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Fluorine-19 Nuclear Magnetic Resonance Study of Some Pentafluorostannate Complexes

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Several octahedral fluorostannate complexes are described. By means of nuclear magnetic resonance and conductivity data the nature of the species was established. This type of anion has the general formula $SnF_5 \cdot B^-$, where B represents various bases or solvents.

Introduction

The existence of $(n\text{-}C_3H_7)_2NH_2^+TiF_5 \cdot ROH^-$ in various alcohol solutions was recently demonstrated.[2] Many other group IV metals should be capable of forming stable pentafluoro complexes, and this has been shown to be the case. Recently, the compound $K_2[SnF_5OH] \cdot H_2O$ was prepared, and its infrared and Raman spectra were recorded.[3] The $[GeF_5OH]^{2-}$ anion has also been reported.[4,5]

In this paper, the investigation of the reaction of stannic fluoride with di-*n*-propylammonium hexafluorostannate and di-*n*-propylammonium fluoride is reported. An octahedral fluorostannate complex was found which has the general formula $SnF_6 \cdot B^-$, where B represents various solvents. The structure of this complex was established by nuclear magnetic resonance spectra and conductivity studies.

Experimental

Chemicals.—Reagent grade solvents were freshly distilled prior to use. The stannic fluoride solutions were prepared in a drybox.

Preparation of Di-*n*-propylammonium Hexafluorostannate.—The hexafluorostannate was prepared by combining acetone solutions of stannic fluoride and di-*n*-propylammonium fluoride, refluxing the solution for 2 hr., cooling to 0°, filtering the product, and washing it several times with cold acetone to remove excess di-*n*-propylammonium fluoride. The F^{19} magnetic resonance spectrum of the SnF_6^{2-}–ethanol solution consisted of a sharp single resonance, thus indicating the absence of fluoride ion.

Anal. Calcd. for $[(C_3H_7)_2NH_2^+]_2SnF_6^{2-}$: N, 6.42. Found: N, 6.48.

Preparation of $(C_3H_7)_2NH_2^+SnF_5 \cdot B^-$ Solutions.—Stannic fluoride solutions of known concentration were added to weighed hexafluorostannate or fluoride samples. The usual concentration for n.m.r. measurements was approximately 0.5 to 1 *M* for each reactant. Equal concentrations were usually used 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-4302 B, equipped with variable temperature accessories. The spectra were calibrated in p.p.m. displacements from the external primary standard trichlorofluoromethane or trifluoroacetic acid. Electrical conductivity was measured with an Industrial Instruments Model RC-1 conductance bridge.

Results

A continuous variation study[6] of the conductivity of a mixture of stannic fluoride and di-*n*-propylammonium fluoride in absolute ethanol was performed. Figure 1 illustrates the data obtained for this system (both compounds at 0.02 *M* concentration). The mole fraction of the stannic fluoride is plotted *vs.* the "change in conductance." The latter refers to the difference in conductance readings between the actually observed value and a straight line connecting the points obtained for pure stannic fluoride and pure di-*n*-propylammonium fluoride representing no interaction. The

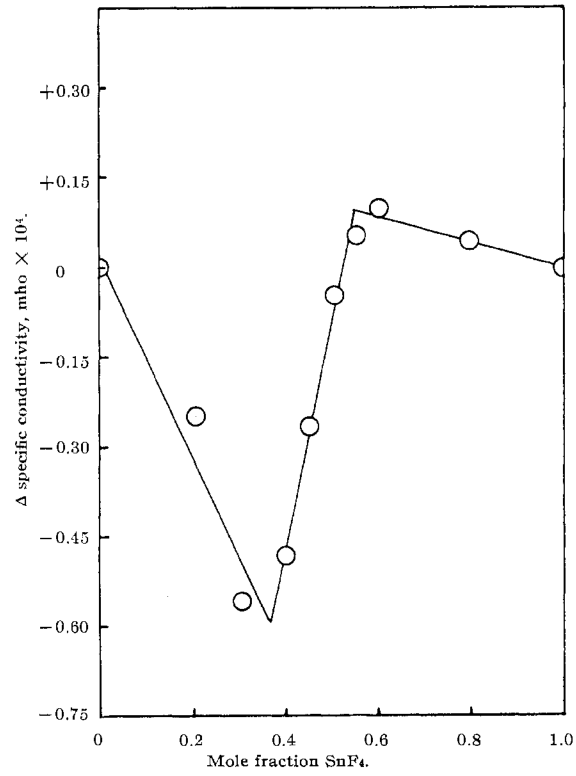

Figure 1.—A continuous variation study for the system $(n\text{-}C_3H_7)_2NH_2^+F^-$–$SnF_4$ in ethanol (sum of $SnF_4 + F^- = 0.02$ *M*).

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TABLE I

F^{19} CHEMICAL SHIFT AND COUPLING DATA

Compound	Multiplet	Chem. shift (p.p.m. external ref.)	Temp., °C.	Coupling constant, c.p.s.	
				~Sn–F[a]	F–F
SnF_6^{2-} in C_2H_5OH	Singlet	158,[b] 79[c]		1550	...
cis-$SnF_4\cdot 2C_2H_5OH$	Complex	167.5[b]	−42	1850	...
trans-$SnF_4\cdot 2C_2H_5OH$	Singlet	162[b]	−42	1800	...
$SnF_5\cdot C_2H_5OH^-$	Doublet	160[b]	−28	~1700	40
	Quintet	167		*d*	
$SnF_5\cdot CH_3OH^-$	Doublet	164.5[b]	−30	~1700	37
	Quintet	172		*d*	
$SnF_5\cdot i\text{-}C_3H_7OH^-$	Doublet	78[c]	−15	*e*	42
	Quintet[f]	83.5			
$SnF_5\cdot HCON(CH_3)_2^-$	Doublet	78.5[c]	−14	*e*	~50[g]
	Quintet	86			
$SnF_5\cdot HOCH_2CH_2OH^-$	Doublet	79[c]	−19	*e*	41
	Quintet[f]	~82			
$SnF_5\cdot ClCH_2CH_2OH^-$	Doublet[f]	81[c]	−18		
	Quintet[f]	86			

[a] The average Sn^{117}–F and Sn^{119}–F coupling constants were measured from the center of the multiplet. For all complexes except SnF_6^{2-} it was not possible to resolve the multiplets; *i.e.*, the downfield members and the upfield members. [b] Chemical shift relative to $CFCl_3$ as an external standard. [c] Chemical shift relative to CF_3COOH as an external standard. Comparison with $CFCl_3$ scale is obtained by adding 76.6. [d] These satellites are detected only for the doublet of intensity four. [e] The concentration of the complex was too low to detect the Sn^{117}–F and Sn^{119}–F splitting. [f] The multiplet was not resolved. [g] Approximate measurement on the oscilloscope.

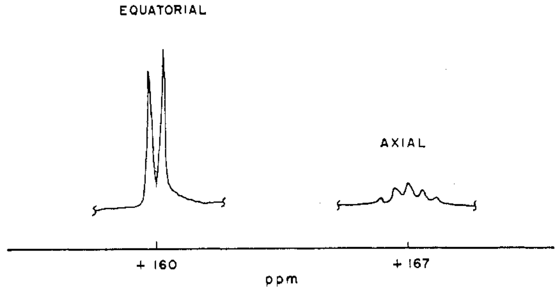

Figure 2.—F^{19} high resolution spectrum of $SnF_5\cdot C_2H_5OH^-$ at −28°. Shifts with respect to external $CFCl_3$.

points of interest are the two distinct breaks in the curve. The one corresponds to a minimum conductivity in the study and occurs at an approximate ratio of two fluorides to one stannic fluoride. This is suggestive of the formation of hexafluorostannate. The maximum conductivity occurs at the second break in the curve at an approximate ratio of one fluoride to one stannic fluoride which corresponds to the empirical formula SnF_5^-. Only a maximum was obtained in the curve of the continuous variation study between stannic fluoride and di-*n*-propylammonium hexafluorostannate. The maximum occurred at a mole ratio of one SnF_4 to one SnF_6^{2-} and is also suggestive of the formation of a complex of an empirical formula SnF_5^-.

The n.m.r. study confirmed the presence of a SnF_5^- species and indicated that a molecule of solvent occupied the sixth position in the octahedron. The predicted first-order spectrum for this type of structure would consist of a quintet for the axial fluorine and a doublet for the equatorial fluorines. The quintet to doublet ratio would be 1 to 4. The multiplets for the ethanol complex are shown in Figure 2 and they correspond to the criteria for the octahedral complex. Nuclear magnetic resonance data for the fluorostannate complexes and some of the reactants are given in Table I. After the F^{19} n.m.r. spectra were recorded for the various pentafluorostannate complexes, excess fluoride was added to each solution and the $SnF_5\cdot B^-$ complex was converted to hexafluorostannate. The chemical shift for hexafluorostannate in each solvent was identical with that obtained when a sample of di-*n*-propylammonium hexafluorostannate was added to the respective solvents.

Discussion

Group IV-A and IV-B metal halides react with most solvents so that a maximum degree of coordination is obtained. It has been shown that titanium tetrafluoride is octahedrally coordinated in various basic solvents and has a structure in which two molecules of solvent occupy *cis* positions in the octahedron.[2,7] Two triplets of equal intensity in the n.m.r. spectra provided proof of the structure assignment. This is in contrast to the spectrum of tin tetrafluoride in ethanol.[8] Both isomers of stannic fluoride diadducts are formed and are in equilibrium. The *cis* complex consists of a complex multiplet (a first-order spectrum is obtained with titanium tetrafluoride). A second-order spectrum indicates that the shielding of the fluorines in *cis*-$SnF_4\cdot 2C_2H_5OH$ is quite similar since a complex multiplet is obtained when the chemical shift difference for the fluorines is of the same order of magnitude as the F–F coupling constants. With only one fluorine *trans* to ethanol in the $SnF_5\cdot C_2H_5OH^-$ complex, the shielding of the *cis* and *trans* fluorines is sufficiently different so that a first-order spectrum is obtained. First-order spectra were found for all of the $SnF_5\cdot B^-$ complexes. In these complexes where B (base) represents methanol, ethanol, 2-propanol, N-dimethylformamide, 1,2-ethanediol, and 2-chloroethanol, the base increased the shielding of the *trans* fluorine as compared to the

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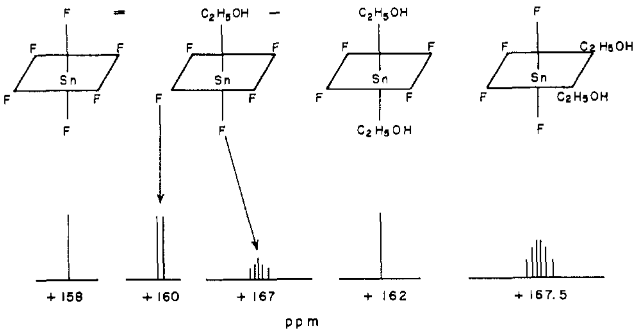

Figure 3.—Comparison of the F^{19} spectra and structures for tin complexes in ethanol. Shifts with respect to external $CFCl_3$.

cis fluorines. A comparison of the difference in chemical shifts of the axial and equatorial fluorines shows that there is a larger difference with the more basic ligands. For example, in the ethanol complex there is a difference of 7 p.p.m. in the chemical shift of the two types of fluorines as compared with 5 p.p.m. for the 2-chloroethanol complex.

It is also of interest to compare the chemical shifts of the stannic fluoride complexes in ethanol with each other (Figure 3). The shielding of the *trans* fluorine in $SnF_5 \cdot C_2H_5OH^-$ is similar to the shielding of the fluorines in *cis*-$SnF_4 \cdot 2C_2H_5OH$, whereas the shielding of the *cis* fluorines in $SnF_5 \cdot C_2H_5OH^-$ is similar to that of the fluorines in SnF_6^{2-}. The chemical shift of the fluorines in *trans*-$SnF_4 \cdot 2C_2H_5OH$ is nearest to that of the *cis* fluorines in the pentafluorostannate complex.

The F–F coupling constants for a given $MF_5 \cdot B^-$ or $MF_4 \cdot 2B$ are quite insensitive to the nature of the ligand employed. This is brought out in Table I and by previous work.[2,9] On the other hand, the $Sn^{117,119}$–F coupling constants are sensitive, and the coupling constants increased with substitution of the fluoride ion in SnF_6^{2-} with a ligand to yield $SnF_5 \cdot ROH^-$. Substitution of a second fluoride to form $SnF_4 \cdot 2C_2H_5OH$ caused a further increase in the magnitude of the coupling constant. The coupling constant for the *cis* complex is larger than that for the *trans* complex. The difference in the coupling constants reflects a difference in hybridization of the fluoride complexes. The magnitudes of the M–F coupling constants depend on the fractional p-character of the bonding hybrid of M, since the p-component of the hybrid can couple with the 2p-orbital of fluorine to yield splitting.[10]

The F^{19} spectra of the $SnF_5 \cdot B^-$ complexes were found to be markedly temperature dependent. Above 0° rapid exchange resulted in the loss of fine structure (in the cases where it was possible to resolve the spectra). Since the complexes are in excess base, it seems probable that the temperature dependency of the F^{19} spectra is due to ligand–solvent exchange. Muetterties[7] has suggested in his studies with titanium tetrafluoride and stannic fluoride complexes that temperature effects were due to ligand exchange. Low solubilities and ligand exchange make it difficult to obtain good spectra, although it was usually possible to obtain fair resolution of the $SnF_5 \cdot B^-$ spectra by cooling the samples in the temperature range from -10 to $-50°$.

The pentafluorostannate complexes can be prepared by the addition of either fluoride ion or hexafluorostannate ion to a solution of stannic fluoride. The formation of $SnF_5 \cdot B^-$ depends strongly on the nature of the solvent, as in the case of acetone, acetonitrile, and nitromethane higher fluoride complexes of undetermined composition are formed. The same observation was made in the preparation of pentafluorotitanates.[2] The solvent needs to be a strong enough base to prevent the fluorine bridging and formation of polymeric fluoride complexes.

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