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Fluorine-19 Nuclear Magnetic Resonance Study of Some Pentafluorotitanate Complexes

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Received December 18, 1962

A new type of octahedral fluorotitanate complex is described. Nuclear magnetic resonance and conductivity data lead to the conclusion that the species consists of one molecule of solvent, one axial fluorine, and four equatorial fluorines coordinated to the titanium. This type of anion has the general formula $\text{TiF}_5 \cdot \text{ROH}^-$, where R represents the alkyl group.

Introduction

The existence of $(\text{TiF}_5^-)_n$ was suggested in a study of the binary system $\text{TiF}_4 - [(n\text{-C}_3\text{H}_7)_2\text{NH}_2^+]_2\text{TiF}_6^{-2}$ in acetone.¹ Solid hexafluorotitanate remained in the acetone solution below $\text{TiF}_4/\text{TiF}_6^{-2}$ mole ratios of approximately one, but above this ratio all material was soluble. The nature of the resulting species was not resolved. In this paper, the investigation of the reaction of titanium tetrafluoride with di-*n*-propylammonium hexafluorotitanate in various alcohols is reported. A new type of octahedral complex was discovered which has the general formula $\text{TiF}_5 \cdot \text{ROH}^-$, where R represents an alkyl group. This type of complex may be considered a unique derivative of TiF_6^{-2} . The structure of this type of complex was established by nuclear magnetic resonance spectra and by a conductivity study.

Experimental

Chemicals.—Reagent grade acetone was freshly distilled from sodium carbonate. Reagent grade ethanol, methanol, 2-propanol, and di-*n*-propylamine were used. All titanium tetrafluoride solutions were prepared in a drybox and filtered in order to remove any insoluble impurities.

Preparation of Di-*n*-propylammonium Hexafluorotitanate.—The hexafluorotitanate was prepared in an inert atmosphere by combining acetone solutions of titanium tetrafluoride and di-*n*-propylammonium fluoride, filtering the product, and washing with purified acetone. Di-*n*-propylammonium fluoride was prepared by slowly adding anhydrous hydrogen fluoride to pre-cooled di-*n*-propylamine. The resulting precipitate was washed with ether.

Anal. Calcd. for $[(\text{C}_3\text{H}_7)_2\text{NH}_2^+]_2\text{TiF}_6^{-2}$: N, 7.6; F, 30.9. Found: N, 7.4; F, 29.7, 30.6.

The melting point of approximately 180° and the X-ray *d*-spacings agreed with published data.²

Preparation of $(\text{C}_3\text{H}_7)_2\text{NH}_2^+ \text{TiF}_5 \cdot \text{ROH}^-$ Solutions.—Titanium tetrafluoride-alcohol solutions of known concentration were added to weighed hexafluorotitanate samples. The usual concentration for n.m.r. measurements was approximately 1 *M* for each reactant. Equal concentrations were chosen since the maximum in the continuous variation study occurred at a 1:1 stoichiometry.

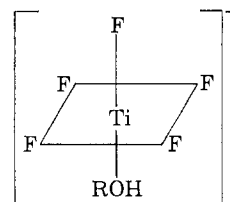
Instrumental.—The F^{19} n.m.r. spectra were obtained with a Varian 56.4 Mc. high resolution spectrometer, Model V-4302B, equipped with variable temperature accessories. The spectra

were calibrated in p.p.m. displacements from the external primary standard trichlorofluoromethane. Electrical conductivity was measured with an Industrial Instruments Model RC-1 conductance bridge. The conductivity cell (cell constant = 0.8) was a Leeds and Northrup No. 4917.

Results

In order to establish the nature of the species formed in the reaction between titanium tetrafluoride and di-*n*-propylammonium hexafluorotitanate, a continuous variation study³ was carried out in absolute ethanol. A plot of conductivity *vs.* mole fraction is given in Fig. 1. The maximum obtained corresponds to the empirical formula TiF_5^- .

The n.m.r. study confirmed the presence of a TiF_5^- species and indicated that a molecule of solvent occupied the sixth position in the octahedron. The following structure is consistent with the data



The predicted first-order spectrum for this type of structure would consist of a quintuplet for the axial fluorine and a doublet for the equatorial fluorines. The quintuplet to doublet ratio would be 1 to 4. The multiplets for the methanol complex are shown in Fig. 2. Nuclear magnetic resonance data for all of the $\text{TiF}_5 \cdot \text{ROH}^-$ complexes and the reactants are given in Table I. In Fig. 3 a typical F^{19} spectrum of the $\text{TiF}_4 - \text{TiF}_6^{-2}$ reaction mixture in ethanol is shown. For all molar ratios studied, titanium tetrafluoride and hexafluorotitanate were observed in the n.m.r. spectra as well as the new pentafluorotitanium complex. So far the pentafluorotitanium complex has not been isolated.

Discussion

Titanium tetrafluoride reacts with most solvents so that a maximum degree of coordination is obtained. For the present systems, titanium is octahedrally co-

(1) J. A. Chandler, J. E. Wuller, and R. S. Drago, *Inorg. Chem.*, **1**, 65 (1962).

(2) J. A. Chandler, R. S. Drago, and R. Latham, *J. Inorg. Nucl. Chem.*, **1**, 283 (1961).

(3) P. Job, *Ann. Chem.*, **9**, 113 (1928); F. Woldbye, *Acta Chem. Scand.*, **9**, 299 (1955); M. M. Jones, *J. Am. Chem. Soc.*, **81**, 4485 (1959).

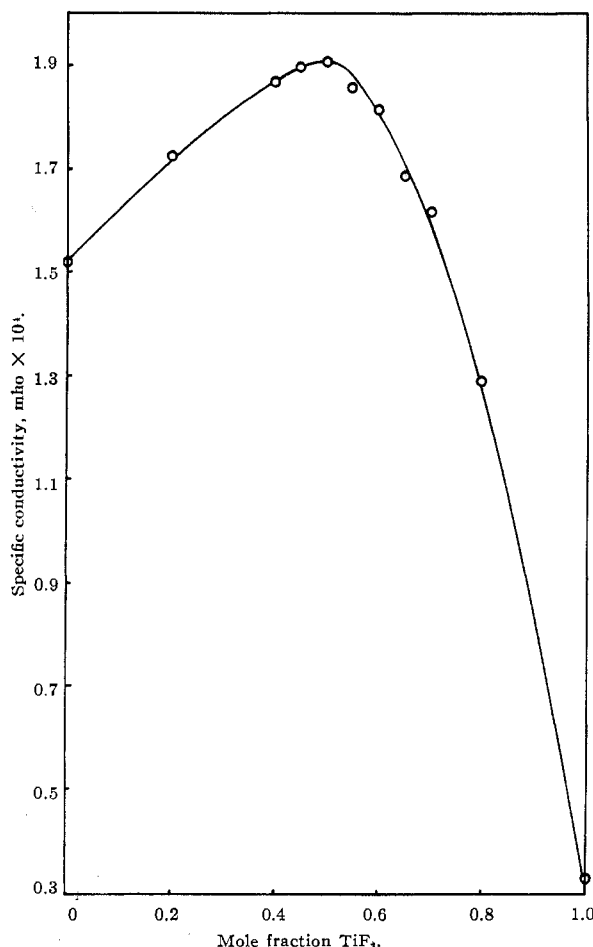


Fig. 1.—A continuous variation study for the system $\text{TiF}_4 - [(\text{n-C}_3\text{H}_7)_2\text{NH}_2^+]_2\text{TiF}_6^{-2}$ in ethanol (sum of $\text{TiF}_4 + \text{TiF}_6^{-2} = 0.02 M$).

TABLE I
 F^{19} CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR SOME FLUOROTITANIUM COMPLEXES

Compound	Multiplet	Relative area	Chem. shift (p.p.m. external CFCl_3 ref.) for F-F	Coupling constant (c.p.s.)
$\text{TiF}_4 \cdot 2\text{CH}_3\text{OH}^a$	Triplet	1	-203 ^b	31 ^c
	Triplet	1	-143	
$\text{TiF}_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}^d$	Triplet	1	-206	32
	Triplet	1	-146	
$\text{TiF}_4 \cdot 2\text{-i-C}_3\text{H}_7\text{OH}^a$	Triplet	1	-206	33
	Triplet	1	-148	
$\text{TiF}_5 \cdot \text{CH}_3\text{OH}^{-e}$	Doublet	4	-96.5	31
	Quintuplet	1	-173	
$\text{TiF}_5 \cdot \text{CH}_3\text{CH}_2\text{OH}^{-e}$	Doublet	4	-99	32
	Quintuplet	1	-182	
$\text{TiF}_5 \cdot \text{i-C}_3\text{H}_7\text{OH}^{-a}$	Doublet	4	-102	ca. 35 ^f
	Quintuplet	1	-184	
TiF_6^{-2} in CH_3OH^g	Singlet	...	-72.5	...
TiF_6^{-2} in $\text{CH}_3\text{CH}_2\text{OH}$	Singlet	...	-74.6, ^h -74.3 ⁱ	...
TiF_6^{-2} in $\text{i-C}_3\text{H}_7\text{OH}^a$	Singlet	...	-77	...

^a -34°. All temperatures are within $\pm 1^\circ$. ^b Accuracy of all chemical shifts is ± 1 p.p.m. ^c Accuracy for the coupling constants is ± 1 c.p.s. ^d -22°. ^e -38°. ^f Estimated from band width. ^g -40°. ^h -18°. ⁱ -4°.

ordinated. It previously was shown⁴ that titanium tetrafluoride in various basic solvents has a structure in which two molecules of solvent occupy *cis* positions in the octahedron.

(4) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

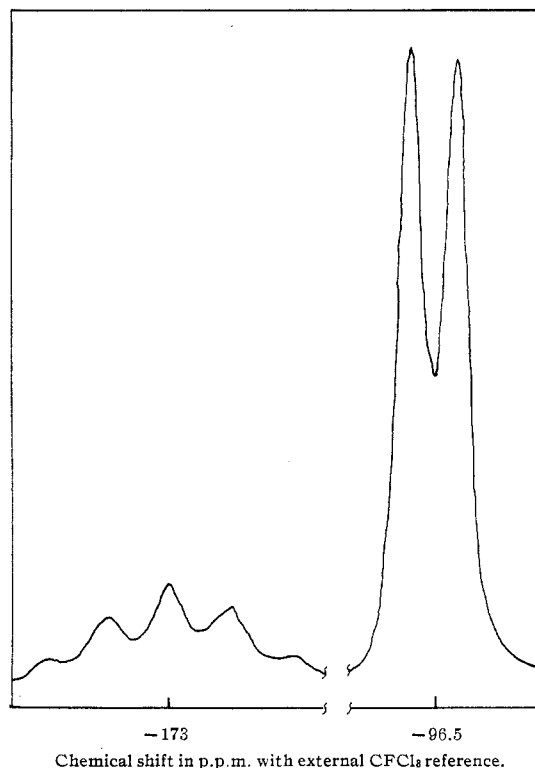
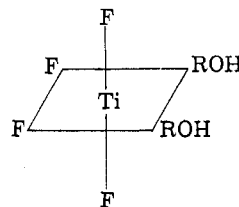


Fig. 2.— F^{19} high resolution spectrum of $\text{TiF}_5 \cdot \text{CH}_3\text{OH}^-$ at -36° .



Two F^{19} triplets of equal intensity in the n.m.r. spectra provided proof of the structure assignment. Our data for titanium tetrafluoride in methanol, ethanol, and 2-propanol also confirmed this type of structure.

The quintuplet downfield from the doublet in the $\text{TiF}_5 \cdot \text{ROH}^-$ complex must be due to the fluorine *trans* to the alcohol group. Therefore, it seems reasonable that the downfield triplet of the $\text{TiF}_4 \cdot 2\text{ROH}$ complex is due to the fluorines which bear a *trans* relationship to the alcohols.

The F^{19} spectra of the $\text{TiF}_4 \cdot 2\text{ROH}$ and $\text{TiF}_5 \cdot \text{ROH}^-$ complexes were found to be markedly temperature dependent. Above -10° rapid exchange resulted in the loss of fine structure. Muetterties⁴ concluded that temperature effects with titanium tetrafluoride and stannic fluoride complexes in excess base were due to ligand exchange. Also his thermal tensiometric studies established base dissociation. Very fast intermolecular fluorine exchange in octahedral MF_6 , MF_6^- , and MF_6^{-2} is generally not observed at moderate temperatures.⁵ It seems probable that the temperature dependency of the $\text{TiF}_5 \cdot \text{ROH}^-$ complexes also is due to ligand-solvent exchange.

The F^{19} chemical shifts of the titanium complexes in Table I show an interesting trend for methanol,

(5) E. L. Muetterties and W. D. Phillips, *ibid.*, **81**, 1084 (1959).

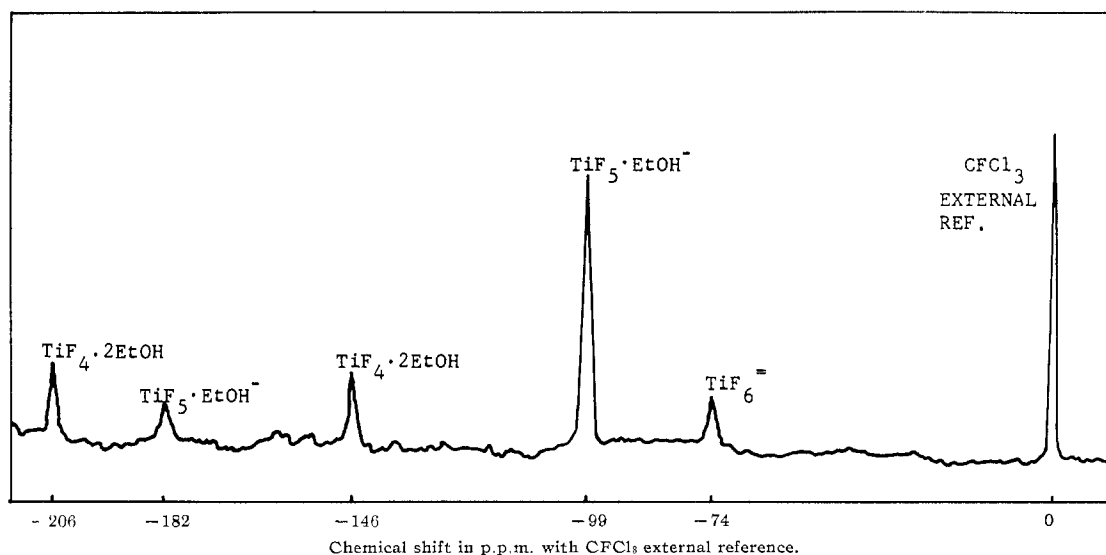
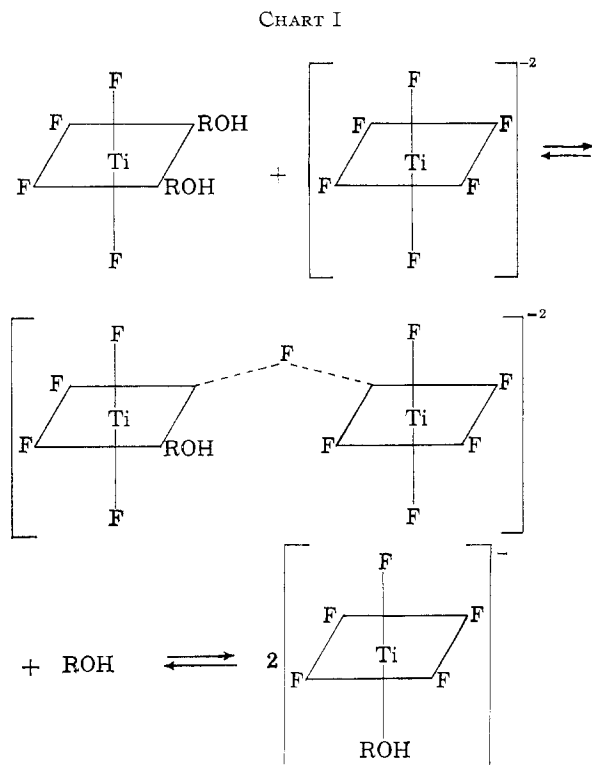


Fig. 3.— ^{19}F Spectrum of the TiF_4 - TiF_6^{-2} reaction mixture in ethanol.



ethanol, and 2-propanol. The more basic ligand might be expected to increase the shielding of the axial and equatorial fluorines but the opposite trend is observed. The "repulsive unshielding" effect⁶ does not seem to

apply since the *trans* fluorine is less shielded than the *cis* fluorines, which are much nearer to the alcohol ligand. Also only a slight change in shielding with change in complex concentration was observed.

A possible mechanism for the formation of $\text{TiF}_5 \cdot \text{ROH}^-$ would be an initial displacement of a molecule of solvent from $\text{TiF}_4 \cdot 2\text{ROH}$ by the formation of a fluorine bridge and subsequent re-entry of solvent in the second octahedron (Chart I).

Pentafluorotitanium complexes undoubtedly can be formed with other Lewis bases but low solubility or side reactions may limit such studies. Efforts to use acetone, acetonitrile, and nitromethane as solvents have not given satisfactory results. On the other hand, it was found that alcohol ligands can be displaced with stronger bases to form new pentafluorotitanium complexes.

Since there may be a large number of anionic metal halide complexes of the generic formula $[\text{MX}_5 \cdot \text{B}]^{\text{Y}}$, where Y represents the charge of the complex, additional studies may prove interesting.

Acknowledgments.—The authors wish to thank Drs. R. S. Drago and J. S. MacKenzie for helpful suggestions and interest. We wish to acknowledge Mr. R. Tepper and staff for elemental analyses and for the preparation of di-*n*-propylammonium fluoride.

(6) G. V. D. Tiers, *J. Am. Chem. Soc.*, **78**, 2914 (1956).