255. Adducts of Niobium(V) and Tantalum(V) Halides. XIV[1]). Structure and Relative Stability of the Adducts with Some Phosphoryl Compounds[2])

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Summary. The adducts of niobium(V) and tantalum(V) halides with some phosphoryl compounds have been studied in chloroform solution by ^{1}H- and ^{19}F-FT-NMR. spectroscopy. These octahedral adducts of general formula $MX_5 \cdot L$ (M = Nb, Ta; X = F, Cl, Br; L = phosphoryl ligand) are monomeric and neutral. Their relative stability constants have been determined at – 60°. The stabilities are controlled by electronic effects of substituents on the phosphoryl group.

1. Introduction. – In dilute solution in inert organic solvents, dimeric niobium(V) and tantalum(V) chlorides and bromides, as well as tetrameric fluorides, react quantitatively with *Lewis* bases to form, in general, monomeric adducts with 1:1 stoichiometry [2] [3] [4].

$$1/n\ (MX_5)_n + L \rightarrow MX_5 \cdot L. \qquad (1)$$

Previous communications of this series have reported the structure, relative stability and kinetic behaviour of adducts with nitriles and dialkylchalcogenides as *Lewis* bases. In the present work we have studied, by ^{1}H- and ^{19}F-FT-NMR., the structure and stability of adducts formed with phosphoryl compounds.

The adduct $NbCl_5 \cdot Cl_3PO$ has been isolated and characterized [5]; the coordination takes place through the oxygen atom. The reactions between $NbCl_5$ and $(Me_2N)_3PO$, $(C_6H_5)_3PO$, $(C_6H_5)_2(C_6H_5CH_2)PO$ [6] show the formation of niobium(V) oxychloride adducts. By X-ray diffraction and IR. spectroscopy *Dorschner* [7] has observed that direct reaction between $(Me_2N)_3PO$ and $NbCl_5$ in $CHCl_3$ leads to a mixture of $NbCl_5 \cdot (Me_2N)_3PO$ and $NbOCl_3 \cdot 2(Me_2N)_3PO$; this reaction also produces $(Me_2N)_3PCl_2$ which was recrystallized and analysed. According to this author the reaction must be carried out in a $CHCl_3$/MeCN mixture to avoid oxychloride formation; $NbCl_5 \cdot MeCN$ is then formed and rapidly substituted by $(Me_2N)_3PO$. Solid adducts $NbX_5 \cdot n(Me_2N)_3PO$ (X = F, n = 2; X = Cl, Br, n = 1) and $TaX_5 \cdot (Me_2N)_3PO$ were isolated by *Masaguer* [8]. Their stoichiometries were determined by chemical analysis; conductimetric and dipole moments measurements showed the absence of ionic species in acetonitrile and nitromethane solutions.

2. Experimental Part. – The work in inert atmosphere, the sample preparation for NMR. measurements and the purification of some of the chemicals is described in [3] and [4]. NbF_5 (*Ozark-Mahoning*) (80°/10^{-1} Torr) and TaF_5 (*Chemie Brunschwig AG*) (60°/10^{-3} Torr) were sublimed;

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[1]) Part XIII: see [1].

[2]) Abstracted, in part, from the Ph. D. Thesis of *C. M. P. Favez*, University of Lausanne, 1976, and from the Ph. D. Thesis of *H. Rollier*, University of Lausanne, 1972.

they may be kept several weeks in evacuated Pyrex tubes. Hexamethylphosphoramide, trimethylphosphate and phosphorus oxychloride (*Fluka*) were distilled twice under vacuum over phosphorus pentoxide.

The following compounds were synthesized: $\mathrm{Cl(MeO)_2PO}$ [9], $\mathrm{Cl_2(MeO)PO}$ [10], $\mathrm{Cl(Me_2N)_2PO}$ [11], $\mathrm{Cl_2(Me_2N)PO}$ [12], $\mathrm{(Me_2N)_2(MeO)PO}$ [10], $\mathrm{(Me_2N)(MeO)_2PO}$ [13], $\mathrm{(MeS)_3PO}$ from MeSNa [14] and $\mathrm{Cl_3PO}$ as described in [15], $\mathrm{(MeO)_3PS}$ [16], $\mathrm{(Me_2N)_3PS}$ from $\mathrm{(Me_2N)_3P}$ [17] and sulfur as in [18].

^{1}H-NMR. spectra were recorded on *Bruker* WP-60 and *Varian* A-60A spectrometers. ^{19}F-FT-NMR. (84.67 HMz) spectra were performed on a *Bruker* HX-90 *Fourier*-transform spectrometer. Concentrations are expressed in molality (m). Chemical shifts ($\delta = (\nu\text{-}\nu_{\mathrm{ref}}) \cdot 10^6/\nu_{\mathrm{ref}}$) are given in ppm with respect to an internal reference as noted.

Table 1. *^{1}H-NMR. chemical shifts* δ (ppm), *chemical shift difference* $\Delta\delta$ (ppm), *coupling constants* J (Hz) *and stoichiometry of the adducts* $MX_5 \cdot L$ *(M = Nb, Ta; X = F, Cl, Br) in* $CHCl_3$ *at* $-60°$ $[\mathrm{M}]_t = 0.03$ m–0.10 m $[\mathrm{L}]_t = 0.03$ m–0.30 m. Reference: internal TMS

$\mathrm{MX_5 \cdot L}$	$\delta(\mathrm{MX_5 \cdot L})$ ± 0.01	$\delta\Delta$[a] ± 0.01	^3J(H,P) $\mathrm{MX_5 \cdot L}$ ± 0.2	^3J(H,P) L ± 0.2	Stoichiometry M:L ± 0.1
$\mathrm{NbF_5 \cdot (Me_2N)_3PO}$[b] [c]	2.74	0.14	10.3	9.4	–
$\mathrm{NbF_5 \cdot (}\mathit{Me}_2\mathrm{N)_2(MeO)PO}$[b]	2.79	0.13	11.0	10.0	1:0.85
$\mathrm{NbF_5 \cdot (Me_2N)_2(}\mathit{Me}\mathrm{O)PO}$[b]	3.83	0.17	12.0	10.5	
$\mathrm{NbF_5 \cdot (}\mathit{Me}_2\mathrm{N)(MeO)_2PO}$[b]	2.85	0.13	10.6	9.8	1:0.9
$\mathrm{NbF_5 \cdot (Me_2N)(}\mathit{Me}\mathrm{O)_2PO}$[b]	3.88	0.18	12.2	11.4	
$\mathrm{NbF_5 \cdot (MeO)_3PO}$[b]	4.10	0.23	11.8	11.0	1:1.0
$\mathrm{TaF_5 \cdot (Me_2N)_3PO}$[b] [c]	2.71	0.09	10.0	9.4	–
$\mathrm{TaF_5 \cdot (}\mathit{Me}_2\mathrm{N)_2(MeO)PO}$[b]	2.80	0.17	10.5	9.8	1:0.85
$\mathrm{TaF_5 \cdot (Me_2N)_2(}\mathit{Me}\mathrm{O)PO}$[b]	3.90	0.26	12.3	11.3	
$\mathrm{TaF_5 \cdot (}\mathit{Me}_2\mathrm{N)(MeO)_2PO}$[b]	2.82	0.13	10.8	9.8	1:0.9
$\mathrm{TaF_5 \cdot (Me_2N)(}\mathit{Me}\mathrm{O)_2PO}$[b]	3.96	0.30	11.9	11.0	
$\mathrm{TaF_5 \cdot (MeO)_3PO}$[b]	4.15	0.30	11.6	11.0	1:0.9
$\mathrm{NbCl_5 \cdot (Me_2N)_3PO}$[c]	2.90	0.20	10.5	9.4	–
$\mathrm{NbCl_5 \cdot (}\mathit{Me}_2\mathrm{N)_2(MeO)PO}$	2.93	0.19	11.0	9.8	1:0.9
$\mathrm{NbCl_5 \cdot (Me_2N)_2(}\mathit{Me}\mathrm{O)PO}$	3.99	0.26	12.5	11.3	
$\mathrm{NbCl_5 \cdot (}\mathit{Me}_2\mathrm{N)(MeO)_2PO}$	2.91	0.18	11.2	10.3	1:0.9
$\mathrm{NbCl_5 \cdot (Me_2N)(}\mathit{Me}\mathrm{O)_2PO}$	4.06	0.33	12.1	11.4	
$\mathrm{NbCl_5 \cdot (MeO)_3PO}$	4.13	0.32	11.8	11.0	1:1.0
$\mathrm{NbCl_5 \cdot Cl(Me_2N)_2PO}$	3.01	0.21	13.8	12.8	1:1.0
$\mathrm{NbCl_5 \cdot Cl_2(Me_2N)PO}$	3.12	0.19	16.4	15.6	1:1.0
$\mathrm{NbCl_5 \cdot Cl(MeO)_2PO}$	4.25	0.29	14.5	13.7	1:1.0
$\mathrm{NbCl_5 \cdot Cl_2(MeO)PO}$	4.39	0.28	17.1	17.3	1:1.0
$\mathrm{NbCl_5 \cdot (MeS)_3PO}$	2.71	0.24	19.1	16.4	1:1.1
$\mathrm{NbCl_5 \cdot (Me_2N)_3PS}$	2.85	0.19	11.2	11.3	1:1.1
$\mathrm{NbBr_5 \cdot Cl_2(Me_2N)PO}$	3.12	0.20	16.7	15.8	1:0.9
$\mathrm{NbBr_5 \cdot (MeO)_3PO}$	4.19	0.33	12.0	11.7	1:0.9
$\mathrm{NbBr_5 \cdot Cl(MeO)_2PO}$	4.38	0.29	16.8	17.5	1:1.0
$\mathrm{NbBr_5 \cdot Cl_2(MeO)PO}$	4.27	0.31	14.7	13.9	1:1.0
$\mathrm{NbBr_5 \cdot ClCH_2CN}$	4.65	0.43			1:1.0
$\mathrm{NbBr_5 \cdot FCH_2CN}$	5.54	0.45	45.6[d]	46.1[d]	1:0.9

[a] $\Delta\delta = \delta(\mathrm{MX_5 \cdot L}) - \delta(\mathrm{L})$.

[b] Measured in $\mathrm{CH_2Cl_2}$ at $-100°$.

[c] Other signals of small intensities are attributed to isomers of $\mathrm{MOX_3 \cdot 2(Me_2N)_3PO}$ and **to** $\mathrm{(Me_2N)_3PX_2}$.

[d] Coupling constant ^2J(H,F).

3. Results and discussion. – 3.1. *Stoichiometry and chemical shifts.* At room temperature, the ^{1}H-NMR.-spectra of the adducts in the presence of an excess of ligand show, in most cases, one doublet (splitting due to $^3J(H,P)$) as a result of the rapid ligand exchange (2).

$$MX_5 \cdot L + L^* \rightleftharpoons MX_5 \cdot L^* + L. \qquad (2)$$

This exchange is slowed down at lower temperature and two doublets are observed for the coordinated and free ligand respectively. The ^{1}H chemical-shift δ of the adducts, the chemical shift differences $\Delta\delta$ due to complexation and the stoichiometries are reported in Table 1.

The 1:1 stoichiometry has been verified on the basis of the known concentrations of metal and ligand, and the integration of NMR. signals. For hexamethylphosphoramide adducts, the 1:1 stoichiometry is not measurable by ^{1}H-NMR. as additional doublets appear in the spectra; for the metal fluoride adducts the structure has been verified by ^{19}F-NMR. (see below). The intensities of the additional doublets are reduced considerably if the adducts are prepared using $MX_5 \cdot MeCN$ solutions. Recalling *Dorschner's* observations [7], we assign these new signals to isomers of $MOX_3 \cdot 2(Me_2N)_3PO$. The spectrum of a $NbOCl_3 \cdot 2(Me_2N)_3PO$ solution confirms this assignment and is consistent with a recent study of oxychloride adduct isomers by *Riess* [19]. In $MX_5 \cdot (Me_2N)_3PO$ solution, one supplementary doublet appears at lower field; it is assigned to $(Me_2N)_3PX_2$ formed during the oxygen abstraction reaction.

The ^{1}H-NMR. resonance of the complexed ligand lies at lower field than the free ligand (Table 1) indicating a decrease of the electron density on the protons, due to coordination. Within the same functional group, $\Delta\delta$'s do not vary for different ligands with the pentachloride and pentabromide adduct series; they are smaller for the pentafluorides. Coupling constants $^3J(H,P)$ are slightly modified by complexation, showing an increase of 5 to 10%.

Fig. 1 shows the typical ^{19}F-FT-NMR. spectrum of an octahedral phosphoryl adduct of tantalum pentafluoride. The spectrum of $TaF_5 \cdot (MeO)_3PO$ is composed of two signals, one decet and one doublet in a 1:4 intensity ratio (Table 2), character-

Table 2. ^{19}*F-NMR. chemical shifts* δ (ppm) *and coupling constants* $^2J(F^1,F^2)$, $^3J(F^1,P)$ (Hz) *of axial fluorine* F^1 *and equatorial fluorine* F^2 *in octahedral* $MF_5 \cdot L$ ($M = Nb, Ta$) *in* CH_2Cl_2 *at* $-100°$
$[M]_t = 0.03$ m $[L]_t = 0.03$ m–0.06 m Reference: internal $CFCl_3$

$MF_5 \cdot L$	$\delta(MF_5 \cdot L)$		$^2J(F^1,F^2)$	$^3J(F^1,P)$	$[F^2]/[^1]$[a])
	F^1	F^2			
$NbF_5 \cdot (Me_2N)_3PO$	142 ± 1	118.8 ± 0.2	–	–	3.7 ± 0.3
$NbF_5 \cdot (Me_2N)_2(MeO)PO$	154 ± 1	124.3 ± 0.2	–	–	3.9 ± 0.2
$NbF_5 \cdot (Me_2N)(MeO)_2PO$	166.9 ± 0.5	130.3 ± 0.2	–	–	3.8 ± 0.2
$NbF_5 \cdot (MeO)_3PO$	175.5 ± 0.5	134.3 ± 0.2	–	–	3.9 ± 0.2
$TaF_5 \cdot (Me_2N)_3PO$	69.5 ± 0.1	51.73 ± 0.06	28 ± 2	7 ± 1[b])	3.9 ± 0.2
$TaF_5 \cdot (Me_2N)_2(MeO)PO$	78.9 ± 0.1	55.22 ± 0.06	27 ± 2	6 ± 1	4.2 ± 0.2
$TaF_5 \cdot (Me_2N)(MeO)_2PO$	89.5 ± 0.1	59.46 ± 0.06	27 ± 2	6 ± 1	3.8 ± 0.2
$TaF_5 \cdot (MeO)_3PO$	96.7 ± 0.1	62.36 ± 0.06	25 ± 2	7 ± 1	4.2 ± 0.2

[a]) Intensity ratio between the two signals.
[b]) Equally measured by ^{31}P-{^{1}H-}NMR.: 7.2 ± 0.3 Hz.

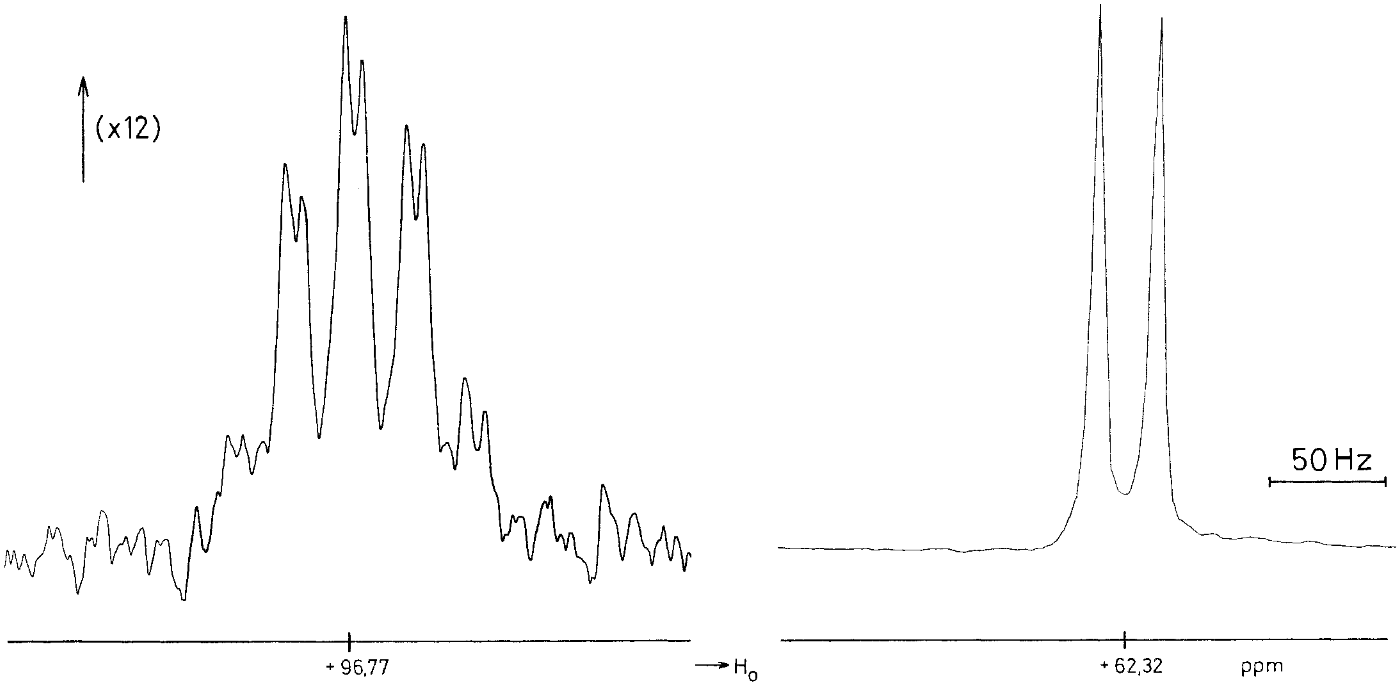

Fig. 1. ^{19}*F-FT-NMR. spectrum* (84.67 MHz) *of the adduct* $TaF_5 \cdot (MeO)_3PO$ *0.03* m *in* CH_2Cl_2 *at −100°.* Reference: internal $CFCl_3$.
(Scale expanded)

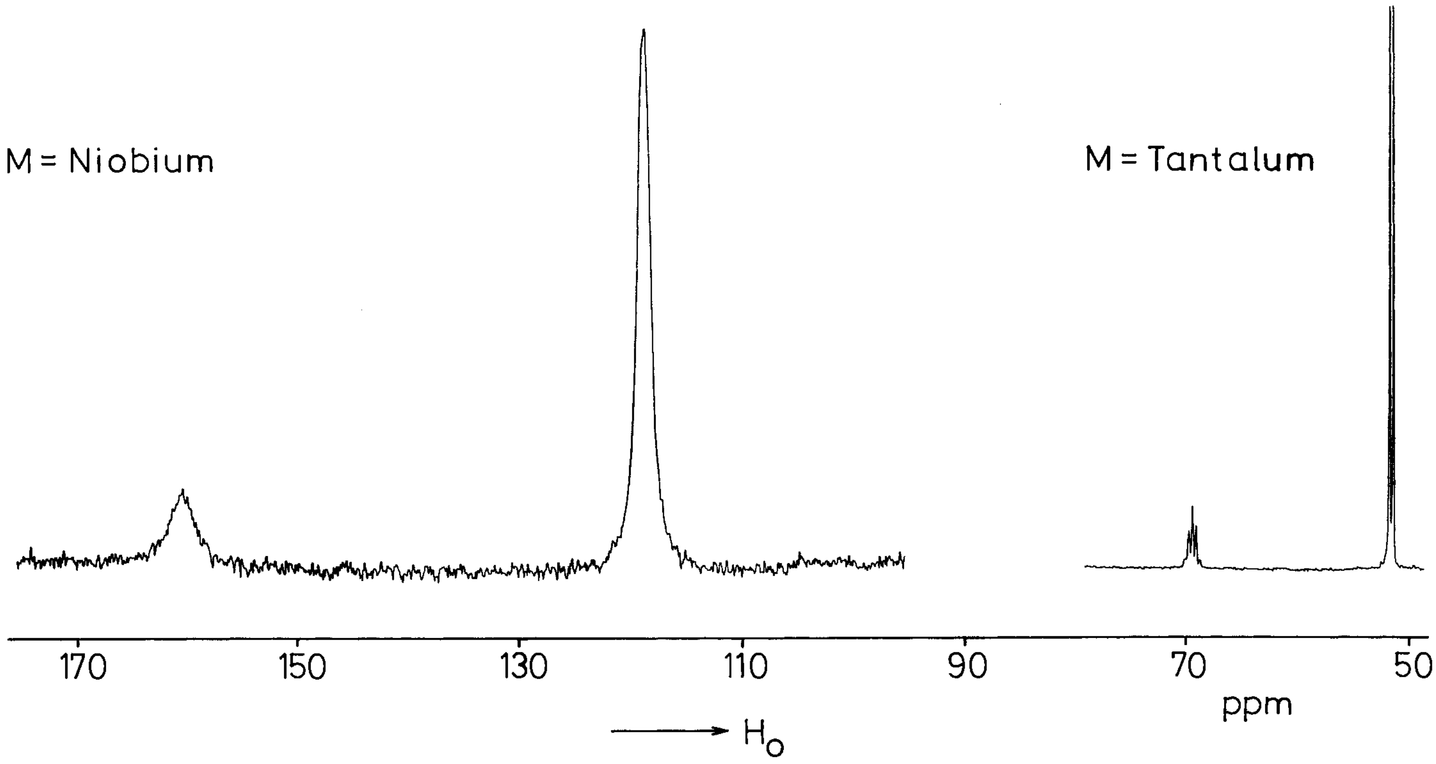

Fig. 2. ^{19}*F-FT-NMR. spectra* (84.67 MHz) *of the niobium and tantalum adducts* $MF_5 \cdot (Me_2N)_3PO$ *0.03 m in* CH_2Cl_2 *at –100°.*
Reference: internal $CFCl_3$

istic of an AM_4X spectrum with $J(M,X) = 0$. The axial fluorine (F^1) is coupled to four equatorial fluorines (F^2), the resulting quintet being further split in two by coupling with the phosphorus. The ^{19}F chemical-shifts and the coupling constants $^2J(F^1,F^2)$ and $^3J(F^1,P)$ for the two types of fluorine in some phosphoryl adducts of MF_5 are reported in Table 2. Coupling constants for NbF_5 adducts cannot be measured owing to the large width of NMR. signals (Fig. 2). This broadening is due to the relatively long quadrupolar relaxation time of ^{93}Nb; for ^{118}Ta the shorter quadrupolar relaxation time decouples the ^{19}F from the spin of the metal, giving rise to well resolved ^{19}F-NMR. spectra. The coupling constants for TaF_5 adducts do not exhibit any marked variation through the series. The ^{19}F chemical-shifts do show a large variation through both series of adducts with NbF_5 and TaF_5. We have assumed that

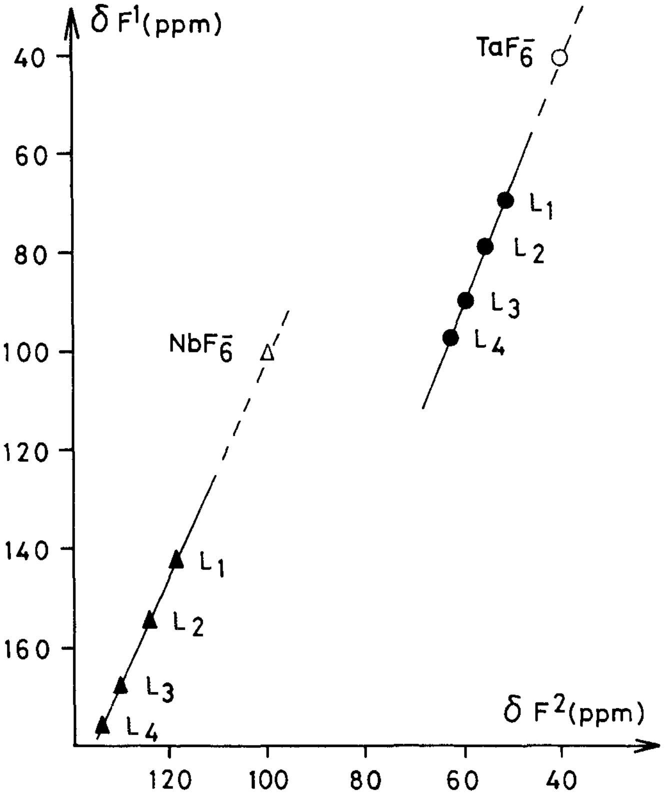

Fig. 3. *^{19}F-FT-NMR. chemical shifts of axial fluorines F^1 (δF^1) in function of equatorial fluorines F^2 (δF^2) for $MF_5 \cdot L$ adducts in CH_2Cl_2 at $-100°$.* Reference: internal $CFCl_3$

$L_1 = (Me_2N)_3PO$

$L_2 = (Me_2N)_2(MeO)PO$

$L_3 = (Me_2N)(MeO)_2PO$

$L_4 = (MeO)_3PO$

slope $= 2.2$ for $NbF_5 \cdot L$ (▲)

slope $= 2,6$ for $TaF_5 \cdot L$ (●)

these shift differences, in similar compounds, are dominated by the paramagnetic shielding parameter [20]. *Gutowsky & Hoffman* [21] showed that fairly good agreement between observed and calculated shifts could be obtained by considering the percent ionic character of the M-F bond. Increasing ionic character results in high field shifts. Our results are in agreement with this observation, *i.e.* the upfield adducts are those with a stronger donor ligand: the phosphoryl ligand electrons induce a decrease of

Table 3. *Relative stability constants for the adducts $NbX_5 \cdot L$ (X = Cl, Br) involving various nitriles, dimethylchalcogenides and phosphoryl compounds, in $CHCl_3$ at −60°*

$$NbX_5 \cdot L_b + L_a \rightleftarrows NbX_5 \cdot L_a + L_b,\ K_{a,b}$$

$[Nb]_t \simeq$ 0.03 to 0.10 m $[L_a]_t + [L_b]_t \simeq$ 0.06 to 0.16 m

MX_5	L_a	L_b	Method	n[a]	$K_{a,b}$	L_c	$K'_{a,b}$[b]	log $K''_{a,b}$[c]
$NbCl_5$	$(MeO)_2(Me_2N)PO$	$Cl(Me_2N)_2PO$	indirect[g]	3	4.5 ± 0.6			0.65
		$(MeO)_3PO$	direct	3	31 ± 6			1.49
	$Cl(Me_2N)_2PO$	$(MeO)_3PO$	indirect	3	13 ± 4			1.11
	$(MeO)_3PO$	$(MeS)_3PO$	direct	3	1.6 ± 0.2			0.20
	$Cl(MeO)_2PO$	$Cl_2(Me_2N)PO$	indirect	3	10.5 ± 1.5			1.02
	$Cl_2(Me_2N)PO$	Me_2S	indirect	3	1.1 ± 0.1			0.04
		Me_3CCN	indirect	3	23 ± 3	Me_2S	23 ± 4	1.36
	Me_2S	Me_3CCN	indirect[h]	3[d]	21 ± 2			1.32
	$(Me_2N)_3PS$	Me_3CCN	direct	2	2.4 ± 0.4			0.38
	Me_3CCN	$MeCN$	direct	15[d]	1.1 ± 0.1			0.04
		$Cl_2(MeO)PO$	direct	4	2.6 ± 0.2	$MeCN$	2.5 ± 0.4	0.40
	$MeCN$	$Cl_2(MeO)PO$	direct	4	2.3 ± 0.2			0.36
	$MeCN$	$ClCH_2CN$			$1.26 \cdot 10^3$			3.10[d]
	$ClCH_2CN$	Cl_3PO	indirect[g]	3[d]	2.5 ± 0.3			0.39
		FCH_2CN	direct	3[d]	3.6 ± 0.3	Cl_3PO	3.7 ± 1	0.56
	Cl_3PO	FCH_2CN	indirect[h]	5	1.5 ± 0.3			0.17
$NbBr_5$	$Cl(MeO)_2PO$	$Cl_2(Me_2N)PO$	direct	3[f]	9 ± 2			0.95
	$Cl_2(Me_2N)PO$	$MeCN$	direct	1[f]	5.3 ± 0.9			0.72
		Me_3CCN	direct	1[f]	6.8 ± 1			0.83
	$MeCN$	Me_3CCN	direct	4[e][f]	1.4 ± 0.2			0.15
	Me_3CCN	$Cl_2(MeO)PO$	direct	3	5.3 ± 0.6			0.72
	Me_3CCN	Me_2O	direct	4[e][f]	48 ± 5			1.68
	$ClCH_2CN$	FCH_2CN	direct	2	3.0 ± 0.3			0.48
	FCH_2CN	Cl_3PO	indirect[g]	3	2.5 ± 0.8			0.40
	$ClCH_2CN$	Cl_3PO	indirect[g]	3	11.5 ± 3			1.06
$TaBr_5$	$Cl_2(Me_2N)PO$	Me_3CCN	direct	1[f]	18 ± 3			1.26
	$Cl_2(Me_2N)PO$	$MeCN$	direct	1[f]	30 ± 4			1.48

[a] Number of determinations.
[b] $K'_{a,b} = K_{a,c} \cdot K_{c,b}$.
[c] $K''_{a,b}$ is the definitive value of $K_{a,b}$ adopted, taking into account the various constants determined.
[d] Determined by *A. E. Merbach & J.-C. Bünzli* [3].
[e] Determined by *R. Good & A. E. Merbach* [4].
[f] Determined in CH_2Cl_2.
[g] Integrations on L_a.
[h] Integrations on L_b.

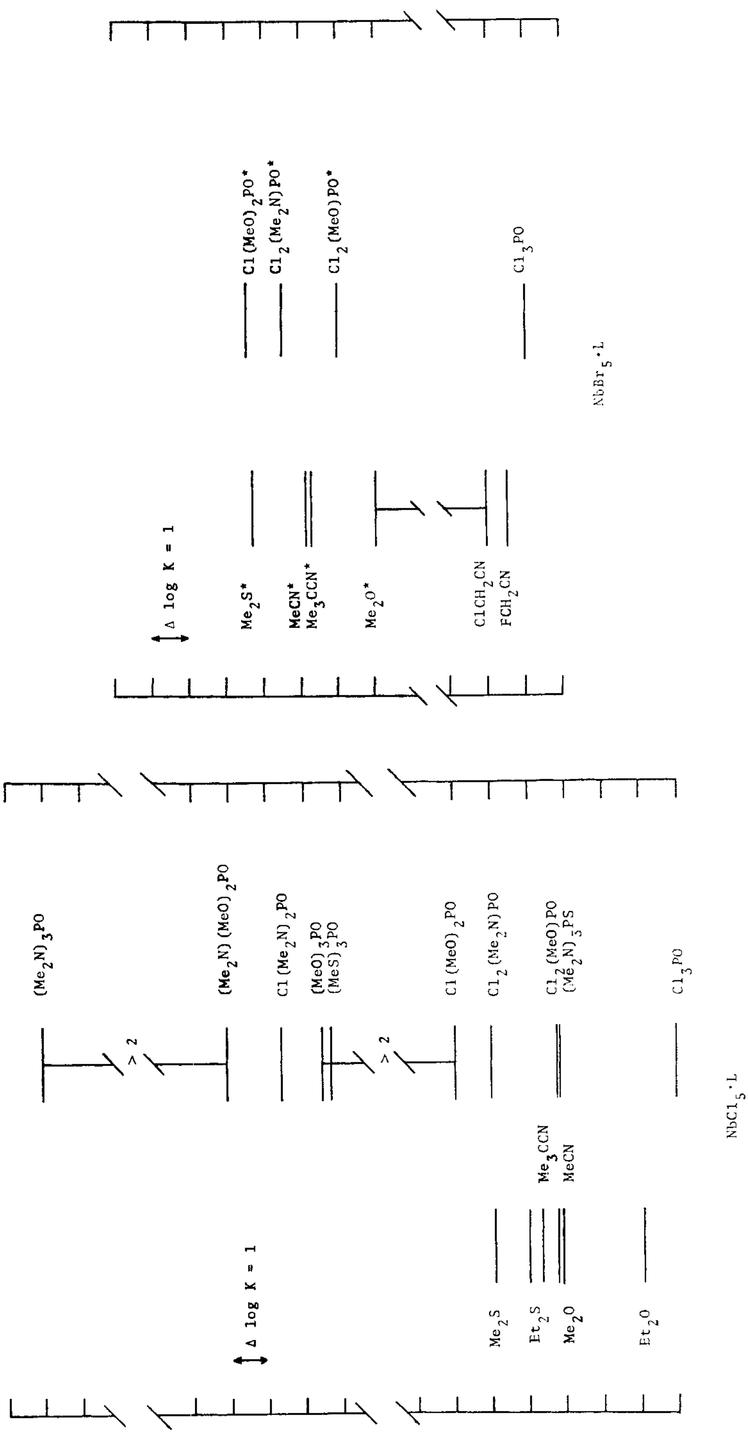

Fig. 4. *Relative stability of the adducts of niobium(V) chlorides and bromides $NbX_5 \cdot L$ at −60° in $CHCl_3$* (or in CH_2Cl_2: *). The stability of the adducts increases from bottom to top. Data taken from Table 3 and reference [4]

charge in the metal which increases the ionic character of the M-F bond, and therefore decreases the fluorine resonance frequencies. The paramagnetic screening tensor being proportional to $-1/\Delta E$ (ΔE is the average value of excitation energies) an increase in ΔE will induce a less negative shielding constant and a downfield chemical shift. We have not studied UV. spectra of the adducts because the charge transfers from fluorine to metal are too energetic to be observed in CH_2Cl_2. However, optical electronegativities determined by *Valloton & Merbach* [22] for niobium(V) (1.85) and tantalum(V) (1.62) suggest a large increase in charge transfer energy from niobium(V) to tantalum(V) adducts. This explains the large upfield chemical shifts for tantalum(V) compared to niobium(V) as shown in Fig. 2 and in Table 2. A closer look at the ^{19}F chemical-shifts in the two series, shows that F^1 is downfield of F^2. In addition we observe over a large range of chemical shifts that the axial fluorine, F^1 is twice as much affected by the nature of phosphoryl ligand as the equatorial fluorines, F^2 (this observation is illustrated by the slopes of 2 in Fig. 3). This fact suggests that the electronic perturbations operate through the dπ orbitals of the metal, since the axial fluorine can interact with the ligand oxygen through two dπ orbitals, while any given equatorial fluorine interacts through only one dπ orbital.

3.2. *Relative stability of the adducts.* We have determined, by ^{1}H-NMR., (*cf.* [3]) the constants $K_{a,b}$ for the competitive equilibria according to equation (3), for the case of slow exchange. The errors on the equilibrium constants (4) are estimated as

$$MX_5 \cdot L_b + L_a \rightleftharpoons MX_5 \cdot L_a + L_b. \tag{3}$$

$$K_{a,b} = ([MX_5 \cdot L_a]\,[L_b]/[L_a]\,[MX_5 \cdot L_b]). \tag{4}$$

a function of the reproducibility of integrations, the number of determinations and the method used. The results are given in Table 2 and Fig. 4.

Numerous experimental and theoretical reports have been devoted to the elucidation of the nature of the P-O bond in phosphoryl compounds [23]. The results show that the bonding can be interpreted in terms of σ donation from phosphorus to oxygen and pπ-dπ backdonation. The availability of the oxygen 2p orbitals for coordinative bonding is influenced by the inductive and conjugative effects of the three other substituents on phosphorus. π-bond order (P-O) and partial charge on the oxygen atom have been used to estimate the donor strength of phosphoryl ligands [24].

The large increase in stability from Cl_3PO to $(MeO)_3PO$ and to $(Me_2N)_3PO$ in the corresponding adducts $MX_5 \cdot L$ (M = Nb; X = Cl, Br) shows that the conjugative effect plays the largest part in complex stability. Lower stability is found for $(Me_2N)_3PS$ than for $(Me_2N)_3PO$ adducts; the same trend is observed for Cl_3PS and Cl_3PO, Cl_3PS forming no adduct with niobium(V) chloride [25]. Nonetheless dialkylsulfur adducts are found to be more stable than dialkyloxide adducts; this suggests that the stability is related to the structure of the donor group rather than to the nature of the donor atoms. Determination of the relative stabilities of adducts formed by chlorides and bromides by the competitive method is not possible owing to the formation of mixed halides. Nevertheless, the comparison between both stability scales shows that the donor strength sequence is the same and that stability differences do not vary from chloride to bromide adducts.

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