a Coderg premonochromator. Below 2000 cm^{-1}, the frequency accuracy was estimated to be approximately ±3 cm^{-1} for the infrared spectra and ±1 cm^{-1} for the Raman spectra; above 2000 cm^{-1}, the accuracy was estimated to be twice these values. The ^{19}F and the ^{1}H NMR spectra of the solutions in standard tubes were obtained on a Varian NV 14 spectrometer and a Bruker WP spectrometer operating at 56.4 and 60 MHz, respectively. Samples were referenced externally with respect to $Si(CH_3)_4$ (^{1}H) and $CFCl_3$ (^{19}F). A positive chemical shift denotes a resonance occurring to high frequency of the reference compound. The chemical shift accuracy was estimated to be approximately ±0.05 ppm.

X-ray Diffraction. X-ray diffraction powder patterns of the samples sealed in 0.3 mm o.d. glass capillaries were obtained by using a Philips camera (diameter 11.46 cm) using Ni-filtered Cu Kα radiation. Crystals suitable for structure determination were selected in the drybox under a microscope and sealed inside 0.3 mm o.d. glass capillaries to protect them from the atmosphere. The crystals were examined with an Enraf-Nonius CAD 4 automated diffractometer. Cell dimensions were obtained by a least-squares refinement of the setting angles of the 25 reflections with θ between 8 and 12°. Intensities were corrected for Lorentz polarization and empirical absorption by using DIFABS.[34] The structures were solved by the heavy-atom method and refined by full-matrix least squares (*F*). The W atom of $WOF_4{\cdot}C_5H_5N$ and W, F, O, and N atoms of $WOF_4{\cdot}2C_5H_5N$ were refined anisotropically. H atoms were included in the refinement at calculated positions: they were not refined but constrained to ride on their C atoms. In $WOF_4{\cdot}2C_5H_5N$, the position of the O atom is based on the symmetry requirement of the space group, whereas in $WOF_4{\cdot}C_5H_5N$, in which no symmetry was imposed, the refinements of the five solutions O/F lead to an unique solution (homogeneity of the *B* values). All calculations were performed on a PDP 11/23 Plus computer with the Enraf-Nonius structure determination package.[35] Analytical scattering factors for neutral atoms[36] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Other experimental details appear with the crystal data in Table II and in the supplementary material.

Materials. Tungsten oxide tetrafluoride was obtained as described in the literature[38] and purified by sublimation under dynamic vacuum at ca. 50 °C. Tungsten hexafluoride used for this preparation was from Comurhex. Pyridine (Prolabo) was refluxed over KOH and distilled; methylene chloride (Prolabo) was refluxed over Na–Pb alloy. Methylene chloride-d_2 and pyridine-d_5 (CEA; 99.3% and 99.6% isotopic enrichment, respectively) were purified as for the non-deuteriated compounds except that a smaller scale apparatus was used. Microanalyses were by Analytische Laboratorien, Elbach, West Germany.

Preparation of $WOF_4{\cdot}2C_5H_5N$. A 0.394-g (1.428-mmol) amount of WOF_4 was loaded in a drybox into a dried 250-cm^3 glass flask. The flask was evacuated on the vacuum line, and 30 cm^3 (0.372 mol) of pyridine was condensed into the flask cooled at liquid-nitrogen temperature. The mixture was slowly warmed up to room temperature and stirred for 1 h. As no sign of reaction occurred and WOF_4 was still in suspension, the mixture was heated to ca. 60 °C, which instantly resulted in a pale yellow homogeneous solution. Cooling of this solution to ca. 40 °C gave a deposit of very pale blue crystals on the walls. The solution was cooled down to room temperature, and the volatiles were removed by pumping. Anal. Calcd for $WOF_4{\cdot}2C_5H_5N$: W, 42.36; F, 17.51; C, 27.67; H, 2.32; N, 6.45. Found: W, 42.15; F, 17.28; C, 27.54; H, 2.24; N, 6.37. These crystals were sublimed at ca. 30 °C under static vacuum to obtain crystals suitable for X-ray structure determination.

Preparation of $WOF_4{\cdot}C_5H_5N$. The initial crystals identified as $WOF_4{\cdot}2C_5H_5N$ were found to decompose under pumping at room temperature. The crystals were ground and loaded into a dried 250-cm^3 glass flask in a drybox. The flask was evacuated and pumped for 5 days at room temperature. The pale blue solid compound left in the flask presented an X-ray powder pattern different from that of WOF_4 or $WOF_4{\cdot}2C_5H_5N$. Anal. Calcd for $WOF_4{\cdot}C_5H_5N$: W, 51.80; F, 21.41; C, 16.92; H, 1.42; N, 3.95. Found: W, 51.55; F, 21.19; C, 16.94; H, 1.55; N, 4.00.

The same compound was also obtained from reaction of 0.3136 g of WOF_4 (1.137 mmol) with 0.092 mL (1.14 mmol) of C_5H_5N in 15 cm^3 of dichloromethane. The very pale blue crystals that grew on standing were isolated, ground in the drybox, and identified as $WOF_4{\cdot}C_5H_5N$ from their X-ray powder patterns. Crystals obtained from sublimation of the powder under vacuum at ca. 50 °C were selected for X-ray structure determination.

In order to help in the interpretation of the vibrational spectra, the adducts were also prepared with pyridine-d_5.

Results and Discussion

Synthesis of the Adducts $WOF_4{\cdot}2C_5H_5N$ and $WOF_4{\cdot}C_5H_5N$. Tungsten oxide tetrafluoride readily dissolves in dry pyridine at ca. 60 °C. Cooling of the solution results in formation of very pale blue crystals with composition $WOF_4{\cdot}2C_5H_5N$, which are easily separated from the mother solution by decantation and filtration. The adduct has a marginal stability at room temperature, and it decomposes under pumping at this temperature into the adduct $WOF_4{\cdot}C_5H_5N$, which sublimes at ca. 50 °C under vacuum without decomposition. Both compounds were found to be very moisture sensitive.

The ^{19}F NMR spectrum of the mother liquor at 300 K showed only the presence of the anion WOF_5^-[7,19,21] in trace amounts. The ^{1}H NMR spectrum at 300 K showed only the lines of pyridine.

As a whole these results are interpreted as follows: gentle heating of a suspension of WOF_4 in pyridine yields depolymerization of the oxide tetrafluoride and its subsequent coordination by pyridine molecules. Probably owing to saturation of the coordination sphere of the central atom, the adduct $WOF_4{\cdot}2C_5H_5N$ that is formed is not soluble at room temperature in an excess of pyridine. Pumping or solvolysis in dichloromethane of this adduct left only one pyridine molecule attached to WOF_4. The traces of ionic species that were observed can be explained as being due to the formation of HF from reaction of WOF_4 with pyridine and subsequent transfer of the ion F^- to the bulk of WOF_4.[7] It must be pointed out that this process occurs only on a trace level as attested by the very weak intensity of the corresponding NMR lines and that the ionic species are not formed in dichloromethane solution.

Vibrational Spectra. The frequencies observed for the infrared and Raman spectra of the adducts $WOF_4{\cdot}2C_5H_5N$ and $WOF_4{\cdot}C_5H_5N$ are summarized in Table I, where the frequencies have, as far as possible, been put in rows corresponding to those of the parent species. Where not obvious, especially in the low-frequency region, assignments of bands to the pyridine ligand or to the vibrations of the other atoms were made by comparison of the spectra with those obtained for the deuteriated adducts (frequencies not shown in the table).

The frequencies attributable to the pyridine ligand are comparable[41–43] with those that have been observed for other complexes. When these frequencies are compared with those of the

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Table I. Vibrational Data[a] for WOF$_4$·2py and WOF$_4$·py: Comparison with Those of Pyridine (py) and WOF$_4$

IR [c]				Raman [c,d]				main assignments [e]
Py	WOF4.2Py	WOF4.Py	WOF4	Py	WOF4.2Py	WOF4.Py	WOF4	ligand Py
	3250 w	3250 w						
	3170 w	3180 w		3173				
3150				3152	3150 (1)	3150 (<1)		
	3120 s	3120 s		3144*				C-H stretching
3085*				3087*	3095 (12)	3096 (5)		
		3090 vw			3083 (17)	3088 sh		
	3060 m	3065 m		3067		3074 (3)		
	3040 w	3040 w						
	3012 w	3015 w						
3055*				3054*				
3030*				3022*				
3005*	2970 w	2970 w		2987*				
2955				2954*				
	2920 w	2920 w		2917				
2910				2909				
	2850 vw	2850 w		2871				
2830				2830				
				2792				
				2705				
				2657				
2600								
2450	2500 w	2485 w		2450				
	2380 vw	2385 w		2372				
2298	2315 w	2320 w		2292				
2205		2230 vw						
	2005 w	2015 mw						
1988*	1990 w	2000 m						
	1955 vw	1958 w						
1920*	1933 m	1933 ms						
	1875 vw	1885 w						
1870*	1850 m	1860 m						
1825	1820 w	1830 w			1835 (5)			
1730	1715 m	1713 m						
1685	1673 m	1663 m						
1633*	1640 m	1643 ms						
1598*	1613 s	1615 s		1596	1610 (8)	1610 (8)		
1580*	1575 m	1575 m		1580*	1575 (7)	1576 (2)		C-C and C-N stretching
1573*	1540 ms	1540 ms		1572*				
1480*	1490 s	1490 s		1481		.1490 (<1)		
1437*	1460 s	1458 s		1436				
1373	1392 m	1395 m						

IR [c]				Raman [c,d]				main assignments [e]	
Py	WOF4.2Py	WOF4.Py	WOF4	Py	WOF4.2Py	WOF4.Py	WOF4	ligand Py	other atoms
1355	1360 ms	1367 m		1355					
	1345 m	1355 mw							
1292	1300 vw	1310 w							
	1248 ms	1245 m				1238 (1)		in-plane C-H bending	
1215*	1213 s	1227 ms		1215*	1215 (12)	1222 (6)			
		1204 m							
	1170 vw	1167 m							
1145*	1160 m	1160 ms		1145	1160 (7)	1158 (2)			
	1120 vw								
	1098 m								
1065*	1073 s	1072 s		1067					
	1053 m	1050 s			1046 (25)	1046 (4)			
	973 s	997 s,br	1053*		969 (62)	996 (100)	1053*		W=O stretching
1027*	1022 ms	1022 ms		1030*	1022 (100)	1020 (13)		in-plane ring def	
990*				989*				sym stretching of the ring	
980				978				out-of-plane C-H bending	
942	950 mw	952 vw		940					
		900 w,br							
	920 vw								
884	875 vw	875 w,br		880					
850 vw		860 w,br							
809		795 w,br		812					
745*	763 s	758 ms		747					
	745 sh	745 sh					740		
			730*		650 (40)	694 (25)	725*		sym W-F stretching
				714			702		
700*	700 sh	700 sh		707				out-of-plane C-H bending	
675	685 s	675 ms						out-of-plane ring def	
	645 ms		665*				660		asym W-F stretching
650				651		657 (4)		in-plane-ring def	
		610 s, br				637 (4)			W-F stretching
597*	603 s			603	597 (51)	606 (2)		in-plane-ring def	
	565 ms				564 (5)		560		W-F stretching
			547*						W...FW stretching
	525 ms	510 w					520		W-F stretching
		457 ms,br							
			470						
403*	465 s	430 ms		406				out-of-plane ring def	
	387 ms	390 w		380	382 (3)				
			386						
	335 s	345 w			335 (16)		325*	def and lattice modes	
						313 (14)	315*		
	290 m	295 w	300		298 (3)	300 (26)			
	280 w				280 (10)	270 (3)			
					252 (1)		260		
						234 (1)	239		
							213		
					178 (21)	186 (2)	182		
						172 (2)			
					134 (46)	145 (19)	51		
							43		
							24		

[a] Frequencies in cm^{-1} are listed in the decreasing order of those of pyridine and WOF$_4$ taken altogether. Abbreviations used: sh, shoulder; br, broad; v, very; s, strong; m, medium; w, weak; def, deformation; sym, symmetric; asym, asymmetric. [b] Spectra recorded for the materials used in the preparations: liquid pyridine (thickness 0.1 mm), crystals of WOF$_4$ between AgBr disks for the IR spectra; liquid pyridine, crystals of WOF$_4$ for the Raman spectra. [c] Asterisks indicate the more intense bands. [d] Uncorrected Raman intensities based on relative peak heights are given in parentheses. [e] Pyridine data from ref 39; WOF$_4$ data from ref 40.

Table II. Crystallographic Data for $WOF_4 \cdot 2C_5H_5N$ and $WOF_4 \cdot C_5H_5N$

	$WOF_4 \cdot 2C_5H_5N$	$WOF_4 \cdot C_5H_5N$
fw	434.05	354.95
space group	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
a, Å	8.248 (3)	7.757 (2)
b, Å	11.465 (3)	14.442 (3)
c, Å	13.507 (3)	7.859 (7)
β, deg	108.10 (2)	105.79 (4)
V, Å^3	1214 (1)	847 (1)
Z	4	4
T, K	295	295
λ, Å	0.71073	0.71073
d(calcd), g cm^{-3}	2.374	2.783
μ, cm^{-1}	97.6	139.5
abs cor min–max	0.80–1.34	0.55–1.60
$R(F_o)$	0.031	0.059
$R_w(F_o)$	0.041	0.073

Table III. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å$^{2\,a}$
		$WOF_4 \cdot 2C_5H_5N$		
W	0.000	0.21402 (4)	0.250	3.43 (1)
F(1)	−0.0655 (8)	0.3454 (5)	0.3157 (4)	6.1 (1)
F(2)	0.2119 (8)	0.2058 (6)	0.3426 (5)	5.8 (2)
O	0.000	0.0484 (6)	0.250	2.5 (1)*
N(1)	−0.1034 (8)	0.1533 (7)	0.3766 (5)	3.6 (2)*
C(1)	−0.022 (1)	0.1808 (8)	0.4756 (7)	3.9 (2)
C(2)	−0.077 (1)	0.1400 (9)	0.5547 (7)	4.4 (2)
C(3)	−0.220 (1)	0.0718 (9)	0.5346 (7)	4.8 (2)
C(4)	−0.304 (1)	0.0447 (9)	0.4326 (7)	5.1 (2)
C(5)	−0.240 (1)	0.0837 (9)	0.3533 (7)	4.4 (2)
		$WOF_4 \cdot C_5H_5N$		
W	0.8711 (4)	0.4267 (2)	0.7122 (4)	5.79 (6)*
F(1)	0.743 (4)	0.466 (2)	0.492 (5)	7.3 (8)
F(2)	0.948 (4)	0.360 (2)	0.919 (5)	9 (1)
F(3)	0.993 (5)	0.356 (3)	0.588 (5)	10 (1)
F(4)	0.702 (4)	0.467 (2)	0.819 (5)	8 (1)
O	1.017 (7)	0.523 (3)	0.774 (7)	11 (1)
N	0.664 (5)	0.308 (3)	0.643 (5)	5 (1)
C(1)	0.691 (5)	0.221 (3)	0.660 (6)	4 (1)
C(2)	0.583 (6)	0.147 (3)	0.619 (7)	5 (1)
C(3)	0.410 (7)	0.171 (4)	0.533 (8)	6 (1)
C(4)	0.359 (7)	0.259 (4)	0.503 (8)	7 (1)
C(5)	0.487 (8)	0.322 (4)	0.551 (9)	8 (2)

[a] Asterisks denote B_{eq} values, equal to $^4/_3\sum_i\sum_j\beta_{ij}\vec{a}_i\vec{a}_j$.

free ligand, splitting or shifts of some bands occur, and the general tendency is toward an increase in frequency. As far as vibrations originating from those of WOF_4 are concerned, in line with a transfer of the electron density from the nitrogen atom to the tungsten atom, a decrease in the W=O and symmetric W—F stretching frequencies is observed. As expected, this effect is more pronounced for the adduct with two pyridine ligands. No indications of the location of the W—N vibration frequency could be found.

The Raman spectra of solutions of $WOF_4 \cdot 2C_5H_5N$ and $WOF_4 \cdot C_5H_5N$ in deuteriated dichloromethane were recorded at room temperature. In the region not obscured by solvent bands, those attributable to species in solution were found at 955 (broad), 992, 1005, 1020, and 1030 cm^{-1} for the former and at 1003 and 1020 cm^{-1} for the latter. From the bands observed for the solid adducts and for pyridine (see Table I), it is concluded that at room temperature the solution of $WOF_4 \cdot 2C_5H_5N$ contains this adduct (955 and 1020 cm^{-1}), $WOF_4 \cdot C_5H_5N$ (1005 and 1020 cm^{-1}), and free pyridine (992 and 1030 cm^{-1}), whereas the solution of $WOF_4 \cdot C_5H_5N$ contains only this adduct (1003 and 1020 cm^{-1}).

Finally it should be stressed that according to the vibrational spectra both adducts are molecular and that bands corresponding to neither the anionic tungsten[7] species (WOF_5^-, $W_2O_2F_9^-$) nor the pyridinium cation[41–43] were found to be present.

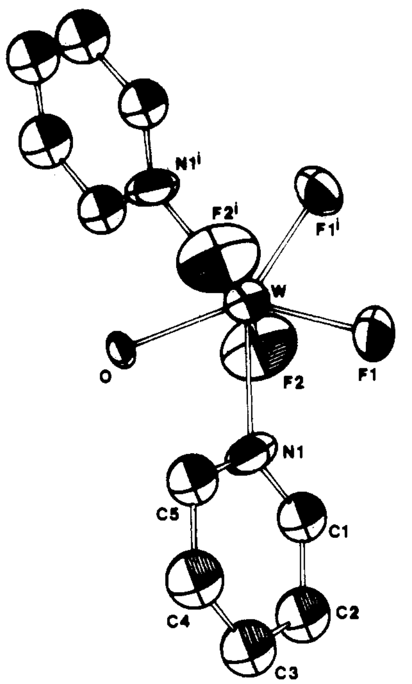

Figure 1. ORTEP[37] drawing of the molecular unit $WOF_4 \cdot 2C_5H_5N$ with the hydrogen atoms omitted (symmetry code for i: $\bar{x}$, y, $\bar{z}$).

Crystal Structure. The molecular stereochemistry of the adducts $WOF_4 \cdot 2C_5H_5N$ and $WOF_4 \cdot C_5H_5N$ was established by single-crystal studies. Crystal data are given in Table II. Final positional and thermal parameters are given in Table III with their estimated standard deviations. The relevant distances and angles are given in Table IV. Figures 1 and 3 show the molecular unit and atomic labeling scheme for $WOF_4 \cdot 2C_5H_5N$ and $WOF_4 \cdot C_5H_5N$, respectively. Figures 2 and 4 give a stereoscopic view of the molecular packing for $WOF_4 \cdot 2C_5H_5N$ and $WOF_4 \cdot C_5H_5N$, respectively.

Both compounds are molecular adducts. The coordination polyhedron of the tungsten atom in $WOF_4 \cdot 2C_5H_5N$ is a bipyramid with a planar pentagonal base made up of one oxygen, two nitrogen atoms of the pyridine ligands, and two fluorine atoms. The two other fluorine atoms are at the apical positions: the almost linear F-W-F axis (F(2)-W-F(2)^i = 174.0 (3)°) is perpendicular to the equatorial plane. A diad axis lies in the base through W and O bisecting the N-O-N angle and the F(1)-F(1)^i contact. The two independent W-F bonds are of significantly different length: 1.909 (6) Å for the F in the equatorial base versus 1.808 (6) Å for the axial F. The pyridine ring is planar (maximum deviations from the least-squares plane ±0.02 (1) Å); the dihedral angles are 60.7 (3)° between the two pyridine planes and the pentagonal base and 109.0 (2)° between each other.

As a whole the structure of $WOF_4 \cdot 2C_5H_5N$ was firmly established from this X-ray diffraction study; however, a different arrangement of the ligands of the tungsten atom could have been expected. With this alternative arrangement, the pentagonal plane would be made up of three fluorine atoms and two nitrogen atoms of the pyridine ligands, whereas the apical positions would be occupied by one oxygen atom and one fluorine atom in statistical distribution. With such an arrangement the observed W-F(2) bond distance (1.808 Å) is the average of the W=O and W—F(apical) bond distances. Taking a W—F(apical) bond distance equal to the mean equatorial W—F bond distance (1.906 Å) results in a W=O bond distance of 1.71 Å. This value is close to the W=O bond distance found in $WOF_4 \cdot C_5H_5N$ (1.77 (5) Å), $XeF_2 \cdot WOF_4$ (1.65 (3) Å),[10] or WOF_4 (1.66 Å, average of W=O and W—F bonds).[44,45]

On the other hand, the low frequency of the W=O vibration observed for $WOF_4 \cdot 2C_5H_5N$ (969 cm^{-1}) as compared with the W=O vibration for $WOF_4 \cdot C_5H_5N$ (996 cm^{-1}), $XeF_2 \cdot WOF_4$ (1033, 1044 cm^{-1}),[9] or WOF_4 (1053 cm^{-1}) certainly reflects a

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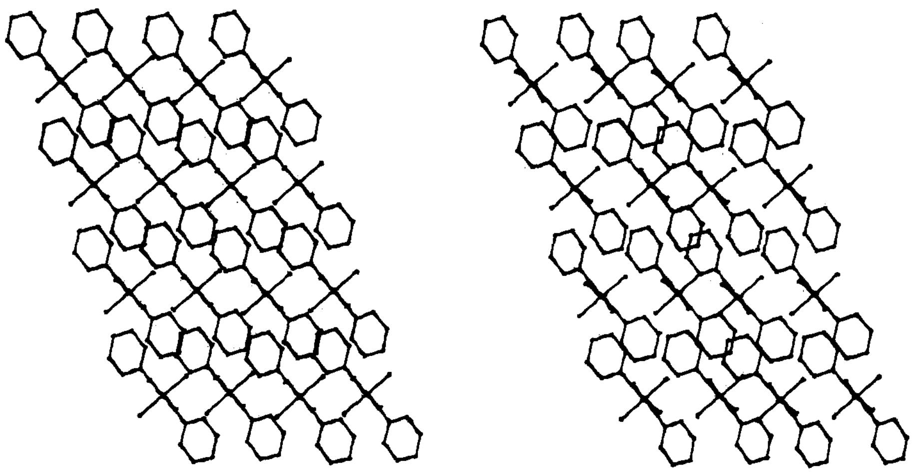

Figure 2. Stereoscopic view of the molecular packing of WOF$_4$·2C$_5$H$_5$N.

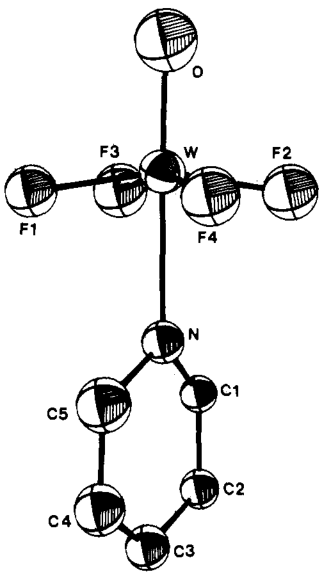

Figure 3. ORTEP[37] drawing of the molecular unit WOF$_4$·C$_5$H$_5$N with the hydrogen atoms omitted.

Table IV. Selected Bond Lengths (Å) and Angles (deg)[a]

WOF$_4$·2C$_5$H$_5$N		WOF$_4$·C$_5$H$_5$N	
W–O	1.900 (7)	W–O	1.77 (5)
W–N(1)	2.246 (8)	W–N	2.30 (4)
W–F(1)	1.909 (6)	W–F(1)	1.83 (3)
W–F(2)	1.808 (6)	W–F(2)	1.85 (4)
		W–F(3)	1.84 (4)
		W–F(4)	1.84 (4)
N(1)–C(1)	1.33 (2)	N–C(1)	1.29 (6)
N(1)–C(5)	1.34 (1)	N–C(5)	1.38 (7)
C(1)–C(2)	1.38 (2)	C(1)–C(2)	1.34 (6)
C(2)–C(3)	1.37 (1)	C(2)–C(3)	1.38 (7)
C(3)–C(4)	1.37 (1)	C(3)–C(4)	1.34 (8)
C(4)–C(5)	1.40 (2)	C(4)–C(5)	1.32 (8)
F(2)–W–F(2)^{i}	174.0 (3)	O–W–N	175 (2)

[a] Symmetry code for i: $\bar{x}$, y, $\bar{z}$.

much weaker W=O bond strength in WOF$_4$·2C$_5$H$_5$N and, consequently, a longer bond distance. The repulsive effect of the W=O bond, which accounts for the distortion of the octahedron of ligands in XeF$_2$·WOF$_4$[10] or WOF$_4$·C$_5$H$_5$N (vide infra), might be not so effective in WOF$_4$·2C$_5$H$_5$N due to the different nature of ligands in the equatorial plane and the different coordination polyhedron of the tungsten atom. In summary, even if the alternative solution were to be considered, the molecular symmetry (2-fold axis) imposed by the crystal symmetry and verified in particular for the pyridine ligands, as well as the preceding considerations, clearly do not support this model.

In WOF$_4$·C$_5$H$_5$N the W atom is six-coordinated at the center of a distorted octahedron involving four F atoms, one O atom, and one N atom of the pyridine ligand. The four F atoms define a rectangle (two F–F = 2.69 (2) Å and two F–F = 2.44 (2) Å; F(1)–F(3)–F(2) = 90 (2)°; F(3)–F(2)–F(4) = 90 (2)°; F(2)–F(4)–F(1) = 91 (2)°; F(4)–F(1)–F(3) = 90 (2)°) with the W atom being displaced 0.28 Å one of this plane toward the O atom. The O and the N are in apical positions; the O–W–N axis, almost

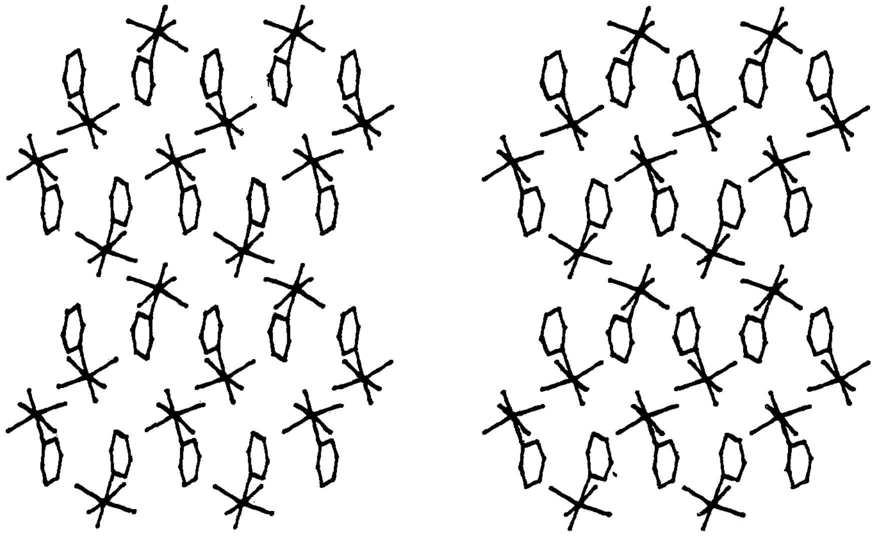

Figure 4. Stereoscopic view of the molecular packing of WOF$_4$·C$_5$H$_5$N.

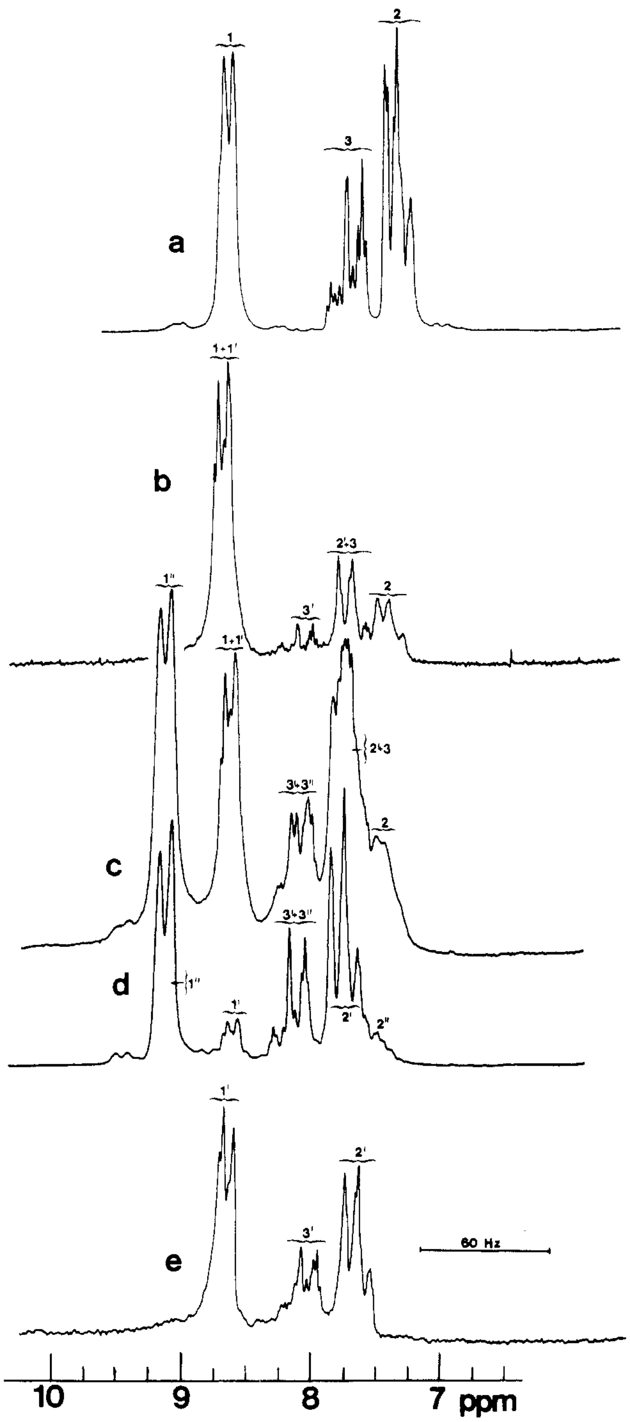

Figure 5. ^1H NMR spectra of solutions of C_5H_5N, $WOF_4{\cdot}2C_5H_5N$, and $WOF_4{\cdot}C_5H_5N$ in dichloromethane: (a) C_5H_5N (300 K); (b) $WOF_4{\cdot}2C_5H_5N$ (303 K); (c) $WOF_4{\cdot}2C_5H_5N$ (243 K); (d) $WOF_4{\cdot}2C_5H_5N$ (213 K); (e) $WOF_4{\cdot}C_5H_5N$ (213 K). The scale on the axis is relative to δ in ppm from TMS. The numbers 1, 2, and 3 refer to the ortho, meta, and para positions of the hydrogen atoms, respectively; the prime and double prime refer to the protons of $WOF_4{\cdot}C_5H_5N$ and $WOF_4{\cdot}2C_5H_5N$, respectively.

linear (175 (2)°), is perpendicular to the plane of F atoms. The displacement of the W atom relative to the equatorial plane may be explained by the repulsive effect of the W=O bond as has been proposed for the fluorine-bridged molecular adduct $XeF_2{\cdot}WOF_4$.[10]

The pyridine ring is planar (maximum deviations from the least-squares plane ±0.02 (6) Å) and perpendicular to the F equatorial plane with its projection parallel to the F(1)–F(3) and F(2)–F(4) edges.

In both structures (Figures 2 and 4) the packing is governed by the pyridine rings, which lie in parallel planes.

Nuclear Magnetic Resonance Spectra. The NMR spectra were recorded for the solutions of WOF_4, $WOF_4{\cdot}C_5H_5N$, and $WOF_4{\cdot}2C_5H_5N$ in dichloromethane. The deuteriated solvent was used for the ^1H NMR spectra. At room temperature the ^{19}F NMR spectrum of WOF_4 in CH_2Cl_2 showed a broad line (fwhm 150 Hz) at δ = 70.5 ppm; the adducts $WOF_4{\cdot}C_5H_5N$ and $WOF_4{\cdot}2C_5H_5N$ showed a single line (fwhm 1 Hz) at δ = 63.9 and 63.6 ppm, respectively. For both adducts the ^{183}W–^{19}F coupling is found to be 67 Hz and no significant changes in the spectra were brought about by temperature variation. The ^1H NMR spectrum of $WOF_4{\cdot}C_5H_5N$ in dichloromethane was similar to that of pyridine, but shifted to higher frequency, and no significant change was observed upon cooling down to 213 K. In contrast, the spectra of $WOF_4{\cdot}2C_5H_5N$ displayed dramatic changes with temperature. At room temperature and down to 243 K they consisted of a mixture of lines attributable mainly to free pyridine and to $WOF_4{\cdot}C_5H_5N$ whereas at 213 K the spectrum also resembles that of pyridine but is shifted to even higher frequency than that of $WOF_4{\cdot}C_5H_5N$. The spectra are shown in Figure 5 and are compared with that of pyridine in the same solvent.

The ^1H NMR spectra are explained by a reversible dissociation of the adduct $WOF_4{\cdot}2C_5H_5N$ in dichloromethane with the degree of dissociation being increased with temperature:

$$WOF_4{\cdot}2C_5H_5N \rightleftharpoons WOF_4{\cdot}C_5H_5N + C_5H_5N \qquad (1)$$

This assumption is supported by Raman spectral data obtained for the same solution (vide supra).

The ^1H NMR and the Raman spectra of $WOF_4{\cdot}C_5H_5N$ in solution as well as the synthesis of this adduct from the stoichiometric amounts of WOF_4 and C_5H_5N in dichloromethane indicate that, in contrast, $WOF_4{\cdot}C_5H_5N$ does not dissociate in this solvent up to room temperature.

The ^{19}F NMR spectrum of WOF_4 is explained by the presence of polymeric species in the noncoordinating solvent.[46] The identical value observed for the ^{19}F chemical shifts of the species of the two adducts $WOF_4{\cdot}C_5H_5N$ and $WOF_4{\cdot}2C_5H_5N$ may be due to rapid intramolecular rearrangement around the tungsten atom and chemical exchange according to equilibrium 1.

Conclusion. Two new adducts of WOF_4 have been prepared and described.

It has been demonstrated from X-ray structure determination, vibrational spectroscopy, and NMR spectroscopy that these two adducts are molecular adducts, with the pyridine molecules bound to the tungsten atom through the nitrogen atom. The seven-coordination of the tungsten atom in $WOF_4{\cdot}2C_5H_5N$ results in a labile character of one of the pyridine ligands as shown by variable-temperature ^1H NMR studies. The dissociation into the more stable adduct $WOF_4{\cdot}C_5H_5N$ restores the six-coordination of the tungsten atom, also found in polymeric WOF_4.[40,44–48]

Acknowledgment. We wish to thank Professor R. Mattes for fruitful discussions.

Supplementary Material Available: Tables of crystal data, bond distances and bond angles, atomic positional parameters, anisotropic thermal parameters, and lattice constants and space group (12 pages); tables of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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