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# Structural and Stereodynamic Studies on Molecular Early Transition Metal Derivatives.
# V. NMR Study of Isolated Tungsten Dioxofluoride Adducts of Type $WO_2F_3L^-$

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*The title compounds (L = phosphine oxide, pyridine N-oxides) have been isolated and characterized, and their $ClCH_2CN$ solutions studied by variable temperature $^1H$, $^{19}F$ and $^{31}P$ NMR. A detailed investigation on $Et_4N[WO_2F_3(OPMe_3)]$ shows that the F atom* trans *to an oxo ligand, as well as the $OPMe_3$ ligand* trans *to the other oxo ligand in the* cis-*dioxo structure A, are rapidly dissociated on the NMR timescale, while the apical F atoms* trans *to each other are not, which illustrates the* trans-*labilizing effect of the oxo ligands. Upon ageing new species are formed in the solutions, including $WO_2F_2(OPMe_3)_2$, $[WO_2F_3(ClCH_2CN)]^-$, $WO_2F_2(ClCH_2CN)_2$, $F^-$ and $OPMe_3$. An equilibrium situation is reached after 4 days' heating at 80 °C. The neutral $WO_2F_2(OPMe_3)_2$ is then largely predominant. Material balance calculations indicate that polynuclear species are also likely to be present.*

## Introduction

The *trans* influence of multiply bonded ligands on the structure of coordination compounds is abundantly documented [1]. However, in Mo(VI) and W(VI) dioxo compounds where a *cis*-$MO_2$ arrangement is always found [1, 2], this *trans* influence becomes in some cases less obvious: for example in $[MoO_2F_4]^{2-}$ only one of the Mo–F bonds *trans* to the oxygen atoms is longer (2.00 Å) while the other is, within experimental error, equal to the Mo–F bonds *trans* to each other (1.94 Å) [3].

The *trans*-labilising effect of the multiply bonded oxygen atoms in Mo(VI) and W(VI) dioxo compounds was first studied by Buslaëv *et al.* They showed, through $^{19}F$ NMR of aqueous solutions of $(NH_4)_2[WO_2F_4]$, that the bonds formed by tungsten with the fluorine atoms in the *trans* positions relative to the oxygens are much more labile: they readily undergo a dissociative exchange at room temperature. A greater reactivity is therefore expected for W–F bonds *trans* to oxygen [4].

As an illustration of this *trans*-labilisation effect, Buslaëv reported on the composition of dioxotungsten(VI) fluoride mixtures formed in hydrofluoric acid solutions and on their *in situ* reactions with a number of ligands. From the NMR spectra measured on the quite intricate solutions obtained in this way, he recognized the formation of $[WO_2F_3L]^-$, $WO_2F_2L_2$ and $WO_2F_2LL'$ (L,L' = DMSO, MeOH, EtOH, MeCN, $SCN^-$); however, none of these derivatives were isolated. The results obtained by Buslaëv again indicate that the ligands *trans* to oxygen are rather labile and are readily substituted by other donors [5, 6].

As part of our search into the fate of early transition metal derivatives in solution [7], we have *isolated* several $[WO_2F_3L]-$ anions (L = phosphine oxide, pyridine N-oxides) as their tetraethylammonium salts. This in turn allowed us to investigate the behavior of these now well characterized isolated species once they are put back in solution under well-defined conditions. We also avoided using aqueous hydrofluoric acid as a solvent, it being too reactive, and preferred $CH_2ClCN$ in which the adducts are still soluble and which was expected to give less complex mixtures. This paper is devoted to the variable temperature $^{19}F$, $^1H$ and $^{31}P$ NMR study of the $[WO_2F_3L]^-$ anions.

## Experimental

The $(Et_4N)(WO_2F_3L)$ compounds were prepared from $(Et_4N)[WO_2F_3(H_2O)]$ through substitution of the aquo ligand by phosphine oxide (I) or pyridine oxides (II–VI) in hot (≅60 °C) acetonitrile solutions [8].

TABLE I. Analytical Data and Principal IR Absorptions of Compounds $Et_4N[WO_2F_3L]$.[a]

| Compounds | Analytical | | | | | | Infra-red | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | F | P | $\nu$(*cis*-$MO_2$) | (M–F) | $\delta$(*cis*-$MO_2$) | (O–M–F) | $\nu$ (PO or NO) | $\Delta\nu$ (PO or NO) |
| I<br>$Et_4N[WO_2F_3(OPMe_3)]$ | calcd | 26.67 | 5.86 | 2.83 | 11.57 | 6.26 | 950 v.s. | 580 s | 376 s | 315 m | 1095 v.s. | 75 |
| | found | 26.81 | 5.85 | 2.94 | 11.34 | 6.72 | 905 v.s. | 555 v.s. | | | | |
| II<br>$Et_4N[WO_2F_3(C_5H_5NO)]$ | calcd | 31.32 | 5.02 | 5.62 | 11.44 | | 960 s | 560 s | 370 m | 305 sh | 1220 s | 25 |
| | found | 31.10 | 5.10 | 5.62 | 11.65 | | 905 v.s. | | | | | |
| III<br>$Et_4N[WO_2F_3(2\text{-}CH_3C_5H_4NO)]$ | calcd | 32.81 | 5.27 | 5.46 | 11.13 | | 960 s | 560 s | | | 1210 s | 10 |
| | found | 32.80 | 5.29 | 5.56 | 10.74 | | 900 s | | | | | |
| IV<br>$Et_4N[WO_2F_3(3\text{-}CH_3C_5H_4NO)]$ | calcd | 32.81 | 5.27 | 5.46 | 11.13 | | 940 s | 575 s | 372 m | 320 m | 1250 s | 15 |
| | found | 32.84 | 5.27 | 5.52 | 10.85 | | 895 v.s. | 545 s | | | | |
| V<br>$Et_4N[WO_2F_3(4\text{-}CH_3C_5H_4NO)]$ | calcd | 32.81 | 5.27 | 5.46 | 11.13 | | 965 s | 560 s | 375 m | 310 sh | 1210 s | 35 |
| | found | 33.14 | 5.55 | 5.66 | 10.59 | | 905 v.s. | | | | | |
| VI<br>$Et_4N[WO_2F_3(4\text{-}CH_3OC_5H_4NO)]$ | calcd | 31.76 | 5.10 | 5.29 | 10.77 | | 950 s | 575 s | 372 m | 315 m | 1210 v.s. | 12 |
| | found | 31.82 | 5.12 | 5.41 | 10.77 | | 900 v.s. | 550 v.s. | | | | |

[a] v.s. = very strong; s = strong; m = medium; w = weak; sh = shoulder.

### *Preparation of* $(Et_4N)[WO_2F_3(H_2O)]$

$Et_4NCl$ (3.3 g, 0.02 mmol) dissolved in HF (20 ml) is added to a solution of $H_2WO_4$ (2.5 g, 0.01 mmol) in HF (20 ml). The solution is then concentrated, the white crystalline precipitate is filtered off, washed with water and dried under vacuum. Yield 3.8 g (90%). *Anal.* Calcd for $WC_8H_{22}F_3NO_3$: C, 22.81; H, 5.22; F, 13.54. Found: C, 22.82; H, 5.29; F, 12.87. Ir (Nujol, cm$^{-1}$): $\nu_s cis(WO_2)$ 997(s); $\nu_{as} cis(WO_2)$ 900(vs); $\delta cis(WO_2)$ 390(m); $\nu$(W–F) 590(sh), 565(vs), 472(s); $\nu$(OH) 3220(s).

### *Preparation of* $(Et_4N)[WO_2F_3(OPMe_3)]$

$(Et_4N)[WO_2F_3(H_2O]$ (420 mg, 1 mmol) is added to a solution of $OPMe_3$ (110 mg, 1.20 mmol) in acetonitrile (40 ml). The mixture is heated to 50–60 °C until dissolution is complete. After cooling the white crystals are filtered off, washed with ethanol and dried under vacuum. Yield 420 mg (85%).

The other $(Et_4N)[WO_2F_3L]$ compounds were prepared according to the same procedure; their analytical and i.r. data are given in Table I.

### *Preparation of* $WO_2F_2(OPMe_3)_2$

A large excess of $OPMe_3$ (370 mg, 4 mmol) dissolved in ethanol (10 ml) is added to a solution of $H_2WO_4$ (250 mg, 1 mmol) in HF (10 ml). The solution is concentrated to *ca.* 10 ml. After 3 days at room temperature the white crystals of $WO_2F_2(OPMe_3)_2$ are collected, washed with ethanol and dried under vacuum. Yield 330 mg (75%). *Anal.* Calcd for $WC_6H_{18}F_2O_4P_2$: C, 16.33; H, 4.08; P, 14.06. Found: C, 16.06; H, 3.97; P, 14.21%.

The i.r. spectra of the $(Et_4N)(WO_2F_3L)$ compounds (Nujol mulls) show the two intense bands at *ca.* 900 and 950 cm$^{-1}$ that are characteristic of a *cis*-dioxo configuration [1, 2]. All the compounds are 1:1 electrolytes in acetonitrile ($\Lambda = 150\ \Omega^{-1}$ mol$^{-1}$ cm$^2$ for $10^{-3}$ solutions).

The NMR spectra were recorded on a Jeol C-60 HL spectrometer ($^{19}$F), A Bruker WH 90/DS spectrometer ($^{31}$P) and, in one case, on a 250 MHz Cameca spectrometer. Infrared spectra were obtained on a Perkin–Elmer 225 spectrometer. Conductance measurements were performed with a Tacussel CD 6AB conductimeter.

## Results and Discussion

### *Low Temperature NMR of Fresh Solutions*

The $^{19}$F spectrum (Fig. 1a) measured on a *freshly* prepared 0.55 *M* solution of $Et_4N[WO_2F_3(OPMe_3)]$ (I), in monochloroacetonitrile at –40 °C, consists of a doublet ($F_a$, $\delta$ = +4.5 ppm from $CF_3COOH$) and a triplet ($F_e$, $\delta$ = –14.3 ppm; $J_{FF}$ = 65 Hz) the areas of which are in a 2:1 ratio. These data are consistent with structure A where $F_a$ is assigned to the axial

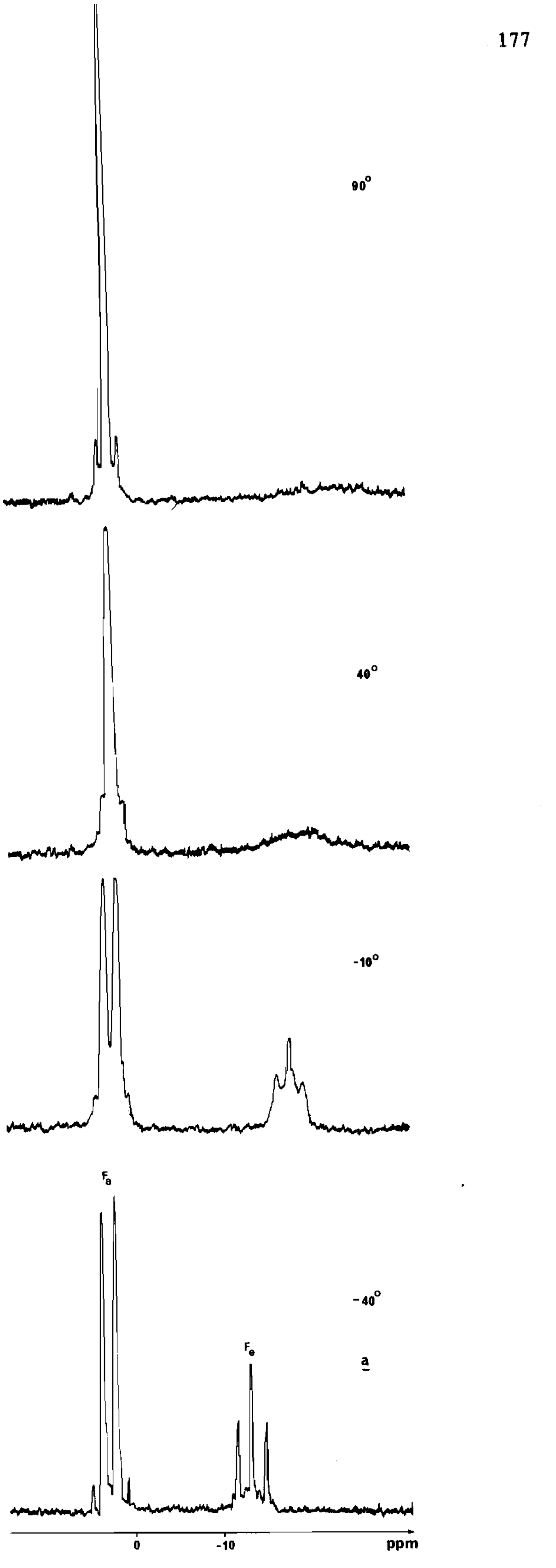


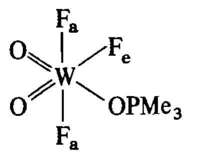
Figure 1. $^{19}$F NMR spectra of a 0.55 *M* solution of $(Et_4N)[WO_2F_3(OPMe_3)]$ in $CH_2ClCN$ (reference: external $CF_3COOH$).

TABLE II. $^{19}F$ NMR Data Measured on 0.7 *M* Chloroacetonitrile Solutions of $Et_4N[WO_2F_3L]$ at –40 °C; external reference: $CF_3COOH$.

| Compound | L | $WO_2F_2L_2$ δ (ppm) | $[WO_2F_3L]^-$ δ $F_{axial}$ (ppm) | δ $F_{eq.}$ (ppm) | J (Hz) | Coalesc.[a] °C |
|---|---|---|---|---|---|---|
| I | $OPMe_3$ | +11.6 | 4.5 | –14.3 | | –8 |
| II | $C_5H_5NO$ | 12.8 | 3.6 | –13.6 | $J_{FF} = 65$ | –20 |
| III | $2\text{-}CH_3C_5H_4NO$ | 13.6 | 5.3 | –15.1 | $J_{WF_{ax}} = 107$ | –18 |
| IV | $3\text{-}CH_3C_3H_4NO$ | 12.7 | 3.4 | –13.5 | | –15 |
| V | $4\text{-}CH_3C_5H_4NO$ | 12.9 | 3.9 | –14.3 | $J_{WF_{eq}} = 73$ | –18 |
| VI | $4\text{-}CH_3OC_5H_4NO$ | 11.3 | 2.4 | –12.9 | | –1 |

[a] Coalescence temperature of the $F_{axial}$ doublets as measured on freshly prepared solutions ($F^-$ and $WO_2F_2L_2$ not yet detectable).

fluorine atoms and $F_e$ to the equatorial one, and which also takes into account the i.r. data



A

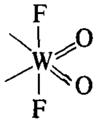
The $^{19}F$–$^{183}W$ coupling satellites are observed for both axial and equatorial fluorines: $J_{F_a\text{–}W}$ = 107 Hz; $J_{F_e\text{–}W}$ = 65 Hz. The significant difference between these one-bond coupling constants indicates that the metal forms a stronger covalent bond with the axial than with the equatorial fluorine atom [9].

Fig. 1 also illustrates the temperature dependence of the $^{19}F$ spectra measured on the same freshly prepared solution of I. The striking features to be noticed when the temperature is increased are: (i) the disappearance of $F_{axial}$–$F_{equatorial}$ coupling; (ii) the slow lowfield shift of signal $F_a$ while signal $F_e$ shifts towards higher fields much more rapidly; (iii) the preservation of the $^{183}W$–$^{19}F$ coupling satellites of signal $F_a$ (axial fluorines) up to 90 °C when compound I starts decomposing. These results imply that the exchange process responsible for the observed change in NMR pattern occurs through dissociation of the equatorial W–F bond.

After the solution has been kept for two hours at room temperature, two new signals become detectable in the low temperature $^{19}F$ spectrum of compound I ($F_c$, δ = +4.35 ppm with $J_{F\text{–}W}$ = 110 Hz and $F_d$, δ = –50.05 ppm). Signal $F_c$ was assigned to $WO_2F_2(OPMe_3)_2$ through comparison with an authentic, independently prepared sample of the latter [8]. The second signal, $F_d$, was assigned to the $F^-$ anion on the basis of its chemical shift [10] and by addition of $Et_4NF$ to the solution. It is noteworthy that the use of aqueous hydrofluoric acid as a solvent made it impossible for Buslaëv to detect the formation of $F^-$ in his tungsten dioxide fluorides solutions.

The *trans* effect of the terminal oxygen atoms was further confirmed by $^1H$ NMR. The proton spectrum measured at –40 °C on the same freshly prepared 0.55 *M* solution exhibits two doublets ($\delta_1$ = 1.60 ppm, 95%; $\delta_2$ = 1.53 ppm, ≅5%; $^2J_{PH}$ = 13.7 Hz). Addition of an excess of free ligand allows the assignment of signal 2 to free $OPMe_3$ which implies partial dissociation (~5%) of I. In a coordinating solvent such as $CH_2ClCN$, it seems reasonable to assume that $OPMe_3$ is then replaced by one molecule of the solvent to give a $[WO_2F_3(CH_2ClCN)]^-$ anion. The coalescence of the signals assigned to free and coordinated $OPMe_3$ is observed at *ca.* 0 °C.

Both $^{19}F$ and $^1H$ NMR results thus demonstrate the *trans* labilising effect of the terminal oxo groups: both W–$OPMe_3$ and W–F bonds located in the *cis*-$WO_2$ plane are immediately partially dissociated in solution, while the *cis*-dioxo *trans*-difluoro scheme:



remains unchanged on the NMR time-scale. A more quantitative study of these phenomena was precluded by the ageing of the solutions: the temperatures of coalescence were found to depend on the amount of the neutral $WO_2F_2L_2$ species present and therefore on time.

The behavior of compounds II to VI in $CH_2ClCN$ solutions was essentially identical with that of compound I. Table II lists the $^{19}F$ chemical shifts measured for the compounds.

### *Ageing of the Solutions*

When a chloroacetonitrile solution of compound I is kept at room temperature for three weeks, the *cis*-

TABLE III. Percentage of the Various Species Detected in Equilibrated Solutions of $Et_4N[WO_2F_3(OPMe_3)]$ at 80 °C.

| Species ($S = CH_2ClCN$ $L = OPMe_3$) | $OPMe_3$ (from $^{31}P$ NMR) % of total $OPMe_3$ | W % of total W | F (from $^{19}F$ NMR) % of Total F |
|---|---|---|---|
| $[WO_2F_3L]^-$ | 4 | 4 | 5 |
| $WO_2F_2L_2$ | 84 | 42 | 28 |
| $[WO_2F_3S]^-$ | 0 | 1 | 1 |
| $WO_2F_2S_2$ | 0 | 2 | 1 |
| $F^-$ | 0 | 0 | 10 |
| $OPMe_3$ | 2 | 0 | 0 |
| non identified species | 10 | 51 | 55 |

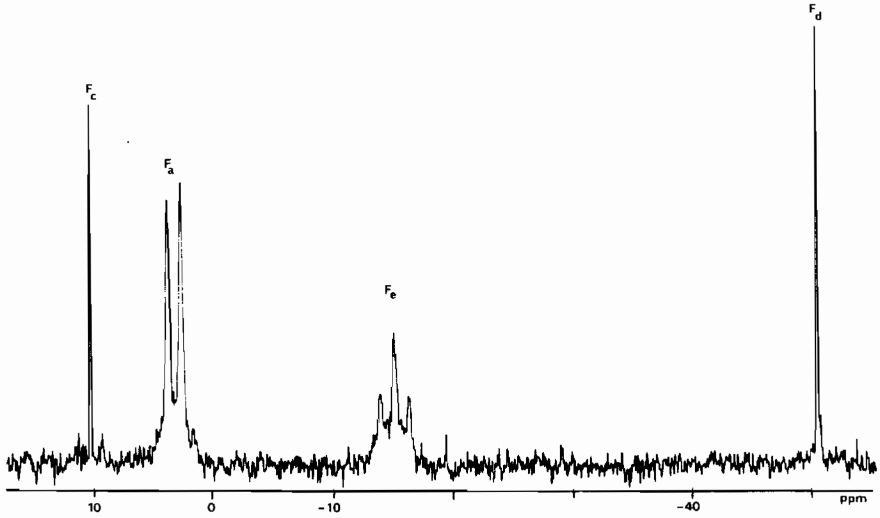


Figure 2. $^{19}F$ spectrum measured at −40 °C on a 0.72 *M* solution of $(Et_4N)[WO_2F_3(OPMe_3)]$ kept at room temperature for three weeks (solvent: $CH_2ClCN$; reference: external $CF_3COOH$).

dioxo *trans*-difluoro structural pattern is still unchanged while the concentration of both the neutral species $WO_2F_2(OPMe_3)_2$ and the $F^-$ ion formed has considerably increased (Fig. 2).

However, we observed that the composition of the solutions of compound I reach an equilibrium – there is no further change in their NMR spectra – after 4 days' heating at 80 °C. This equilibrium does not depend on the concentration of the solution in the 0.03 to 0.72 *M* range and no changes were observed in the spectra even after a year.

The molecular constitution of these solutions at equilibrium is very intricate and could only partially be elucidated through low temperature $^{19}F$ and $^{31}P$ NMR (Table III). The $^{19}F$ spectrum exhibits very numerous signals in as wide a range as from +140 to −30 ppm! (a portion of this spectrum measured at 250 MHz on a Cameca spectrometer is presented in Fig. 3).

Only *ca.* 4% of the initially dissolved $[WO_2F_3(OPMe_3)]^-$ anion remains present at equilibrium, while the preponderant species has become the neutral $WO_2F_2(OPMe_3)_2$ (it represents 84% of the total $OPMe_3$, 42% of the tungsten and 28% of the fluorine). This once more illustrates the stability of the *cis*-dioxo *trans*-difluoro structural pattern. The $[WO_2F_3(CH_2ClCN)]^-$ anion (1%) and $WO_2F_2(CH_2ClCN)_2$ (1% in fluorine) could also be identified. Surprisingly no $[WO_2F_4]^{2-}$ was detected at equilibrium. Free $OPMe_3$ accounts for 2% of the $^{31}P$ spectrum, while the amount of $F^-$ present at equilibrium is quite large (10% of the fluorine).

The starting material being $[WO_2F_3(OPMe_3)]^-$, this implies that, whatever species are present at equilibrium, the overall composition of the solution still corresponds to 3 F atoms for 1 $OPMe_3$ group and one W atom. Taking into account the abundance

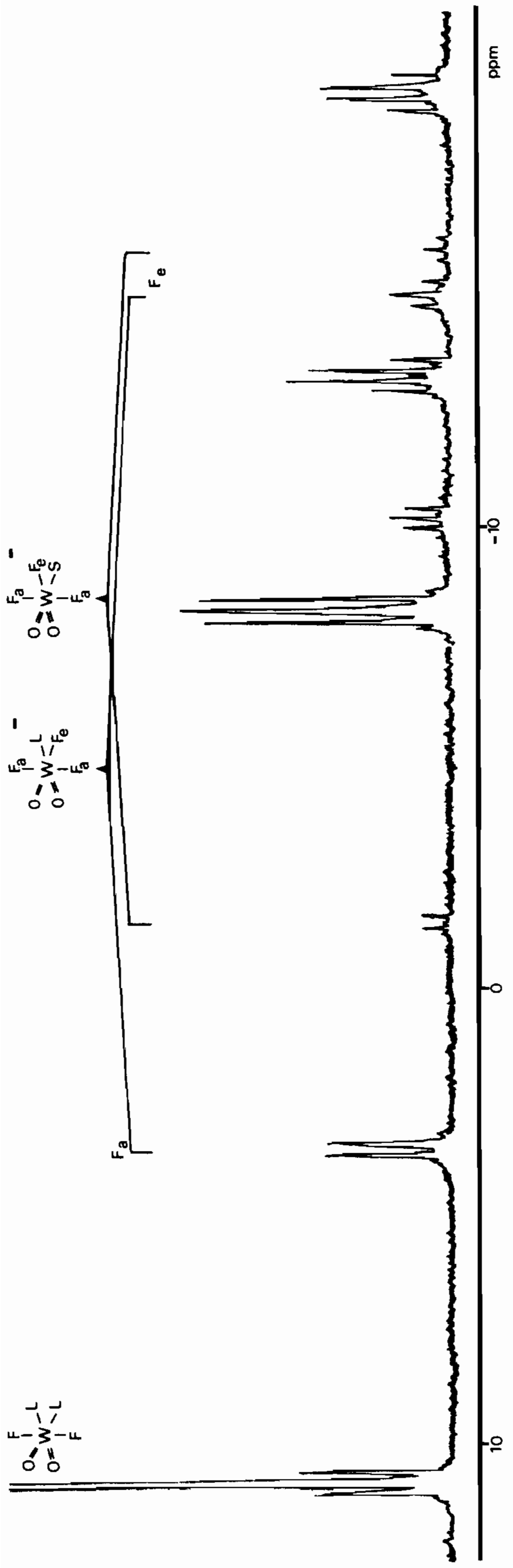


Figure 3. Part of a 250 MHz $^{19}$F NMR spectrum measured at equilibrium on a 0.55 *M* solution of $(Et_4N)[WO_2F_3(OPMe_3)]$ in $CH_2ClCN$.

of the *identified* species (Table III), one is left with 3.3 F and 0.2 $OPMe_3$ per W atom to fit the remaining signals in both the $^{19}$F and the $^{31}$P spectra. This, and the fact that the unidentified signals appear mostly at low fields in the $^{19}$F spectra, may be taken as an indication of the formation of polynuclear species having bridging axial fluorine atoms [9, 11].

These results again illustrate the drastic changes that early transition metals derivatives, that are well-defined in the solid state, often undergo once they are put in solution [7].

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