Fluorine-19 Nuclear Magnetic Resonance Study of some Pentafluorotitanate Complexes with Neutral Ligands

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A ^{19}F n.m.r. study of the reactions of $[TiF_5]^-$ with neutral Lewis bases is reported. The factors which contribute to the formation of $[TiF_5]^-\cdot D$ complexes are considered. Fluorine-19 n.m.r. data for over 30 complexes are presented and the effects of donor basicity, $p_\pi-d_\pi$ bonding, and solvent interactions on the chemical shifts are discussed.

ONLY three complexes of the type $[TiF_5]^-\cdot D$ (D = a neutral ligand) have been previously reported.[1] These complexes were the methanol, ethanol, and propan-2-ol adducts. Attempts to form $[TiF_5]^-$ adducts in acetone, acetonitrile, and nitromethane, where the solvent is also the donor molecule, were unsuccessful. In contrast to the $[TiF_5]^-\cdot D$ complexes, a number of complexes of the type $[TiF_5]^-\cdot D^-$ have been reported (D = an anion) [2,3] and many $TiF_4\cdot 2D$ complexes have been characterized in which the donor is a neutral molecule.[4-7] Consequently it was of interest to carry out a more thorough study of the reactions between $[TiF_5]^-$ and neutral molecules and to investigate the factors which contribute to the formation of $[TiF_5]^-\cdot D$ complexes.

EXPERIMENTAL

Materials.—Titanium tetrafluoride was obtained from Allied Chemical Corp. and used without further purification. The solvents acetonitrile, chloroacetonitrile, dichloromethane, nitromethane, chloroform, and ethanol were purified by standard procedures. Di-n-propylammonium fluoride was prepared by passing hydrogen fluoride gas through a solution of di-n-propylamine in acetone. The precipitate was filtered off and then washed with water-free acetone.

Preparation of Complexes.—The complexes were prepared by one of two methods. The first method consisted of dissolving TiF_4 in a solvent of choice, after which a slight excess of $[NPr^n_2H_2]F$ and a stoicheiometric amount of the donor were added. The second method involved adding a stoicheiometric amount of $[NPr^n_2H_2]_2[TiF_6]$ to a solution of $TiF_4\cdot 2D$. All the complexes were prepared under an atmosphere of dry nitrogen.

Instrumental.—The fluorine n.m.r. spectra were obtained with a Varian A 56/60A high-resolution n.m.r. spectrometer equipped with a V-6057 variable-temperature accessory. The spectra were recorded at -40 °C except where noted, and were calibrated in p.p.m. displacements from internal $[TiF_6]^{2-}$.

RESULTS AND DISCUSSION

In order to help establish the nature of the fluorotitanate species in a number of TiF_4–$[NPr^n_2H_2]F$ solutions, continuous-variation conductivity experiments were made. The donors (and solvents) studied were acetonitrile, 1,2-dimethoxyethane, and *NN*-dimethylformamide (dmf). The conductivity minima in each case corresponded to formation of $[TiF_6]^{2-}$. The maximum for the acetonitrile solution indicated the formation of a polymeric species of stoicheiometry $[Ti_2F_9]^-$. For dimethoxyethane, the maximum corresponded to the formation of a complex with the stoicheiometry $[Ti_4F_{17}]^-$. The measurements for the dmf system indicated that a $[TiF_5]^-$ monomer is formed, and ^{19}F n.m.r. experiments confirmed this. Recently, the formation and identification by ^{19}F n.m.r. techniques of $[Ti_2F_9]^-$, $[Ti_2F_{10}]^{2-}$, and $[Ti_2F_{11}]^{3-}$ in liquid sulphur dioxide was reported,[3] lending support to the conclusion that polymeric species can be formed in some solvents.

A partial list of the donors which promote formation of $[TiF_5]^-\cdot D$ and those which do not is given in Table 1 together with some dielectric-constant, dipole-moment, and basicity data for the donor molecules. Perusal of the data shows that there is no apparent correlation between the dielectric constant or dipole moment of the donor in predicting the formation of a $[TiF_5]^-\cdot D$ complex. The relative basicity of the donors in Table 1 were measured by visible spectroscopy from the interaction of the base with the reference acid $[VO(pd)_2]$ (pd = pentane-2,4-dionato).[8] This technique allows measurement of the relative basicity of the very weak bases and

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TABLE 1

Formation of $[TiF_5]^-\cdot D$ and $[Ti_2F_{11}]^{3-}$ related to some of the physical properties of the donor molecules

Donor	Solvent	$[TiF_5]^-\cdot D$ Formed	$[Ti_2F_{11}]^{3-}$ Formed	Dipole moment of donor [a]/D	Dielectric constant of donor [b]	$D_{II.I}$ [c]/cm^{-1}
H_2O	EtOH	Yes	No	1.85	78.5	5 490
MeOH	MeOH	Yes	No	1.70	32.6	4 420
py	MeCN	Yes	No	2.19	12.3	4 390
EtOH	EtOH	Yes	No	1.69	24.3	4 260
SMe_2O	MeCN $ClCH_2CN$	Yes	No	3.96	47.6	4 180
$Me_2NC(O)H$	$ClCH_2CN$	Yes	No	3.82	37.6	3 940
$(NH_2)_2CO$	$ClCH_2CN$	Yes	Yes			
4-NCpy	MeCN	Yes	Yes			
3-NCpy	MeCN	Yes	Yes			
2-MeOpy	MeCN	No	Yes			
2-Mepy	MeCN	No	Yes			
$MeO(CH_2)_2OMe$	$MeO(CH_2)_2OMe$	No	No			
Me_2CO	Me_2CO	No		2.88	20.7	
$(MeCO)_2O$	$ClCH_2CN$	No	Yes		20.7 (20)	
$(Me_2N)_2CS$	$ClCH_2CN$	No	Yes			
MeCN	MeCN	No	Yes	3.92	37.5 (20)	2 600
$ClCH_2CN$	$ClCH_2CN$	No	Yes			
$MeNO_2$	$MeNO_2$	No	No	3.46	35.9 (20)	2 260
$CHCl_3$	$CHCl_3$	No	No	1.01	4.8 (20)	1 940

[a] In the gas phase; 1D ≈ 3.33 × 10^{-30} C m (' Handbook of Chemistry and Physics,' ed. R. C. Weast, Chemical Rubber Co., 1973). [b] In the liquid phase at 25 °C, except where indicated in parentheses (' Handbook of Analytical Chemistry,' ed. L. Meites, McGraw-Hill, 1963). [c] Ref. 8.

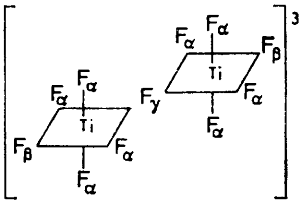
TABLE 2

^{19}F N.m.r. data for $[TiF_5]^-\cdot D$ complexes in various solvents [a]

Donor	σ(doublet)	σ (quintet)	J/Hz	θ_c/°C	Solvent	Other peaks [b]
NEt_3	−20.9				EtOH	
NPr^n_2H	−19.1				EtOH	
3,4-Me_2py	−30.4	−87.4	36	−40	MeCN	
3,5-Me_2py	−30.8	−88.4	36	−40	MeCN	
4-Mepy	−30.6	−86.8	36	−40	MeCN	
3-Mepy	−30.9	−89.1	36	−40	MeCN	
Isoquinoline	−30.6	−91.1	36	−40	MeCN	
Pyridine	−30.4	−91.2	36	−40	MeCN	
3-$NCCH_2$py	−31.1	−94.2	36	−40	MeCN	
3-$MeCO_2$py	−31.1	−94.2	36	−40	MeCN	
4-MeO_2Cpy	−31.4	−97.2	36	−40	MeCN	
3-MeOCpy	−31.3	−95.5	36	−40	MeCN	
3-MeO_2Cpy	−31.1	−97.0	36	−40	MeCN	
3-Clpy	−31.4	−98.0	36	−40	MeCN	
3-Brpy	−31.5	−98.0	36	−40	MeCN	
4-NCpy	−32.1	−98.7	36	−40	MeCN	−20.8, J 44 (triplet)
3-NCpy	−32.2	−100.4	36	−40	MeCN	−20.4, J 43 (triplet)
H_2O	−20.3	−99.0	36	−40	EtOH	
OEt_2	−20.8	−100.5		−40	EtOH	
$MeOC_2H_4OH$	−28	−110		−20	$MeOC_2H_4OH$	
4-MeOpyo	−19.6	−52.0	37	−40	$ClCH_2CN$	
4-Mepyo	−21.1	−57.0	38	−40	$ClCH_2CN$	
4-Mepyo	−21.8	−65.1	37	−20	$ClCH_2CN$	
4-Mepyo	−17	−54		−20	EtOH	
4-Mepyo	−20.8	−57.9	37	−20	CH_2Cl_2	
4-Mepyo	−20	−53		−20	$CHCl_3$	
pyo	−22.9	−61.9	37	−40	$ClCH_2CN$	
4-Clpyo	−22.5	−67.1	36	−40	$ClCH_2CN$	
4-MeO_2Cpyo	−24.0	−72.3	36	−40	$ClCH_2CN$	
4-O_2Npyo	−25.6	−81.7	36	−40	$ClCH_2CN$	
$MeCO_2H$	−26	−108		−20	$MeCO_2H$	
$(EtO_2C)_2$	−23	−94		−20	$(EtO_2C)_2$	
$HCONMe_2$	−25.6	−85.4	37	−40	$ClCH_2CN$	
$HCONEt_2$	−26	−99		−20	$HCONEt_2$	
$HCONEt_2$	−24	−93		−20	$CHCl_3$	
$HCONEt_2$	−24.3	−93.6	36	−30	CH_2Cl_2	
$HCONEt_2$	−25.3	−91.4	36	−40	MeCN	
$MeCONMe_2$	−23	−89		−20	$CHCl_3$	
	−24.3	−91.9	39	−40	CH_2Cl_2	
	−24.2	−89.9	39	−40	$MeNO_2$	
	−24.2	−83.2	39	−40	$ClCH_2CN$	
$(NH_2)_2CO$	−19.7		42	−40	$ClCH_2CN$	−23.1, J 44 (triplet)
$(MeNH)_2CO$	−18.6	−79.8	42	−40	$ClCH_2CN$	−21.3, J 45 (doublet)
SMe_2O	−21.5	−83.9	36	−35	MeCN	
	−24.2	−79.5	37	−40	$ClCH_2CN$	

[a] Chemical shifts (p.p.m.) relative to internal $[TiF_6]^{2-}$; py = pyridine, pyo = pyridine 1-oxide. [b] Assigned to $[Ti_2F_{11}]^{3-}$.

the values are reported as the difference, $D_{\mathrm{II,I}}$, between the first and second absorption bands. It can be seen that acetonitrile, nitromethane, and chloroform, which do not form $[TiF_5]^-\cdot D$, are rated as relatively weak bases on the basis of $D_{\mathrm{II,I}}$ values. The bases listed in Table 1 for which $D_{\mathrm{II,I}}$ is not given (with the exception of the substituted pyridines), which would be expected to be weaker bases than urea or dmf, also do not form $[TiF_5]^-\cdot D$. Thus the basicity of the donor determines the particular titanium fluorine spectra. In the ^{19}F n.m.r. spectra of the solutions of TiF_4 and $[NPr^n{}_2H_2]F$ with some of the bases in Table 1 which did not form $[TiF_5]^-\cdot D$ (and with four of the complexes listed in Table 2) there appears to be a triplet at *ca.* −20 p.p.m. with a coupling constant of between 43 and 45 Hz. Since the solutions were prepared with an excess of $[NPr^n{}_2H_2]F$ in order to provide $[TiF_6]^{2-}$ as a reference, and since $[TiF_5]^-\cdot D$ was not formed, it is reasonable to assume that the resonance at −20 p.p.m. is due to a complex of the two species, $[Ti_2F_{11}]^{3-}$.

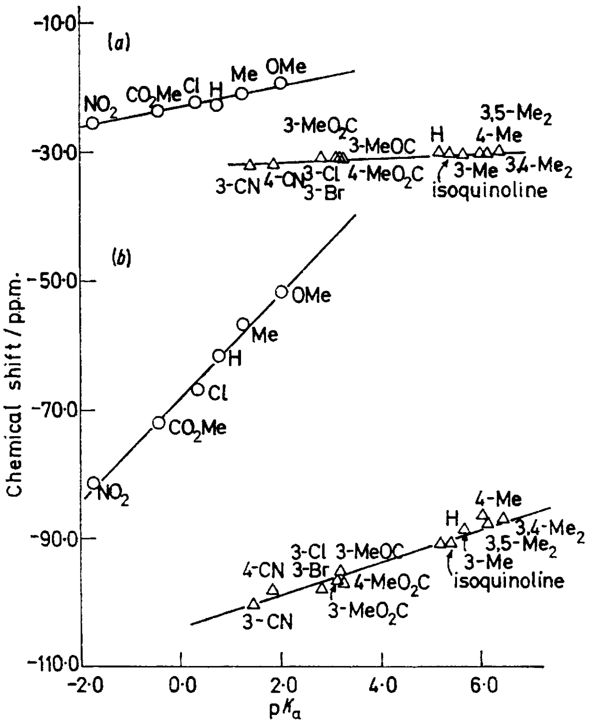


The ^{19}F n.m.r. spectra of this complex would consist of a resonance due to the α-fluorines split into a doublet of doublets by the β- and γ-fluorines and much less intense resonances due to the β- and γ-fluorines. At low concentrations with appropriate coupling constants, the doublet of doublets could appear to be a triplet. In fact, it has been reported that the $[Ti_2F_{11}]^{3-}$ ion is formed in liquid SO_2 and that the ^{19}F n.m.r. spectrum contains an intense doublet of doublets at *ca.* −20 p.p.m.[3] The couplings of this peak are such that at low concentration the resonance could easily be mistaken for a triplet. A necessary condition for the stability of $[TiF_5]^-\cdot D$ is that the donor be a strong enough Lewis base to prevent formation of polymeric fluorotitanate complexes held together by fluorine bridges. It is interesting to note that although the 2-substituted pyridines are relatively strong Lewis bases, there is enough steric interaction through the substituted 2 position to prevent the formation of $[TiF_5]^-\cdot D$.

Over 30 neutral Lewis bases have been used in the preparation of $[TiF_5]^-\cdot D$ complexes. Solutions of these complexes in excess of donor or other solvents were studied by ^{19}F n.m.r. spectroscopy and the chemical shifts and the coupling constants are reported in Table 2. The ^{19}F n.m.r. spectra were consistent with those obtained previously [1] and are taken as sufficient evidence for the formation of $[TiF_5]^-\cdot D$, even though isolation of a complex containing this anion has not been reported. Each spectrum consisted of two principle resonances, one of which had four times the area of the other. At lower temperatures (depending on the donor and the solvent) the larger peak split into a doublet, and the smaller peak became a quintet. This type of spectrum is exactly the predicted first-order spectrum for a complex ion containing Ti^{IV} octahedrally co-ordinated by five fluoride ions and one donor molecule. The chemical shifts of the doublets in Table 2 range from −17 to −32 p.p.m., whereas the shifts of the quintet range from −52 to −110 p.p.m. This indicates that the fluorine *trans* to the donor is much more sensitive to the effect of the donor than are the *cis* fluorines.

Most of the complexes of TiF_4 and $[TiF_5]^-$ with neutral donors have been with oxygen donors such as pyridine 1-oxides, sulphoxides, and alcohols.[4-7] In Table 2 are listed a number of complexes with nitrogen donors, among them a series of aromatic amines. It is of interest to compare the ^{19}F n.m.r. data of these nitrogen-donor complexes with some of the oxygen-donor complexes. As an example, consider the chemical shifts of the $[TiF_5]^-$ complexes of 4-cyanopyridine and 4-methoxypyridine 1-oxide, two ligands with approximately the same pK_a values (1.90 and 2.05, respectively). Comparing the *trans* fluorines in the two complexes, it is found that the chemical shift of the *trans* fluorine for the pyridine complex is 47 p.p.m. farther downfield. It has been shown for complexes of TiF_4 that steric interactions between the fluorines and the donors have a small but definite effect on the fluorine chemical shifts.[6] In comparing the steric effects of pyridine 1-oxides and quinoline 1-oxides on TiF_4 it was found that the *cis* fluorines (as would be expected) were influenced more by the bulkiness of the donor. The chemical shift for the *cis* fluorine moved upfield for the more hindered complexes, whereas the chemical shift of the *trans* fluorine moved slightly downfield. This steric effect would not be expected to be as large in the case of $[TiF_5]^-\cdot D$ complexes since only one donor is complexed to the titanium. Thus steric interaction cannot account for the great difference in the chemical shifts between the pyridine and pyridine 1-oxide adducts of $[TiF_5]^-$. These results indicate that there is a fundamental difference between the complexing characteristics of the pyridines and the pyridine 1-oxides. This difference is the ability of pyridine 1-oxides to contribute to ligand to metal π bonding because of the lone pairs of electrons on the oxygen.[4-6] In contrast, the pyridines cannot readily function as π donors since they have no available nitrogen lone pairs, but rather are good π acceptors. Thus they will facilitate the ability of the fluorine to π bond to titanium. In Ti^{IV} there are low-lying unfilled *d* orbitals with which the ligands, especially fluorines, may π bond. When fluorine–metal π bonding occurs the fluorine experiences a paramagnetic shift which increases with the amount of π bonding. That is, as fluorine to titanium π bonding increases, the less shielded the fluorine becomes and the lower its chemical shift. The ability of a donor *trans* to a given fluorine to compete for the π-bonding orbitals greatly influences the chemical shifts of the fluorines. If the *trans* ligand competes effectively for the titanium π-bonding orbitals, the π donation from the *trans* fluorine to titanium is lessened, the fluorine is shielded more, and the resulting chemical shift of the fluorine is observed at a higher value.

The chemical shift of the fluorines *cis* to the donor is upfield from that of the *trans* fluorine, and the chemical shift of the *trans* fluorine is more affected by the basicity of the donor. The fluorine *trans* to the donor can compete more successfully for the available titanium *d* orbitals than can any of the four fluorines which are *trans* to each other. Since the deshielding of both types of fluorines (compared to $[TiF_6]^{2-}$) occurs because of the π donation to the titanium *d* orbitals, a fluorine *trans* to the donor must have a greater double-bond character than a *cis* fluorine.



Plots of chemical shifts of substituted pyridine and 4-substituted pyridine 1-oxide complexes against the respective pK_a values. (*a*), *cis*-Fluorine; (*b*), *trans*-fluorine; △, pyridine complexes; ○, pyridine 1-oxide complexes

It has been shown for complexes of TiF_4 with a series of substituted pyridine 1-oxides that there is a direct relation between the chemical shifts of the fluorines and the basicities of the donors.[5] It was of interest to determine if a similar relation exists for the $[TiF_5]^- \cdot D$ species, and to compare the results of the substituted pyridine 1-oxide complexes with those of the substituted pyridine complexes. The Figure shows the chemical shifts of the substituted pyridine and pyridine 1-oxide complexes plotted against the corresponding pK_a values. There is a near linear correlation between the basicities of the donor molecules and chemical shifts in both cases. As the basicity of the donor increases, the chemical shift moves upfield. The pK_a of a donor depends on the σ-bonding characteristics of the donor atom. An increase in the titanium–fluorine bond distance as the donor becomes more basic decreases the overlap of the fluorine non-bonding *p* orbitals with the titanium *d* orbitals, the fluorine is shielded more, and the chemical shift increases. The gradients of the lines due to the *cis* and *trans* fluorines of the pyridine 1-oxide complexes of $[TiF_5]^-$ are 1.6 and 8.1 respectively. In comparison, the gradients of the lines for the *cis* and *trans* fluorines of the corresponding $TiF_4 \cdot 2D$ complexes are 3.7 and 9.2 respectively (calculated from data from ref. 5). It appears, as would be expected, that the fluorines of the $TiF_4 \cdot 2D$ complexes are more sensitive to the donors, since each complex contains two donors instead of one for the $[TiF_5]^- \cdot D$ complexes. The same relation holds for the TiF_4 [9] and $[TiF_5]^-$ complexes of the substituted pyridines.

It is also of interest to compare the gradients of the lines due to the *cis* and *trans* fluorines of the substituted pyridine 1-oxide complexes with those of the substituted pyridine complexes of $[TiF_5]^- \cdot D$, which are 0.31 and 2.7 respectively. As can be seen, there is a tremendous difference in gradients of the lines due to the pyridine and pyridine 1-oxide complexes. Again this shows the difference between the two series of complexes. The greater p_π–d_π bonding of the pyridine 1-oxides over that of the pyridines enhances the sensitivity of the fluorines toward the basicity of the donor.

The data in Table 2 also indicate that the chemical shifts in the ^{19}F n.m.r. spectra of $[TiF_5]^- \cdot D$ complexes are influenced to some extent by the nature of the solvent. For example, there is a difference of more than 10 p.p.m. for the quintet of the 4-methylpyridine 1-oxide complex in acetonitrile solution as compared with ethanol or chloroform solution. Likewise the quintet of the *NN*-dimethylacetamide complex is shifted 8.7 p.p.m. further downfield with the solvent chloroacetonitrile than with dichloromethane. There are a number of solvent properties which could cause this effect, including dipole moment, dielectric constant, dispersion (van der Waals) forces, and hydrogen bonding. It has been suggested that for some organic fluorine compounds the variation in fluorine chemical shifts with different solvents is mainly due to dispersion forces between the fluorine-containing compound and the solvent, while polar forces seem not to be very important.[10] The data in this study are insufficient to show the relation of chemical shifts with the solvent properties. Significantly, all the $[TiF_5]^- \cdot D$ solutions contained the di-n-propylammonium ion, and alkyl-substituted ammonium ions are known to form ion pairs with various complex anions.[11] The influence of the solvent on the stability constant of a $[NPr^n_2H_2][TiF_5 \cdot D]$ ion pair might affect the chemical shifts significantly.

Coupling Constants.—The fluorine spin–spin coupling

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[9] H. G. Lee and R. O. Ragsdale, unpublished work.

[10] D. F. Evans, *J. Chem. Soc.*, 1960, 877.

[11] D. W. Larsen, *Inorg. Chem.*, 1966, **5**, 1109.

constants listed in Table 2 range from 36 to 42 Hz. The couplings for all the pyridine complexes are 36 Hz, whereas the couplings for the pyridine 1-oxide complexes are 37 ± 1 Hz. Since the couplings vary little in both series of complexes, it can be concluded that there is no correlation between the coupling constants and the basicities of the ligands in the $[\mathrm{TiF_5}]^-\cdot\mathrm{D}$ complexes. The coupling constant of a $[\mathrm{TiF_5}]^-\cdot\mathrm{D}$ complex is approximately the same as that of the corresponding $\mathrm{TiF_4\cdot 2D}$ complex, and seems to be affected by the bulkiness of the ligand at the donor site. This observation is in agreement with the 'through-space' mechanism.[12] This type of nuclear interaction is thought to arise as a result of overlap between the electronic clouds of the coupled fluorine atoms.

Exchange Processes.—The ^{19}F n.m.r. spectra of the $[\mathrm{TiF_5}]^-\cdot\mathrm{D}$ complexes are temperature dependent. The fine structure coalesces and the two main peaks collapse into a single resonance as the temperature is raised. Therefore, a fast exchange of fluorine nuclei between the two electronic environments must be occurring. A reasonable mechanism for this exchange would be a dissociation–inversion process analogous to that proposed

$$[\mathrm{TiF_5}]^-\cdot\mathrm{D} \rightleftharpoons [\mathrm{TiF_5}]^- + \mathrm{D} \qquad (1)$$

$$[\mathrm{TiF_5}]^-\ (\mathrm{A}) \rightleftharpoons [\mathrm{TiF_5}]^-\ (\mathrm{B}) \qquad (2)$$

for $\mathrm{TiF_4\cdot 2D}$ complexes.[13] The inversion step is thought to involve isomerization of $[\mathrm{TiF_5}]^-$ through trigonal-bipyramidal and tetragonal-pyramidal intermediates.

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[12] D. S. Dyer and R. O. Ragsdale, *J. Phys. Chem.*, 1967, **71**, 2309.

[13] D. S. Dyer and R. O. Ragsdale, *J. Amer. Chem. Soc.*, 1967, **89**, 1528.