COMPLEX FORMATION OF POLYMERIC NIOBIUM AND TANTALUM PENTAFLUORIDES IN NON-AQUEOUS SOLVENTS

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SUMMARY

^{19}F NMR and i.r. spectroscopy were employed to study complex formation of niobium and tantalum pentafluorides with triphenylphosphine oxide, ethyl diphenylphosphinate and S-ethyl diphenylthiophosphinate in methylene chloride and in acetonitrile. In methylene chloride solution MF_5L, $M_2F_{10}L$, $MF_4L_2^+$ and $M_2F_{11}^-$ complexes were found (M=Nb, Ta; L- phosphoryl-containing ligand). I.r. frequencies are assigned. Solvent properties (electric conductivity and donor capacity) affect the relative stability of complexes. The dependence of ^{19}F NMR parameters on the donor capacity of the ligands is discussed.

INTRODUCTION

Tantalum and niobium halides form halogen-bridged compounds. The crystalline pentafluorides of these elements are tetramers with cis-fluorine bridges [1,2] . The penta-chlorides are dimers, sharing one edge of two octahedra [3]. In mixed compounds of the $MFCl_4$ type (M=Nb or Ta) the fluorine atoms bridge [4] . The dimeric Nb and Ta anions $M_2F_{11}^-$ [5,6] have two distorted octahedra sharing one fluorine. Recently the titanium complex $Ti_2F_{11}^{3-}$ has been characterized by NMR [7] . In the NMR spectra of such anions (I) the signal of the bridge fluorine atom F_3 lies to stronger field than the equatorial fluorines F_2, whereas the F_I lines lie to weaker field

(I)
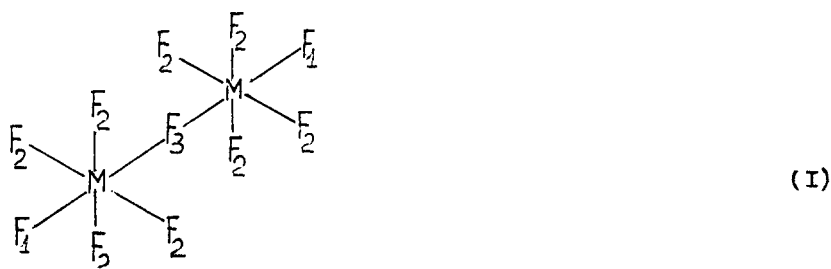
Antimony (V) and arsenic (V) give complex anions $Sb_2F_{11}^-$ and $As_2F_{11}^-$. Sb can also form dimeric molecular complexes with donor ligands of the type $Sb_2F_{10}L$ (L=SO_2, SOF_2, SO_2ClF, $MeSO_2F$, H_2O, H_2SO_4, $(CH_3)_2O$), where the ligand molecule occupies a cis-position with respect to the bridge fluorine [8-11].

The present work deals with preparation, NMR, and i.r. characterisation of complex compounds of Nb and Ta formed from interaction between the pentafluorides and S-ethyl diphe-nylthiophosphinate (L^I), ethyl diphenylphosphinate (L^{II}) and triphenylphosphine oxide (L^{III}) in methylene chloride and ace-tonitrile. Previous studies on the complex formation of Nb and

Ta pentafluorides with some phosphoryl-containing compounds in non-aqueous solvents showed formation of I:I adducts [I2-I3] as well as formation of anionic and cationic complexes in the case of tributylphosphine oxide.

EXPERIMENTAL

Nb and Ta pentafluorides were prepared by direct fluorination of the corresponding metal in quartz apparatus. S-ethyl diphenylthiophosphinate was synthesized by the reaction between potassium diphenylthiophosphinate and ethyl bromide [I4].Ethyl diphenylphosphinate was obtained by the reaction of sodium ethoxide with the corresponding phosphoryl chloride [I5]. Triphenylphosphine oxide ("Chemapol", grade "pure") was recrystallized from toluene. Methylene chloride was dried by repeated distillation over $CaCl_2$ and CaH_2; acetonitrile was distilled over P_2O_5.

^{I9}F NMR spectra (Table I) were recorded on a Varian A 56/60 spectrometer at temperatures from 30 to -I00°. Chemical shifts were measured with respect to CCl_3F and recalculated with respect to F_2.

I.r. spectra of starting materials and complexes were recorded in CH_2Cl_2 and in CH_3CN solution (c 0.35 M/l) on a UR-20 spectrometer (400-4000 cm^{-I}) in KBr or NaCl cuvettes. Results are given in Table 2.

Studies on the interaction of Ta and Nb pentafluorides with ligands were made in methylene chloride and in acetonitrile with the overall concentration of components (MF_5+L) up to 50

TABLE I

^{19}F NMR parameters complexes (w.r.t. F_2; to reference w.r.t. CCl_3F subtract 430.6 p.p.m.)

Complex	Solvent	F_I	F_2	F_3	F_4	F_5	F_6	$J(F_I-F_2)$ ±5 Hz	$J(F_I-F_3)$ ±5 Hz	$J(F_6-F_3)$ ±5 Hz	$\Delta\Sigma=\delta F_I - \delta F_2$ p.p.m.
TaF_5L^I	CH_2Cl_2	372.2	345.4	-	-	-	-	28	-	-	26.8
	CH_3CN	372.8	348.I	-	-	-	-	28	-	-	24.7
cis-$TaF_4L^I_2$ +	CH_2Cl_2	355.4	329.6	-	-	-	-	28	-	-	25.8
	CH_3CN	355.9	330.6	-	-	-	-	28	-	-	25.3
trans-$TaF_4L^I_2$ +	CH_2Cl_2	356.4	-	-	-	-	-	-	-	-	-
	CH_3CN	356.9	-	-	-	-	-	-	-	-	-
$Ta_2F_{II}^-$	CH_2Cl_2	3I4.9	359.I	5II.5	-	-	-	-	I65	-	-
$Ta_2F_{IO}L^I$	CH_2Cl_2	3II.2	357.0	509.3	343.4	320.6	300.2-	-	I60	I75	-
TaF_5L^{II}	CH_2Cl_2	37I.7	343.5	-	-	-	-	28	-	-	28.2
	CH_3CN	372.I	344.2	-	-	-	-	28	-	-	27.9
cis-$TaF_4L^{II}_2$ +	CH_2Cl_2	353.5	326.4	-	-	-	-	29	-	-	27.I
	CH_3CN	353.9	327.0	-	-	-	-	29	-	-	26.9
trans-$TaF_4L^{II}_2$+	CH_2Cl_2	354.4	-	-	-	-	-	-	-	-	-
	CH_3CN	354.6	-	-	-	-	-	-	-	-	-

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Ta$_2$F$_{10}$L^{II}	CH$_2$Cl$_2$	310.9	356.7	509.0	342.6	319.5	299.2	-	140	180	-
TaF$_5$L^{III}	CH$_2$Cl$_2$	373.8	349.0	-	-	-	-	29	-	-	24.8
	CH$_3$CN	374.1	350.6	-	-	-	-	28	-	-	23.5
cis-TaF$_4$L$^{III}_2$ +	CH$_2$Cl$_2$	356.8	337.0	-	-	-	-	28	-	-	19.8
Ta$_2$F$_{10}$L^{III}	CH$_2$Cl$_2$	312.0	357.4	509.9	345.0	323.0	303.4	-	165	200	-
NbF$_5$L^{I}	CH$_2$Cl$_2$	302.6	271.1	-	-	-	-	49	-	-	31.5
	CH$_3$CN	302.9	272.7	-	-	-	-	49	-	-	30.2
cis-NbF$_4$L$^{I}_2$ +	CH$_2$Cl$_2$	279.6	251.1	-	-	-	-	50	-	-	28.5
Nb$_2$F$_{11}^{-}$	CH$_2$Cl$_2$	239.3	285.0	487.0	-	-	-	-	200	-	-
Nb$_2$F$_{10}$L^{I}	CH$_2$Cl$_2$	236.9	281.4	483.0	263.4	245.8	207.5	-	160	185	-
NbF$_5$L^{II}	CH$_2$Cl$_2$	301.1	266.7	-	-	-	-	49	-	-	34.4
	CH$_3$CN	301.7	267.8	-	-	-	-	49	-	-	33.9
cis-NbF$_4$L$^{II}_2$ +	CH$_2$Cl$_2$	278.3	248.2	-	-	-	-	50	-	-	30.1
Nb$_2$F$_{10}$L^{II}	CH$_2$Cl$_2$	236.1	281.1	482.5	261.8	245.6	206.7	-	175	200	-
NbF$_5$L^{III}	CH$_2$Cl$_2$	305.1	274.6	-	-	-	-	49	-	-	30.5
	CH$_3$CN	305.7	275.8	-	-	-	-	49	-	-	29.9
cis-NbF$_4$L$^{III}_2$ +	CH$_2$Cl$_2$	281.0	255.6	-	-	-	-	49	-	-	26.4
cis-Nb$_2$F$_{10}$L^{III}	CH$_2$Cl$_2$	237.4	281.6	483.8	267.1	246.6	209.1	-	200	200	-

TABLE 2

I.r. spectral data (cm^{-I}) for complexes of Ta and Nb pentafluorides with phosphoryl containing ligands

Complex	γ(P=O)	$\Delta\gamma$(P=O)	γ(M-F)
OPPh$_2$SC$_2$H$_5$(L^I)	I200	-	-
OPPh$_2$OC$_2$H$_5$(L^{II})	I230	-	-
OPPh$_3$(L^{III})	II90	-	-
TaF$_5$L^I	II30	70	620, 595
TaF$_5$L^{II}	II45	85	600
TaF$_5$L^{III}	II30	60	605
NbF$_5$L^I	II25	75	630
NbF$_5$L^{II}	II40	90	640
NbF$_5$L^{III}	II30	60	630
Ta$_2$F$_{I0}$L^I	II25	75	630, 6I0, 5I5
Ta$_2$F$_{I0}$L^{II}	II45	85	620, 525
Ta$_2$F$_{I0}$L^{III}	II35	55	6I5, 520
Nb$_2$F$_{I0}$L^I	II30	70	630, 600
Nb$_2$F$_{I0}$L^{II}	II40	90	625, 585
Nb$_2$F$_{I0}$L^{III}	II35	55	635, 585

weight % and the MF$_5$:L ratios 0.5; I and 2. Upon interaction between the initial components the solutions warmed up and became dark brown in colour [I3] .

RESULTS AND DISCUSSION

   After two hours an equimolecular methylene chloride solu-
tion of TaF_5 and S-ethyl diphenylthiophosphinate gave a ^{19}F NMR
spectrum. consistent with the I:I complex (II) and the cis- and
trans- cationic species $TaF_4L_2^{I+}$(III) and (IV). The relative
amounts of these latter species is 8:I; the statistical ratio
would be 4:I. At -80° the $Ta_2F_{II}^-$ anion is observed. Fine
structure is not observed.
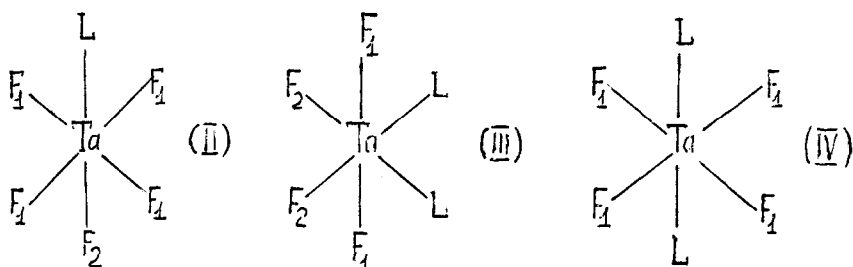
   After 5 days at room temperature the signal from the
$Ta_2F_{II}^-$ anion had disappeared, the intensity of $TaF_4L_2^{I+}$
resonance signals decreased, while that of the MF_5L^I molecu-
lar complex increased. At -45° fine structure a doublet and
quintet was observed (Fig. Ia).

   In methylene chloride solution complex formation between
equimolecular amounts of TaF_5 and S-ethyl diphenylthiophosphinate
begins by dissociation of the tetramer:

$$Ta_4F_{20} + 4(L^I) \xrightarrow{CH_2Cl_2} TaF_4(L^I)_2^+ + Ta_2F_{II}^- +$$
$$TaF_5L^I + L^I \qquad (I)$$

$$Ta_2F_{II}^- + TaF_4(L^I)_2^+ + L^I \xrightarrow{CH_2Cl_2} 3\ TaF_5L^I \qquad (2)$$
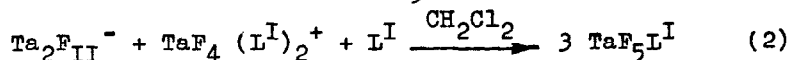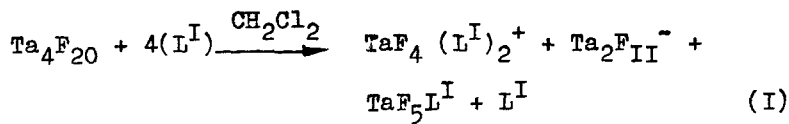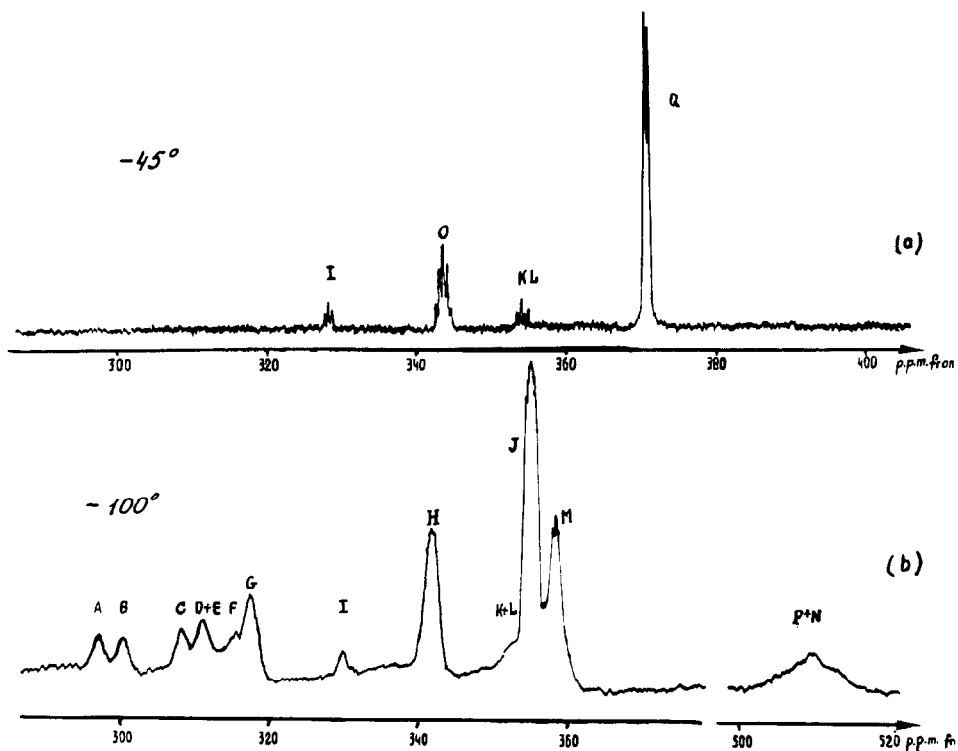
Fig. 1. ^{19}F NMR spectra Ta-F complexes with S-ethyl diphenyltio-
phosphinate in methylene chloride solution: (a) 1 : 1 solution
after 5 days at room temperature; b) 2 : 1 solution.

A, B - F_6 $Ta_2F_{10}L$; C, D - $F_1Ta_2F_{10}L$; E, F -F_1 $Ta_2F_{11}^{-}$; G - F_5
$Ta_2F_{10}L$; I - F_2 cis -$TaF_4L_2^{+}$; H -F_4 $Ta_2F_{10}L$; J - F_2 $Ta_2F_{10}L$; K - F
cis -$TaF_4L_2^{+}$; L - F_1 trans -$TaF_4L_2^{+}$; M - F_2 $Ta_2F_{11}^{-}$; N - F_3 Ta_2F_{11}
P - F_3 $Ta_2F_{10}L$; O - F_2 TaF_5L; Q - F_1 TaF_5L.

At high concentrations of the thioester (TaF_5:L^I = 0.5)
the NMR spectrum recorded two hours after the solution had
been prepared showed only the molecular complex TaF_5L^I.

In excess of TaF_5 (TaF_5 : L^I = 2) the spectrum was more
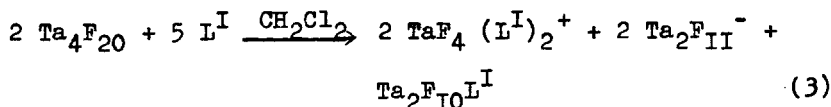complex, consisting of fourteen resonance lines (Fig. Ib).

The spectrum is interpreted to show cis-$\mathrm{TaF_4L_2^{I+}}$; the dimeric anion $\mathrm{Ta_2F_{II}}^-$ (I); and the dimeric molecular complex $\mathrm{Ta_2F_{IO}L^I}$ (V).

(V)
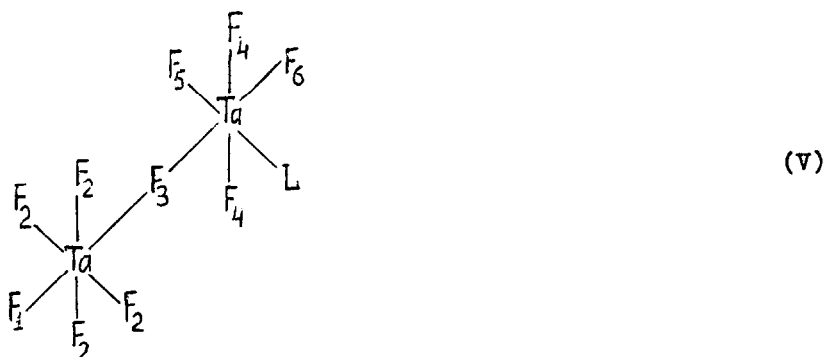
The most intense signals H and J belong to the F_4 and F_2 atoms respectively.

It is of interest that in the spectra of dimeric anions of d^0-transition metals ($\mathrm{Ta_2F_{II}}^-$, $\mathrm{Nb_2F_{II}}^-$ and $\mathrm{Ti_2F_{II}}^{3-}$) the J(F-F) of non-equivalent trans- fluorine atoms e.g. $\mathrm{J(F_I\text{-}F_3)}$; $\mathrm{J(F_3\text{-}F_6)}$ is much greater than J(F-F) for cis- fluorines e.g. $\mathrm{J(F_I\text{-}F_2)}$, so that the signal of the F_I atom of the anion (I) is a double quintet. In complex (V) F_I and F_6 are unresolved and looked like doublets. This is consistent with the occupation of positions trans- to F_3 by non-equivalent fluorines (F_I and F_6) with a cis-phosphoryl ligand. The low field signals are ascribed to the F_6 atom.

The reaction in methylene chloride solution is as follows:

$$2\ \mathrm{Ta_4F_{20}} + 5\ \mathrm{L^I} \xrightarrow{\mathrm{CH_2Cl_2}} 2\ \mathrm{TaF_4}\ (\mathrm{L^I})_2{}^+ + 2\ \mathrm{Ta_2F_{II}}^- + \mathrm{Ta_2F_{IO}L^I} \qquad (3)$$

$\mathrm{OPPh_2OC_2H_5}$ and $\mathrm{OPPh_3}$ react similarly with tantalum pentafluoride in methylene chloride but in case of $\mathrm{OPPh_3}$ the

^{19}F NMR spectrum of an equimolecular solution one hour after preparation showed only the signals of the TaF_5L^{III} molecular complex.

Signals of $TaF_4L_2^{III}$ $^+$ cations were observed only at the ratio TaF_5 : L^{III} = 2, when the solution also contained dimeric complexes $Ta_2F_{11}^-$ and $Ta_2F_{10}L^{III}$, Table I.

Niobium pentafluoride reacts more rapidly than TaF_5. At the ratio NbF_5 : L = I or 0.5 only NbF_5L molecular complexes were present in the solution (Table I) after one hour. The spectra show fine structure at low temperatures (-80°). The resonance lines were considerably broader than those of tantalum complexes, probably due to longer times of nuclear relaxation.

It has recently been shown by ^{19}F NMR techniques that tantalum fluoride complexes are more stable in solution than niobium complexes [16] . We may thus assume that the ligand-induced repture of M-F bonds in the Me_4F_{20} tetramer occurs more readily for Nb than for Ta.

At a NbF_5 : L 2 : I ratio the ^{19}F NMR spectrum showed the dimeric anion $Nb_2F_{11}^-$ (I) [5] and the dimeric molecular complex $Nb_2F_{10}L$ with the ligand L cis- to the bridge fluorine.

Accordingly, in dimeric molecular complexes $M_2F_{10}L$ of transition and non-transition elements a molecular ligand appears to prefer to occupy a cis-position with respect to the bridge fluorine. In all the d^o-complexes $Ta_2F_{11}^-$, $Nb_2F_{11}^-$ [5,7], $Ta_2F_{10}L$ and $Nb_2F_{10}L$ the spin-spin interaction constant $J(F_I-F_3)$ is several times higher than $J(F_I-F_2)$, in contrast to the similar compounds of non-transition elements $As_2F_{11}^-$, $Sb_2F_{11}^-$ and $Sb_2F_{10}L$, where $J(F_I-F_3)$ is small [8-II].

This may indicate that in the transition element complexes the strongest interaction occurs between the trans-ligands, whereas in non-transition elements this type of interaction through the central atom is weaker.

It has been previously shown [13] that the difference between chemical shifts $\Delta\delta = \delta F_I - \delta F_2$ of MF_5L complexes (M = Nb or Ta, L is a phosphoryl-containing ligand) increases with the decreasing donor capacity (trans activity) of the ligand, as the bond between the trans-F_2 atom and the metal becomes more covalent. For the Nb and Ta complexes studied the value $\Delta\delta = \delta F_I - \delta F_2$ increased in the series $Ph_3PO - Ph_2OPSC_2H_5 - Ph_2OPOC_2H_5$ (Table I) parallel to the change in trans-influence. The effect is greater for niobium complexes. The difference between chemical shifts $\Delta\delta = \delta F_I - \delta F_2$ for the signals of complex cations cis-$MF_4L_2^+$ (III) increases which reflects the increasing covalency of the M-F_2 bond with respect to M-F_I, and also follows the same order.

It is significant that upon changing from L^{III} to L^{II} (lower trans effect) signals of the non-equivalent fluorine atoms in dimeric complexes $M_2F_{10}L$ also move towards weaker fields in accordance with less ionic character for the metal fluorine bond.

For all the MF_5L (M=Nb,Ta) complexes considered the resonance signals of the F_I fluorine atoms (trans- position with respect to each other) are at higher field than those of F_2 signals trans- to the phosphoryl-containing ligand [12-13].

As solvent properties are responsible for the extent of solvation and association of ions and neutral particles, it

appeared of interest to study the influence of solvent nature
upon the composition of complexes in solution. On addition of
nitromethane (dielectric constant ξ = 38.6) to methylene
chloride solution containing dimeric molecular complexes
$M_2F_{10}L$, $MF_4L_2^+$ cations and dimeric anions $M_2F_{11}^-$ the signals
of the neutral complex disappeared, whereas those of cations
and anions became more intense. Addition of a less polar solvent
only caused small changes from the initial spectrum. This indicate
that in media with a higher dielectric constant that $M_2F_{10}L$
dissociates, though the corresponding anion $M_2F_{11}^-$ remains
as a dimer. In contrast to nitromethane, addition of a donor
solvent, i.e. ethyl acetate to the initial solution cause the
signals of all dimeric forms to disappear and the spectra
show only molecular complexes and the anion MF_6^-. Addition of
acetonitrile produces the same effect. Strong donor ligands
as tributyl phosphate and hexamethylphosphoramide do not form
dimeric molecular complexes in methylene chloride solution
and only MF_5L adducts are present [13] .

At a MF_5:L ratio of 1:2 substitution of acetonitrile for
methylene chloride as solvent does not affect the composition
of the complexes in solution although the signals are at
slightly higher fields, presumably owing to solvation effects.
The equimolecular solution immediately after preparation
shows only the MF_5L, cis- and trans-$MF_4L_2^+$ complexes and the
dimeric anion $M_2F_{11}^-$ is absent. No acetonitrile complexes
are present. The F_2 signals in acetonitrile solution undergo
a larger shift to higher fields and therefore the chemical
shift differences of the complexes are lower than in
methylene chloride solution (Table I).

At the ratio $MF_5:L = 2$ the acetonitrile solution showed only the MF_5L molecular complexes.

The P=O stretching frequency (Table 2) decreases on complexation. In MF_5L and $M_2F_{10}L$ complexes the $\Delta\sqrt{}$(P=O) values were the same for Nb and Ta complexes. In the i.r. spectrum of ethyl diphenylphosphinate the P-O-C band, a doublet with maxima at 1040 and 1030 cm^{-1} [17-18] , was virtually unaffected by complex formation, as are the aromatic bands at 1450 and 1600 cm^{-1}. S-ethyl diphenylthiophosphinate has an intense band at 575 cm^{-1} attributed to the P-S-C stretching mode [18]. Upon complex formation this band moves to 590 cm^{-1}. It seems that owing to charge transfer from the phosphoryl group to the metal atom the effective positive charge at the phosphorus increases and in its turn this may affect electron density in the P-S bond. The P-S-C bond would thus become stronger and $\sqrt{}$ (P-S) should move to higher frequency. The absence of such an effect in $OPPh_2OC_2H_5$ complexes is likely to be due to the higher electronegativity of the oxygen atom. We believe that the intense broad symmetrical bands with two maxima at 600-610 and at 620-640 cm^{-1} can be atributed to M-F vibrations [19-23] . The increase in frequency of the M-F stretching mode as compared with normal values for Nb and Ta fluorine compounds (560-585 cm^{-1} for $\sqrt{}$(Ta-F) and 560-610 cm^{-1} for $\sqrt{}$(Nb-F)) [19-23] probably indicates that the M-F bond becomes stronger on complexation.

The broad band at 510-520 cm^{-1} in the spectra of dimeric molecular complexes $M_2F_{10}L$ is attributed to the bridge M-F-M vibration [20] , and the presence of the bridge M-F-M is also shown by the considerable broadening of the absorption band

in the 600-640 cm^{-1} region in the spectra of these compounds as compared with the corresponding band for the MF_5L complexes.

The i.r. spectra of free and complexed ligands were virtually the same in acetonitrile solution and in methylene chloride. The corresponding absorption bands, in acetonitrile, however, were situated at lower frequencies, presumably on account of dipole-dipole interaction [24] .

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