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Molecular structure of the $WOF_4 \cdot 2py$ (py = pyridine) adduct as refined by ^{19}F NMR spectroscopy

L. Arnaudet, R. Bougon *, B. Buu

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

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Abstract

The structure of the heptacoordinated adduct of tungsten(VI), $WOF_4 \cdot 2py$, has been refined using ^{19}F NMR spectroscopy. The oxygen atom and one fluorine atom are located at the apical positions of the pentagonal bipyramid of ligands. To comply with X-ray diffraction data previously obtained, a statistical distribution of oxygen and fluorine atoms must be implied at the apical positions.

Keywords: Tungsten(VI) oxide tetrafluoride; Pyridine; Tungsten(VI) fluoro adducts; NMR spectroscopy

1. Introduction

The crystal structures of the tungsten(VI) adducts $WOF_4 \cdot py$ and $WOF_4 \cdot 2py$ (py = pyridine) have been determined previously [1] by X-ray diffraction methods. As far as the molecular structure of $WOF_4 \cdot 2py$ is concerned, the X-ray study showed that the coordination polyhedron of the tungsten atom was a bipyramid with a planar pentagonal base made up of two nitrogen atoms, two fluorine atoms and one oxygen atom. The two other fluorine atoms were located at the apical positions. However, a different arrangement of the ligands could also fit the data. In this alternative arrangement, the pentagonal plane was made up of three fluorine atoms and two nitrogen atoms, whereas the apical positions were occupied by one oxygen atom and one fluorine atom in a statistical distribution. The first arrangement was preferred on the basis of a comparison of the stretching vibrations in similar compounds.

Since that work was reported, improvements in NMR facilities have made possible a thorough ^{19}F NMR spectroscopic study of $WOF_4 \cdot 2py$ in solution, from which a more accurate model of its molecular structure has been obtained.

2. Experimental details

The experimental procedures, materials, apparatus and instrumentations were as described previously [1]. The NMR spectra were recorded on a Bruker AC-200 spectrometer at 200.13, 188.3 and 50.32 MHz for ^1H, ^{19}F and ^{13}C, respectively. Samples were referenced externally with respect to $Si(CH_3)_4$ or $CFCl_3$, with positive shifts being downfield from the standards. The $WOF_4 \cdot 2py$ adduct was prepared as described previously [1], its purity being checked by examining its X-ray diffraction powder pattern and its IR vibrational spectrum.

3. Results and discussion

The ^1H, ^{19}F and ^{13}C NMR data obtained for solutions of $WOF_4 \cdot 2py$ in CD_2Cl_2 are listed in Table 1 and the ^{19}F NMR spectrum is shown in Fig. 1.

The reversible dissociation of the adduct in CD_2Cl_2 solution [1], i.e.

$$WOF_4 \cdot 2py \rightleftharpoons WOF_4 \cdot py + py \qquad (1)$$

has been confirmed by the present study. At temperatures higher than 273 K, only $WOF_4 \cdot py$ and py were observed. At 273 K and below, the exchange is slowed down and the relative concentration of $WOF_4 \cdot 2py$ increases as the temperature decreases. In agreement with the molecular structure previously determined by X-ray diffraction [1], the ^{19}F NMR spectrum showed the equivalence of the fluorine atoms of $WOF_4 \cdot py$. The ^{19}F NMR spectrum of $WOF_4 \cdot 2py$ is of the A_2MX type. The doublet of doublet at δ 13.5 ppm (at 203 K) was assigned to the two equivalent fluorine atoms F(A) located in the pentagonal plane, and the doublets of triplets

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* Corresponding author.

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Table 1
^1H, ^{13}C and ^{19}F NMR data [a] for solutions of $WOF_4 \cdot 2py$ in CD_2Cl_2

Temperature (K)	Chemical shifts, δ (ppm)									Species [b]
	^1H			^{13}C			^{19}F			
	δ_2	δ_3	δ_4	δ_2	δ_3	δ_4	δ_A	δ_M	δ_X	
298	8.65	7.34	7.74	149.8	124.4	136.9				py
	8.65	7.62	8.05	148.1	126.0	141.3		63.67		1/1
273	8.64	7.62	8.05					63.81		1/1
	9.1	7.4	7.8				17.39	−8.49	−74.44	1/2
263	8.62	7.62	8.05					63.87		1/1
	9.14	7.36	8.6				16.80	−8.82	−74.83	1/2
243	8.60	7.60	8.05	148	126.3	141.7		63.97		1/1
	9.13	7.70	8.09	148.2	126.6	141.2	15.72	−9.42	−75.54	1/2
223	8.60	7.45	7.87					64.07		1/1
	9.10	7.68	8.10				14.60	−10.04	−76.31	1/2
203	8.58	7.52	7.96	146.3	125.0	143.3		64.07		1/1
	9.09	7.68	8.10	150.0	128.4	139.9	13.52	−10.66	−77.17	1/2

Temperature (K)	Coupling constant (Hz)	Species [b]
203	$J_{^{183}W-F} = 63$	1/1
	$J_{F(A)F(M)} = 50$; $J_{F(A)F(X)} = 42$; $J_{F(M)F(X)} = 75$; $J_{^{183}WF(X)} = 62$	1/2

[a] Temperature in K, chemical shifts δ in ppm from TMS (^1H and ^{13}C) or $CFCl_3$ (^{19}F).

[b] Species 1/1 and 1/2 refer to $WOF_4 \cdot py$ and $WOF_4 \cdot 2py$, respectively. Subscripts 2, 3 and 4 refer to the hydrogen and carbon atoms in the *ortho*, *meta* and *para* positions to the nitrogen atom, respectively. Subscripts A, M, and X for $WOF_4 \cdot 2py$ refer to the two equivalent equatorial fluorine atoms, the third equatorial fluorine atom and the apical fluorine atom, respectively. The four equivalent fluorine atoms of $WOF_4 \cdot py$ are referred to as δ_M. The coupling constants for $WOF_4 \cdot 2py$: $J_{^{183}WF(M)}$ and $J_{^{183}WF(A)}$, which are probably smaller than $J_{^{183}WF(X)}$ (62 Hz), could not be determined. The connection between δ ^1H and δ ^{13}C was obtained from the 2D heterocorrelation spectra (program XHCORR.D from Bruker).

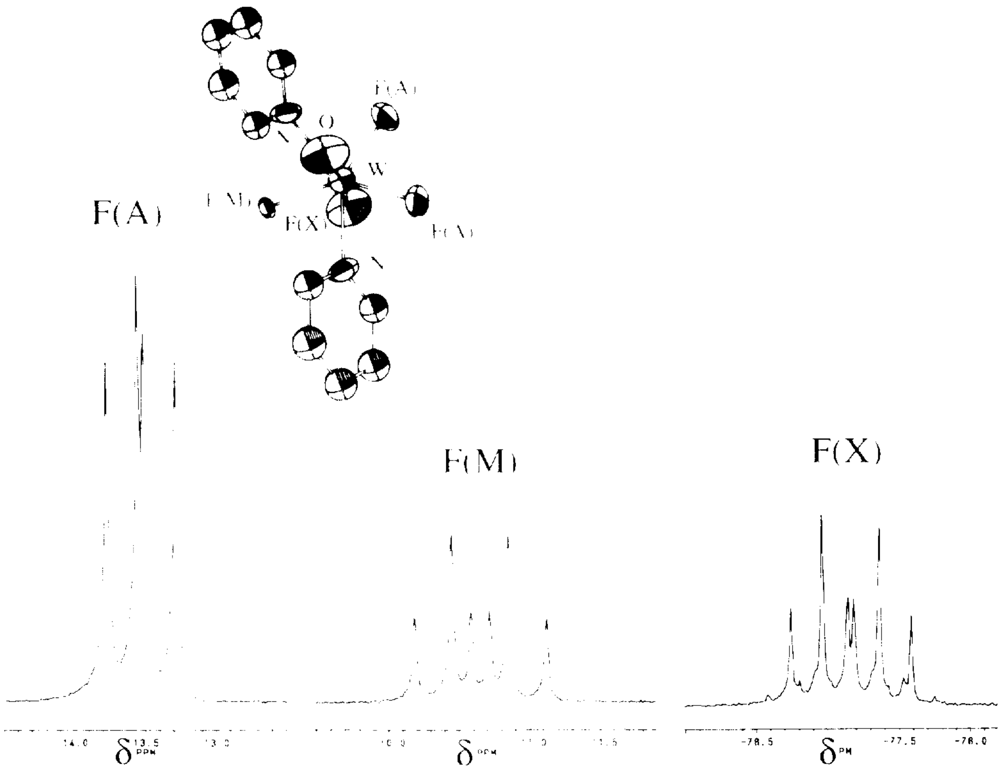

Fig. 1. ^{19}F NMR spectrum of a solution of $WOF_4 \cdot 2py$ in CD_2Cl_2 at 203 K. The F, O, W and N atoms on the ORTEP drawing of the $WOF_4 \cdot 2py$ molecular unit obtained previously from X-ray diffraction studies [1] are labelled according to the results of the present study.

at δ −10.7 and −77.2 ppm were assigned to the in-plane F(M) and the apical F(X) fluorine atoms, respectively. The assignment of the two doublets of triplets relative to each other was based on the *trans* effect of the oxygen ligand which is expected to shift the apical fluorine atom to higher field [2].

These results rule out the arrangement with the oxygen atom in the equatorial plane of the pentagonal bipyramid, which would correspond to an A_2X_2-type spectrum. A model in accord with the ^{19}F NMR spectrum has the oxygen atom and one fluorine atom at the apical positions while the equatorial plane is made up of two nitrogen atoms of the py ligands, two equivalent fluorine atoms and the fourth fluorine atom. This arrangement may reasonably be expected to be the same in the solid state, with the apical positions occupied by one fluorine atom and one oxygen atom in a statistical distribution. Taking into account the X-ray diffraction data previously obtained [1] and assuming that the W–F(X) (apical) bond distance is equal to the mean bond distance found in the equatorial plane (1.906 Å), leads to a W=O bond distance of 1.71 Å which is in better agreement with its usual value [3] in monooxo complexes than that (1.900 Å) based on the alternative model.

References

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