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AFML-TR-71-224

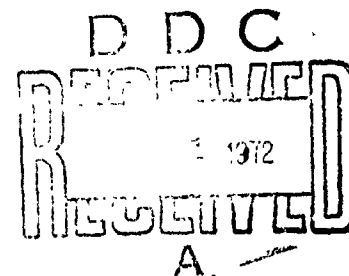
FLUORINE-19 NUCLEAR MAGNETIC RESONANCE

RONALD O. RAGSDALE

UNIVERSITY OF UTAH

TECHNICAL REPORT AFML-TR-71-224

DECEMBER 1971



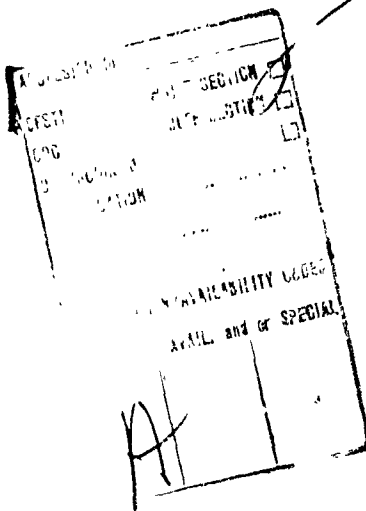
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UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) University of Utah Salt Lake City, Utah		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE FLUORINE-19 NUCLEAR MAGNETIC RESONANCE		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report - March 1969 to June 1971		
5. AUTHOR(S) (First name, middle initial, last name) Ronald O. Ragsdale		
6. REPORT DATE	7a. TOTAL NO. OF PAGES 49	7b. NO. OF REFS 41
8a. CONTRACT OR GRANT NO. F33615-69-C-1016	9a. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO. 7367		
c. Task No. 736702	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFML-TR-71-224	
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory (LPA) Wright-Patterson AFB, Ohio 45433
13. ABSTRACT Several series of diadducts of titanium tetrafluoride were studied with high resolution fluorine-19 nuclear magnetic resonance spectroscopy. These consisted of studies with aromatic amine oxides, amides and sulfoxides as bases. Mixed diadducts of TiF_4 with the aromatic amine oxides and tetramethylurea as a reference base were also investigated. Both basicity and steric interactions were found to affect the ^{19}F chemical shifts. Some aromatic amine oxide, amide and sulfoxide adducts with tin tetrafluoride were also investigated. <u>Cis</u> and <u>trans</u> isomers were found for all complexes in which the donor molecule was small. With large bulky ligands only the <u>trans</u> isomers were detected. First order spectra for the <u>cis</u> adducts were measured when the donor molecule was a very weak base. Only second order spectra were found for $SnF_4 \cdot 2D$ complexes formed with the relatively strong bases. The ^{19}F chemical shifts, in contrast to TiF_4 data, were found to be relatively insensitive to the basicity of the donor molecules.		

DD FORM 1473
1 NOV 65

UNCLASSIFIED

Security Classification

UNCLASSIFIED
Security Classification

14	KEY WORDS		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nuclear Magnetic Resonance						
Fluorine-19						
Titanium Tetrafluoride						

AFML-TR-71-224

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RONALD O. RAGSDALE

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FOREWORD

This report was prepared by Professor Ronald C. Ragsdale of the Department of Chemistry, University of Utah, Salt Lake City, Utah. The work was initiated under Project No. 7367, "Research on Characterization and Properties of Materials for Air Force Systems," Task 736702, "Physical-Chemical Methods for Materials Analysis."

This report was prepared by Professor Ragsdale under University of Utah Contract F33615-69-C-1016. Dr. Daniel S. Dyer of the Analytical Branch, Materials Physics Division, Air Force Materials Laboratory, was the Project Engineer.

The report covers work conducted from March 1969 to June 1971. It was submitted by the author in June 1971.

This technical report has been reviewed and is approved.


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Air Force Materials Laboratory

ABSTRACT

Several series of diadducts of titanium tetrafluoride were studied with high-resolution fluorine-19 nuclear magnetic resonance spectroscopy. These consisted of studies with aromatic amine oxides, amides and sulfoxides as bases. Mixed diadducts of TiF_4 with the aromatic amine oxides and tetramethylurea as a reference base were also investigated. Both basicity and steric interactions were found to affect the ^{19}F chemical shifts.

Some aromatic amine oxide, amide and sulfoxide adducts with tin tetrafluoride were also investigated. Cis and trans isomers were found for all complexes in which the donor molecule was small. With large bulky ligands only the trans isomers were detected. First order spectra for the cis adduct were measured when the donor molecule was a very weak base. Only second order spectra were found for $\text{SnF}_4 \cdot 2\text{D}$ complexes formed with the relatively strong bases. The ^{19}F chemical shifts, in contrast to TiF_4 data, were found to be relatively insensitive to the basicity of the donor molecules.

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SECTION I

INTRODUCTION

Previous Fluorine-19 nuclear magnetic resonance studies of the $\text{TiF}_4 \cdot 2\text{D}$ complexes have involved the efforts of Muetterties¹ and Ragsdale and co-workers.²⁻⁹ The data reported by Muetterties contained chemical shift values for only one complex ($\text{TiF}_4 \cdot 2\text{C}_2\text{H}_5\text{OH}$). In contrast the more recent studies included cis and trans isomerism^{4,9} chemical shifts of the diadducts² and the mixed diadducts³, fluorine-fluorine coupling constants⁶, the mechanism of fluorine-19 exchange in the $\text{TiF}_4 \cdot 2\text{D}$ complexes⁵ and the hydrolysis of titanium tetrafluoride.⁷

Even though a number of ^{19}F nmr investigations have been made on the $\text{TiF}_4 \cdot 2\text{D}$ complexes both quantitative and qualitative information are lacking on the cis and trans isomers. No systematic studies of the chemical shifts of the $\text{TiF}_4 \cdot 2\text{D}$ complexes had been carried out. Also only one series of mixed diadducts³ ($\text{TiF}_4 \cdot \text{IMA}, 4\text{ZC}_5\text{H}_4\text{NO}$) had been studied. Essentially one chemical shifts for $\text{TiF}_4 \cdot 2\text{D}$ complexes involved some aromatic amine oxide adducts.^{4,9} In this report we present a further study of cis and trans isomerism of $\text{TiF}_4 \cdot 2\text{D}$ complexes and the chemical shifts for both the diadducts and mixed diadducts.

In contrast to the literature on the TiF_4 complexes little work has been done with SnF_4 . The chemical shifts of only two neutral adducts of SnF_4 have been reported.^{10,11} One of the reasons that studies of SnF_4 are lacking is that the complexes which are formed have limited solubility. Another possible reason is that some of the

spectra are difficult to interpret as it appears that a number of different species are present. Also both first¹⁰ and second¹¹ order spectra have been noted. Studies of $\text{SnF}_4 \cdot 2\text{D}$ complexes, cis and trans isomerism, first and second order ^{19}F spectra, chemical shifts, and coupling constants, are presented in this report. The data for the SnF_4 adducts are compared and contrasted to those for the TiF_4 adducts.

SECTION II

EXPERIMENTAL PROCEDURE

1. INSTRUMENTATION

The fluorine-19 nmr spectra were obtained with a Varian A-56/60A spectrometer operating at 56.4 MHz. The spectrometer was equipped with the Varian V-6057 variable temperature accessory.

An internal reference, CFCl_3 , was used in all samples. Each sample was placed in a thin-walled 5 mm OD sample tube. A tight fitting plastic cap was secured over the mouth of the tube, and the nrm spectrum was obtained as quickly as possible. The spectra were obtained at -40°C for all TiF_4 complexes and some SnF_4 complexes. The nmr spectra for some tin adducts were measured at room temperature.

2. MATERIALS

The solvent chloroacetonitrile was purified by distillation. Titanium tetrafluoride was obtained from Allied Chemical Corp. and used without further purification. Most of the $\text{TiF}_4 \cdot 2\text{D}$ (D = donor) adducts which were isolated were prepared by addition of ethanolic solutions of the respective donor molecules to the TiF_4 solutions in absolute ethanol. If precipitation did not occur immediately some anhydrous diethyl ether was added to induce precipitation. The precipitates were filtered and then washed with anhydrous diethyl ether and dried in vacuo.

Tin tetrafluoride was obtained from Clark-Mahoning Co. and used without further purification. The addition compounds were prepared by the addition of ethanolic tin tetrafluoride to a solution

of the ligand in ethanol or methylene chloride. In general the product precipitated immediately. The precipitates were washed with anhydrous diethyl ether and dried in vacuo.

All para-substituted pyridine 1-oxides except 4-chloro- and 4-bromopyridine 1-oxides and methyl pyridine-4-carboxylate 1-oxide were obtained from Aldrich Chemical Company. Pyridine 1-oxide was purified by vacuum sublimation. 4-Methoxypyridine 1-oxide was purified by recrystallization from an acetone-ether solvent. The remaining commercial pyridine 1-oxides were used with no further purification. 4-Chloro- and 4-bromopyridine 1-oxides were prepared from the 4-nitro compound by the method of Ochiai.¹² Methyl pyridine-4-carboxylate, 2-methylpyridine, 2-ethylpyridine, 2,4-dimethylpyridine, 2,6-dimethylpyridine, and 3,5-dimethylpyridine were obtained from Aldrich Chemical Co. These compounds were oxidized to the respective substituted pyridine 1-oxides with H_2O_2 in glacial acetic acid.¹³

Quinoline 1-oxide was prepared once by the method of Ochiai¹² and subsequently was obtained from Aldrich Chemical Co. The 4-chloro, -methyl, and -nitro derivatives were prepared by the method of Ochiai.¹² The 4-methoxy was prepared according to Tanaka.¹⁴ 6-Methoxyquinoline N-oxide was obtained from Aldrich Chemical Company. 6-Methylquinoline N-oxide was prepared from 6-methylquinoline (Eastman) by the method of Colonna and Risaliti.¹⁵ 6-Bromo, 6-chloro-, and 6-nitroquinoline N-oxides were prepared from the corresponding quinolines (Aldrich Chemical Company) by the method of Bachman and Cooper.¹⁶

All the primary and tertiary amides were obtained from Eastman Organic Chemicals. All the sulfoxides were acquired from Aldrich Chemical Co. (except dimethyl sulfoxide which was obtained from Eastman Organic Chemicals).

3. SAMPLE PREPARATION

The nmr samples were prepared in a glove bag under an atmosphere of dry nitrogen. The $\text{MF}_4 \cdot 2\text{D}$ samples were prepared either by dissolving the metal fluoride in an excess of organic donor, or, when possible by isolating the diadduct and dissolving it in chloroacetonitrile. The $\text{TiF}_4 \cdot \text{D}, \text{D}'$ samples were prepared by adding weighed quantities of the appropriate aromatic amine oxide to $\text{TiF}_4 \cdot 2\text{TMU}$ (TMU = tetramethylurea) -chloroacetonitrile solutions. The nmr samples were approximately 2 molar.

4. ANALYSES

Representative compounds were analyzed by using excess Ti(III) to reduce the amine oxide to the amine. The excess Ti(III) is destroyed with excess $\text{Cr}_2\text{O}_7^{=}$ which is then back titrated with Ti(III)^{17} . These analyses confirmed the formation of 2:1 adducts. The similarity of the ^{19}F nmr and infrared spectra of all the complexes supports a 2:1 stoichiometry. These results are in agreement with previous work^{1,9,11} where 2:1 adducts of SnF_4 and TiF_4 were formed with oxygen donors.

SECTION III

COMPLEXES OF TITANIUM TETRAFLUORIDE

1. COMPLEXES WITH AROMATIC AMINE OXIDES

The donor properties of various aromatic amine oxides have recently been reviewed.^{18,19} It has been demonstrated that the 4-substituted pyridine 1-oxides and the 4-substituted quinoline 1-oxide systems are similar in their interaction toward some transition metals^{19,20} and also toward phenol.^{21,22} Enthalpies of reaction of pyridine 1-oxides and quinoline 1-oxides with $\text{VO}(\text{acac})_2$ have shown that there is a steric difference.^{23,24}

The aromatic amine oxides mentioned above together with 6-substituted quinoline 1-oxides form two to one addition compounds with the Lewis acid, titanium tetrafluoride. Previous infrared studies by Dickson, et al²⁵ have shown that for the 4-substituted pyridine 1-oxide addition compounds a linear correlation exists between $\bar{\nu}_{\text{Ti-O}}$ and the appropriate substituent constants. A similar study²⁶ with the 4-substituted quinoline 1-oxide adducts of both titanium tetrafluoride and tin tetrafluoride showed no correlation between $\bar{\nu}_{\text{M-O}}$ and the σ_{PyNO} constants.¹⁹ In contrast a linear correlation between ^{19}F chemical shift and substituent constants was observed for some mixed diadducts of 4-substituted pyridine 1-oxide with titanium tetrafluoride.³

In this phase of our work the ^{19}F nmr spectra of three series of aromatic amine oxide- TiF_4 diadducts were measured and correlations between the chemical shifts and the σ_{PyNO} substituent constants were investigated. In previous studies geometrical isomers were found for some TiF_4 diadducts.⁹ Therefore, we wished to determine the effect

various ligands had upon the geometry of the complexes and thus gain some knowledge of the factors influencing their stereochemistry. Lastly this study will allow a comparison of the relative donor ability of the pyridine 1-oxide and quinoline 1-oxide systems toward a d^0 acceptor.

As noted earlier there are two possible geometrical isomers for $TiF_4 \cdot 2D$ compounds. The cis isomer has two different fluorine environments each containing two fluorines. Two fluorines are cis to both ligands (F_α) and trans to the other ligand (F_β) (see Figure 1). A first order ^{19}F nmr spectrum of this isomer will contain two 1:2:1 triplets of equal intensity. In the trans isomer all of the fluorines will be equivalent, cis to both ligands. This isomer will give rise to a ^{19}F nmr spectrum containing only a single resonance.

In Table I are listed the ^{19}F chemical shifts for the complexes which were studied. All of the spectra contained two equal intensity triplets indicative of the cis isomer, while some also contained a singlet in the region of the upfield triplet. This singlet, indicative of the trans isomer, was observed only for some of the 4- and 6-substituted quinoline 1-oxides. The ^{19}F - ^{19}F coupling constants are also tabulated in the Table. Within a given system the coupling constants do not vary with changing substituents.

In Figure 1 the ^{19}F chemical shift values are plotted versus the σ_{PyNO} substituent constants for the 4-substituted pyridine 1-oxides and the 4-substituted quinoline 1-oxides. There are several points of interest here. First there is a linear correlation between the chemical shift and σ_{PyNO} for both sets of triplets and the singlet. Secondly for the cis

Figure 1. Correlation plot of the σ_{PyNO} constants versus the chemical shifts for the fluorines of cis and trans $\text{TiF}_4 \cdot 2\text{D}$ where D represents either 4-substituted pyridine 1-oxides or 4-substituted quinoline 1-oxides.

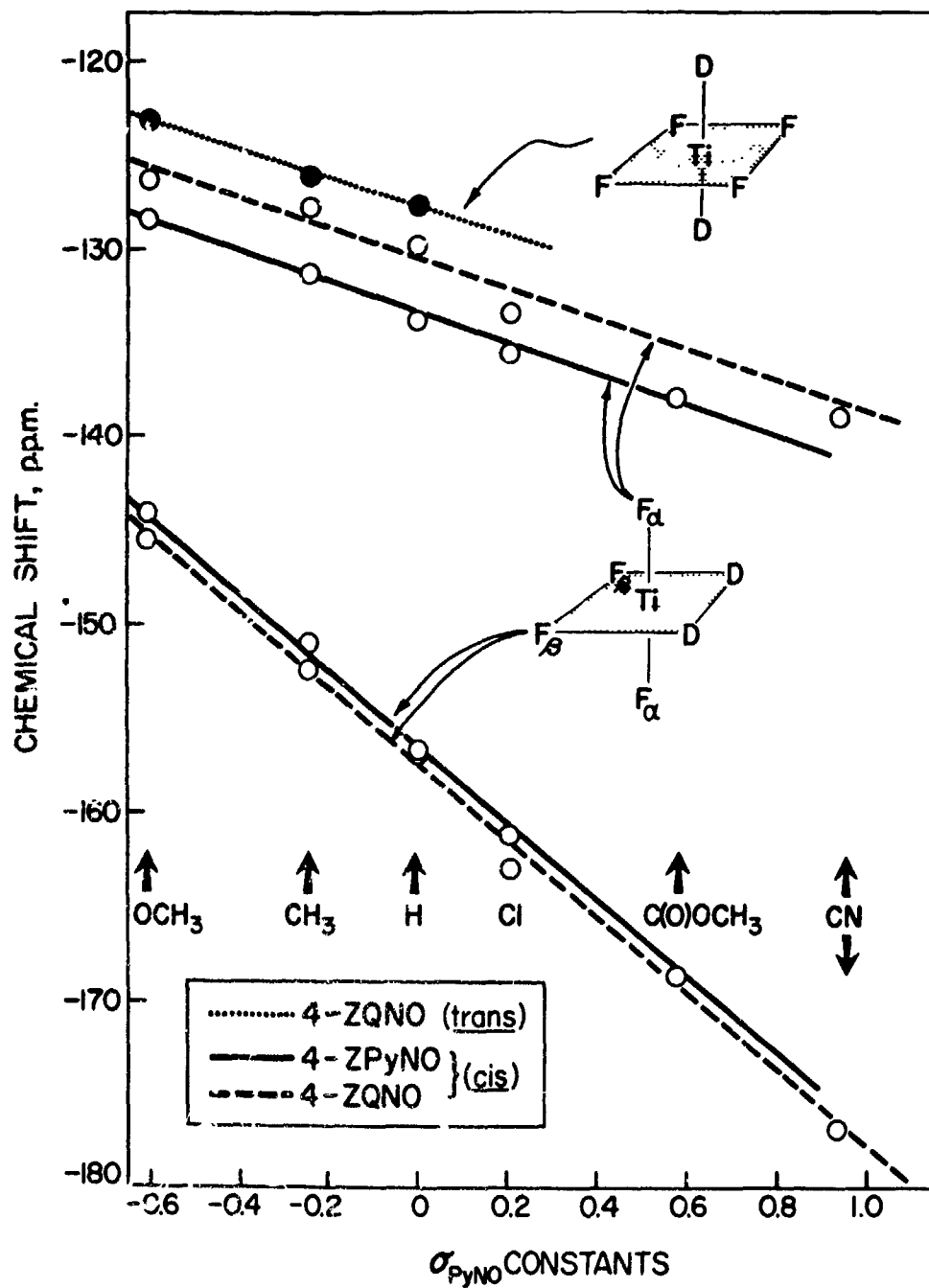


TABLE I

^{19}F nmr Data^a for the Diadducts of TiF_4 with
Various Aromatic Amine Oxides in Chloroacetonitrile

Donor Molecule	Chemical Shifts ^b (ppm)			%trans ^c	^{19}F - ^{19}F ^d Coupling Constants (cps)
	Singlet	Upfield Triplet	Downfield Triplet		
4ZPyNO					
OCH ₃		-128.4	-144.1		35
CH ₃		-131.3	-151.0		35
H		-133.9	-156.9		35
Cl		-135.7	-161.1		34
CH ₃ OC(O)		-138.0	-168.6		34
4ZQNO					
OCH ₃	-123.2	-126.3	-145.5	20.0	37
CH ₃	-126.1	-127.8	-152.4	6.0	37
H	-117.7	-129.9	-156.6	8.0	36
Cl		-133.5	-163.0		36
CN		-138.9	-176.9		36
6ZQNO					
OCH ₃	-128.3	-130.5	-156.3	8.0	38
CH ₃	-128.9	-131.2	-156.7	9.0	36
Cl	-131.5	-133.2	-162.0	3.0	36
Br		-133.0	-162.5		37

^a -40°C

^b ±0.5 ppm

^c ±1.0%

^d ±1 cps

complexes the slope of the line through the upfield triplets (F_{α} type fluorines) is different than the slope of the line through the downfield triplets (F_{β} fluorines). However, the slope of the line for the F_{α} fluorines in the pyridine 1-oxides is the same as the slope for the F_{α} fluorines in the quinoline 1-oxides. A similar trend was noted for the F_{β} fluorines. Thirdly the slope of the line for the trans isomer was very nearly the same as that for the F_{α} fluorines. Lastly there is essentially no difference between the F_{β} fluorines in pyridine and quinoline 1-oxides. However, the F_{α} fluorine for the two systems are separated by approximately 3 ppm with the quinoline 1-oxides being upfield from the pyridine 1-oxides.

It is suggested from a consideration of the above nmr data that the primary difference between the two systems is steric. The 4-substituted pyridine 1-oxides do not form the trans isomer while some of the 4- and 6-substituted quinoline 1-oxides do. There is not a great deal of difference in relative basicity for these two systems²². The F_{α} fluorines cis to both ligands are the fluorines which one would expect to be affected most by changes in the bulkiness of the ligand. The average separation of the F_{α} fluorines is six times the separation of the F_{β} fluorines. The increase in coupling constant is going from the pyridine 1-oxide to the quinoline 1-oxide system is also indicative of a larger steric effect.⁶

Since titanium (IV) is a d^0 case there are low lying unfilled d orbitals with which the ligands, especially fluorine, may π bond. If fluorine to metal π bonding occurs the fluorine will experience a paramagnetic shift which moves the fluorine resonances downfield.²⁷ As the amount of π bonding increases this shift will become larger.

Previous work has suggested that the cis isomer will maximize the π bonding in these compounds.^{2f} In the cis isomer the F_{β} fluorine competes with an oxygen donor trans to it for a given π bonding orbital whereas the F_{α} fluorine competes with another fluorine. One notes that in the trans isomer where the fluorines are trans to other fluorines that the resonance occurs upfield from the triplet for the F_{α} fluorines. This seems to indicate less fluorine to metal π bonding in the trans isomer. From this argument the chemical shifts for the F_{α} fluorines should be much less sensitive to basicity changes than the F_{β} fluorines. As the base strength of the ligand decreases, its ability to compete with a fluorine for a π bonding orbital will decrease. This will allow more fluorine to metal π bonding in the F_{β} fluorines and thus a greater downfield shift.

Since the F_{β} fluorines are more sensitive to changes in the π bonding ability of the ligand, we suggest that the π donating ability of the pyridine 1-oxides and quinoline 1-oxides is almost identical. In contrast nickel and cobalt complexes which have metal to ligand π bonding, the quinoline 1-oxides were found to be better π acceptors than pyridine 1-oxides.²⁰ Perhaps the explanation for this difference lies in the fact that in accepting π electron density the quinoline 1-oxide system has an extra ring in which to delocalize the electron density. However, when donating electron density this extra ring system does not have much effect on the electron density in the N-O bond, since the relative basicities of the quinoline 1-oxides and pyridine 1-oxides are quite similar.²²

In the cases where the trans isomer is formed the largest amount is found with the strongest base. This is in agreement with previous work.⁹ In all cases, however, the amount of trans isomer formed is less than the 25% expected from statistical considerations. This is probably a result of the stabilization of the cis configuration due to maximization of π bonding in this isomer.

The quinoline 1-oxides substituted in the 6-position fall into two groups. The methoxy and methyl complexes are in one class and the chloro and bromo are in the other. The resonance effect of the sixth position proceeds to a position one atom removed from the nitrogen in the quinoline 1-oxides. Since the methoxy and methyl substituents act primarily by a resonance effect, moving these substituents from the 4 to the 6 position should give a ligand with the same donor properties as quinoline 1-oxide. A comparison of the data in Table I bears this out. The chloro and bromo substituents act primarily by an inductive effect and moving them from the 4 to the 6 position will decrease this effect slightly since they are effectively one bond further removed from the nitrogen. It appears from the data that the 6-Cl and 6-Br are nearly identical to the 4-Cl and are different than the unsubstituted quinoline 1-oxide. This seems to indicate that the inductive effect is still quite strong from the 6 position.

2. COMPLEXES WITH AMIDES

A number of papers have been published describing various coordination complexes with primary,^{29,30} secondary³¹⁻³³ and tertiary³²⁻³⁴ amides functioning as monodentate ligands. In contrast to the large number of coordination compounds formed with the amides only the dimethylformamide,^{1,35} dimethylacetamide,^{1,3} diethylformamide⁵ and diethylacetamide³⁵ diadducts with TiF_4 have been reported.

It is of interest to compare the chemical shifts for the amide complexes with those formed with other bases, since the amides as a group are quite weak bases. The pK_a values as for the aliphatic amides are ~ -1 .³⁶ In contrast to the amides the aromatic amine oxides as a group are stronger bases with many of them having pK_a values greater than 1.³⁷

In Table II the nmr data for 17 different amides with titanium tetrafluoride are reported. First order spectra, two triplets of equal intensity, provided proof for the cis isomer. The trans isomer was detected with the two larger amides, N, N-di-n-butylpropionamide and N, N-diphenylacetamide. This result is in agreement with earlier work where the trans isomer was formed with the more bulky ligands.⁹

In the series of adducts with the N, N-dimethyl- and N, N-diethyl-amides the ^{19}F - ^{19}F coupling constants increased with an increase in the size of the amide. The increase in the magnitude of the coupling constant is consistent with a greater steric interaction between the amides and the cis fluorines.⁹ (As noted in Table II.)

TABLE II
¹⁹F NMR Data for the Diadducts of
 TiF₄ with Various Amides in Chloroacetonitrile at -40°

Donor Molecule	Chemical Shifts ^a (ppm)			Coupling Constant ^b , cps	
	Trans	Cis		¹⁹ F - ¹⁹ F	
	Singlet	Upfield Triplet	Downfield Triplet	Δδ ^c	
acetamide		-126.9	-193.9	67	42
propionamide		-126.1	-194.5	68	d
butyramide		-125.0	-193.4	58	42
isobutyramide		-122.8	-192.9	70	d
trimethylacetamide		-123.6	-191.6	68	42
N,N-dimethylformamide ³⁵		-137.0	-189.3	52	38
N,N-dimethylacetamide ³⁵		-135.3	-187.4	52	39
N,N-dimethylpropionamide		-129.6	-188.0	59	42
N,N-dimethylbutyramide		-127.8	-187.4	60	45
N,N-diethylformamide		-136.8	-188.1	51	38
N,N-diethylacetamide		-134.0	-186.9	53	42
N,N-diethylpropionamide		-133.7	-187.9	54	43
N,N-diethylbutyramide		-133.2	-184.9	52	45
N,N-di-n-butylformamide		-137.3	-194.0	57	d
N,N-di-n-butylpropionamide	-136.2	-143.7	-191.0	47	d
N,N-diphenylformamide		-141.8	-220.3	78	d
N,N-diphenylacetamide	-136.8	-142.4	-218.4	76	d

^a Relative to internal CFCl₃ as a reference, + 0.5 ppm.

^b + 1 cps

^c Chemical shift of the upfield triplet minus the downfield triplet

^d Could not measure due to exchange broadening

The coupling constants could not be measured for a number of the adducts due to exchange broadening. The more rapid exchange for some of the amide complexes in contrast to other adducts³⁸ at -40° is probably due to the weak bases.

Examining the chemical shifts that are reported in Table II, there are several points of interest. Except for the N, N-diphenyl-substituted amides the chemical shift values for the downfield triplet have a range of less than 10 ppm. Since the downfield triplet has been shown to have a greater sensitivity to the basicity of the ligand,³ this indicates that the base strength of the various amides is about the same. The downfield shift for the N, N diphenyl-substituted amides could be the result of a great decrease in basicity since the phenyl substituents are strong electron withdrawing groups. The upfield triplet has been shown to be less sensitive to base strength³ and more sensitive to a steric interaction (see preceding section) than the downfield triplet. One would expect the upfield triplet to be more sensitive to the size of the donor molecule since these fluorines are adjacent to the donor molecules. In general as the size of the ligand increased the chemical shift for the upfield triplet shifted upfield.

Perhaps the best indication of the donor ability of the amides toward TiF_4 could be found by taking the difference between the chemical shifts of the upfield and downfield triplets. This difference is reported in Table II. The results break into three groups. The values for the N, N-dialkyl substituted amides is ~ 54 ppm., the primary amides is ~ 68 ppm. and the diphenyl substituted amides is ~ 77 ppm. The relative basicity of the amides towards TiF_4 is N, N-dialkyl substituted amides > primary amides > N, N-diphenyl

substituted amides.

3. COMPLEXES WITH SULFOXIDES

The sulfoxides are quite weak bases, as a result there is much disagreement on the basic strength of the most common sulfoxides.³⁹ The sulfoxides used in this study have pK_a values around -2.³⁹ As a group they have basicities similar to that of the amides. It is of interest to compare the sulfoxide results with those of the amides. The dimethylsulfoxide complex was first prepared by Muetterties¹ and the ^{19}F nmr data were obtained by Dyer.³⁵

In this study we have investigated the reaction of 8 sulfoxides with titanium tetrafluoride. The ^{19}F nmr data are given in Table III. From the chemical shift differences, $\Delta\delta$, there is a fair difference in the relative basicity of the aliphatic sulfoxides and the aromatic substituted sulfoxides. This difference is especially noted when the chemical shifts of the downfield triplets are compared. It is also interesting to compare the chemical shift differences for the downfield triplets of p-chloro and p-methylphenylsulfoxide with that for 4-chloro- and 4-methylpyridine 1-oxide, 11.8 ppm and 10.1 ppm respectively. Direct conjugation between the substituent and the donor oxygen atom is possible with the 4-substituted pyridine 1-oxides whereas it is not possible with the di-p-substituted phenylsulfoxides. From our limited data it appears that two substituted phenyl groups have about the same effect as the 4-substituent on the pyridine 1-oxide. The aliphatic sulfoxides have a relative basicity towards titanium tetrafluoride which is near to that of the tertiary amides since the $\Delta\delta$ values are quite similar. Also it is interesting to note that more rapid exchange

processes occurred with the aromatic sulfoxides than with the aliphatic sulfoxides since the coupling constants could not be measured with the former ligands.

TABLE III

^{19}F NMR Data for the Diadducts of
 TiF_4 with Various Sulfoxides in Chloroacetonitrile at -40°

Donor Molecule	Chemical Shifts ^a (ppm)			Coupling Constant ^b , cps	
	Trans	Cis		¹⁹ F - ¹⁹ F	
	Singlet	Upfield Triplet	Downfield Triplet	$\Delta\delta^c$	
dimethylsulfoxide ³⁵		-133.5	-182.7	49	37
di-n-propylsulfoxide		-135.6	-178.8	43	36
di-n-butylsulfoxide		-133.5	-178.4	45	38
tetramethylenesulfoxide ^d		-133.1	-177.5	44	38
dibenzylsulfoxide	-134.2	-142.1	-215.9	74	e
diphenylsulfoxide	-139.1	-144.2	-221.2	77	e
di-p-chlorophenylsulfoxide	-140.9	-144.6	-222.7	78	e
di-p-methylphenylsulfoxide	-135.6	-142.2	-210.9	69	e

^aRelative to internal CFCl_3 as a reference, ± 0.5 ppm

^b ± 1 cps

^cChemical shift of the upfield triplet minus the downfield triplet

^dMeasured at -20°

^eCould not measure due to exchange broadening

4. MIXED ADDUCTS OF TITANIUM TETRAFLUORIDE

Recently an ^{19}F nmr study of some mixed adducts of TiF_4 ($\text{TiF}_4 \cdot \text{DD}'$) complexes was reported.³ A series of $\text{TiF}_4 \cdot \text{DD}'$ complexes was studied, where D is N,N-dimethylacetamide and D' is a para-substituted pyridine 1-oxide. Also three additional mixed diadducts of TiF_4 were reported.⁸

A fluorine-19 nmr study of $\text{TiF}_4 \cdot 2\text{TMU}$, $\text{Z-C}_5\text{H}_4\text{NO}$ (TMU = 1,1,3,3 tetramethylurea and Z = CN, Cl, 2CH_3 , 4CH_3 , $2,4(\text{CH}_3)_2$, OCH_3 , $2,6(\text{CH}_3)_2$, NO_2 , H) solutions was conducted. The experimental evidence indicates that $\text{TiF}_4 \cdot 2\text{TMU}$ undergoes an exchange reaction in which one or more of the TMU molecules is replaced by a substituted pyridine 1-oxide.

The nmr spectra were run on samples which were of approximately 2 molar concentration with respect to both $\text{TiF}_4 \cdot 2\text{TMU}$ and the substituted pyridine 1-oxide in chloroacetonitrile. The spectra of all the systems, except where Z = $2,6-(\text{CH}_3)_2$, consisted of two 1:2:1 equal-intensity triplets assignable to cis- $\text{TiF}_4 \cdot 2\text{TMU}$, two 1:2:1 triplets due to cis- $\text{TiF}_4 \cdot 2(\text{Z-C}_5\text{H}_4\text{NO})$, and a doublet of doublets and two doublets of 1:2:1 triplets assignable to cis- $\text{TiF}_4 \cdot (\text{TMU})(\text{Z-C}_5\text{H}_4\text{NO})$. See Figure 2 for a representative spectrum. In Figure 3 a spectrum is shown for the reaction mixture of $\text{TiF}_4 \cdot 2\text{TMU}$ plus 4- $\text{NO}_2\text{C}_5\text{H}_4\text{NO}$. No resonances are observed for cis- $\text{TiF}_4 \cdot 2(4\text{-NO}_2\text{C}_5\text{H}_4\text{NO})$ because of its low solubility. In some cases, other trans-complexes were also observed. Where Z = $2,6(\text{CH}_3)_2$, two 1:2:1 triplets and singlet attributable to cis- $\text{TiF}_4 \cdot 2\text{TMU}$ and trans- $\text{TiF}_4 \cdot 2\text{TMU}$, respectively were observed. However, only singlets were found for both $\text{TiF}_4 \cdot 2,6(\text{CH}_3)_2\text{-C}_5\text{H}_3\text{NO}$ and

$\text{TiF}_4 \cdot 2,6(\text{CH}_3)_2\text{-C}_5\text{H}_3\text{NO}$ (TMU), indicating each has the trans-configuration. These results are shown in Figure 4.

In the mixed diadduct for the cis isomer the doublet of doublets has twice the area of either of the doublets of triplets. These spectra are typical of an A_2MX system and clearly indicate a structure in which there are two equivalent and two nonequivalent fluorine atoms. The only structure consistent with the data is a $\text{TiF}_4 \cdot 2D$ complex in which two nonidentical donor molecules occupy positions cis to each other in the octahedron. The upfield doublet of doublets is due to the two equivalent fluorines (F_α) which are cis to both of the donor molecules. The resonance of these two fluorines is split into a doublet of doublets by the two nonequivalent trans-fluorines, F_β and $F_{\beta'}$ (see Figure 5). The downfield peaks are due to the latter fluorines. Each of these two principal resonances is split into a triplet by the cis-fluorines and each of the triplets is further split into a doublet of triplets by the other nonequivalent trans-fluorine, F_β or $F_{\beta'}$. The nmr data are given in Tables IV and V.

The chemical shifts for the cis- and trans- fluorines are plotted versus the σ_{PyNO} substituent parameter to study the effect of the para-substituent on the chemical shift. A linear correlation was obtained for each type fluorine (Figure 5).

As we have suggested previously,³ the large perturbation produced by the substituent Z in the shielding of the fluorine, F_β , trans to 4- $\text{ZC}_5\text{H}_4\text{NO}$ in the $\text{TiF}_4 \cdot \text{DMA}$, 4- $\text{ZC}_5\text{H}_4\text{NO}$ complex is transmitted through the titanium d orbitals by a π mechanism. The progressive downfield shift in the spectra as the para substituent becomes more electron attracting is brought about by an increase in the relative amount of fluorine π donation to the titanium d orbitals.

Figure 2. ^{19}F nmr spectrum of a $\text{TiF}_4 \cdot \text{TMU}$, $2\text{-CH}_3\text{C}_5\text{H}_4\text{NO}$ solution in chloroacetonitrile at -30° . The chemical shifts are in ppm displacements from internal CFCl_3 as a reference.

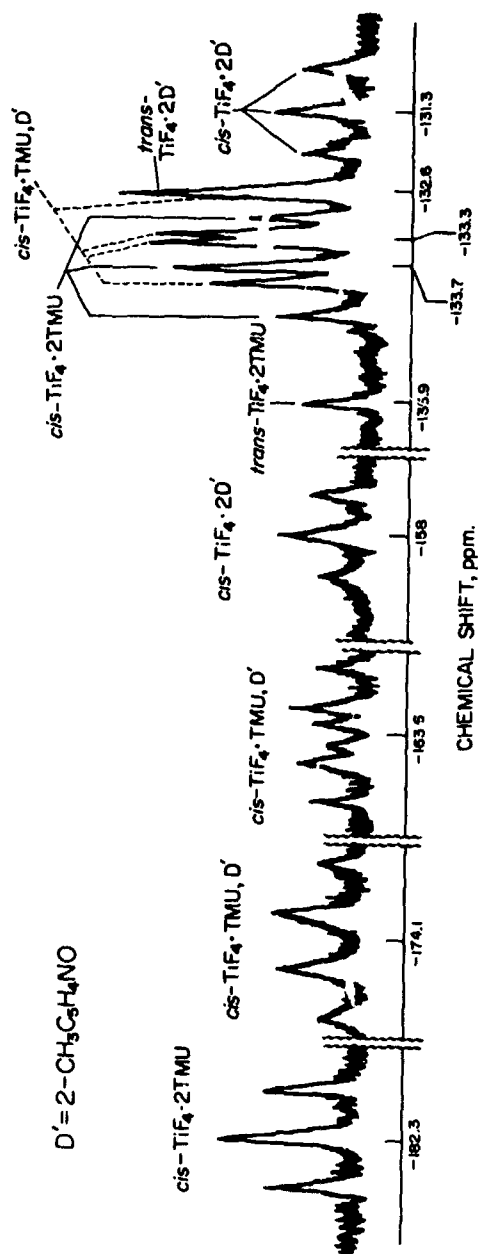


Figure 3. ^{19}F nmr spectrum of a $\text{TiF}_4 \cdot \text{TMU}$, $4\text{-NO}_2\text{C}_5\text{H}_4\text{NO}$ solution in chloroacetonitrile at -30° . The chemical shifts are in ppm displacements from internal CFCl_3 as a reference.

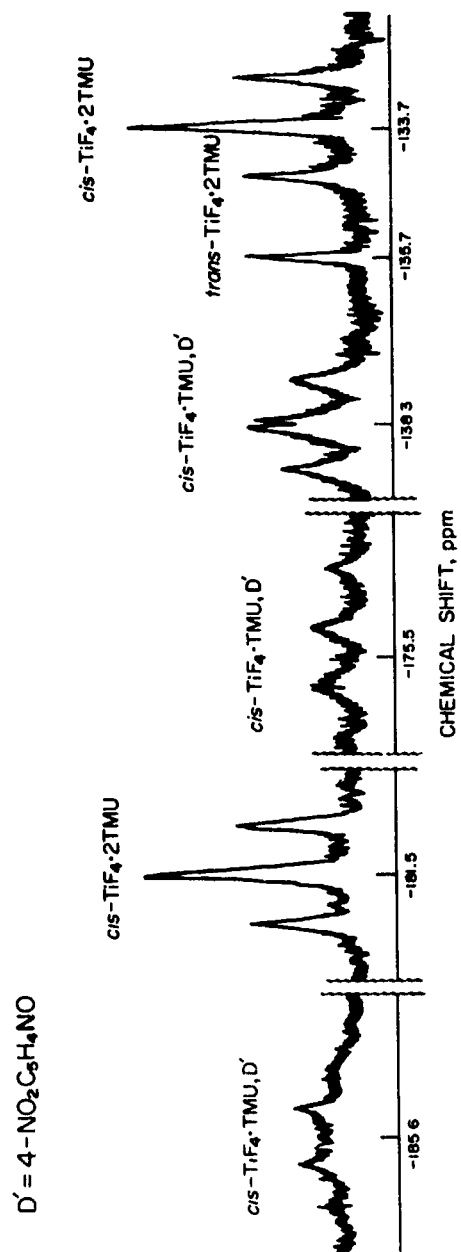


Figure 4. ^{19}F nmr spectrum of a $\text{TiF}_4 \cdot \text{TMU}$, 2,6- $(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NO}$ solution in chloroacetonitrile at -30° . The chemical shifts are in ppm displacements from internal CFCl_3 as a reference.

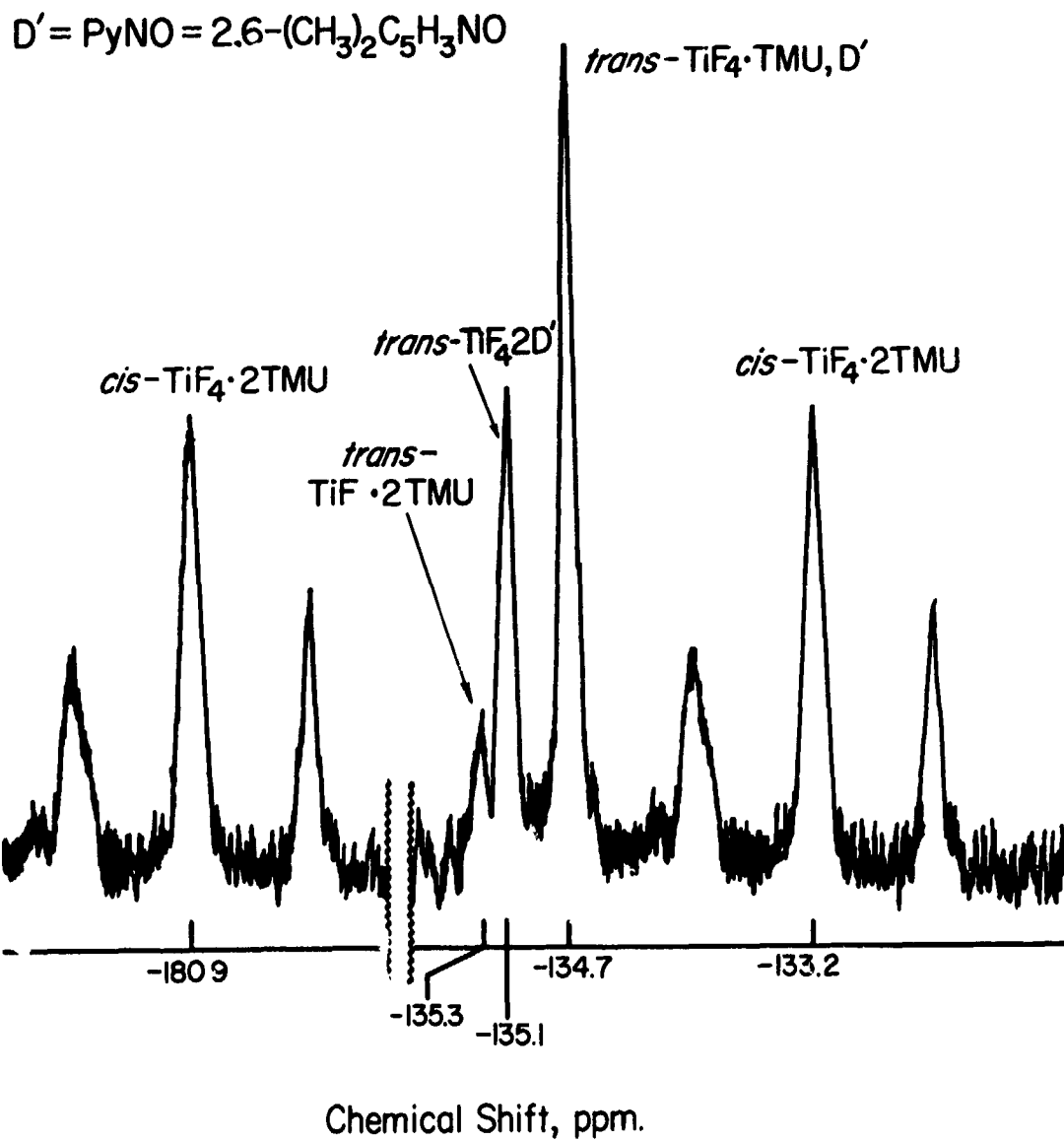


Figure 5. Correlation plot of the chemical shifts for F_α , F_β and F_β' , vs. the σ_{PyNO} substituent parameters.

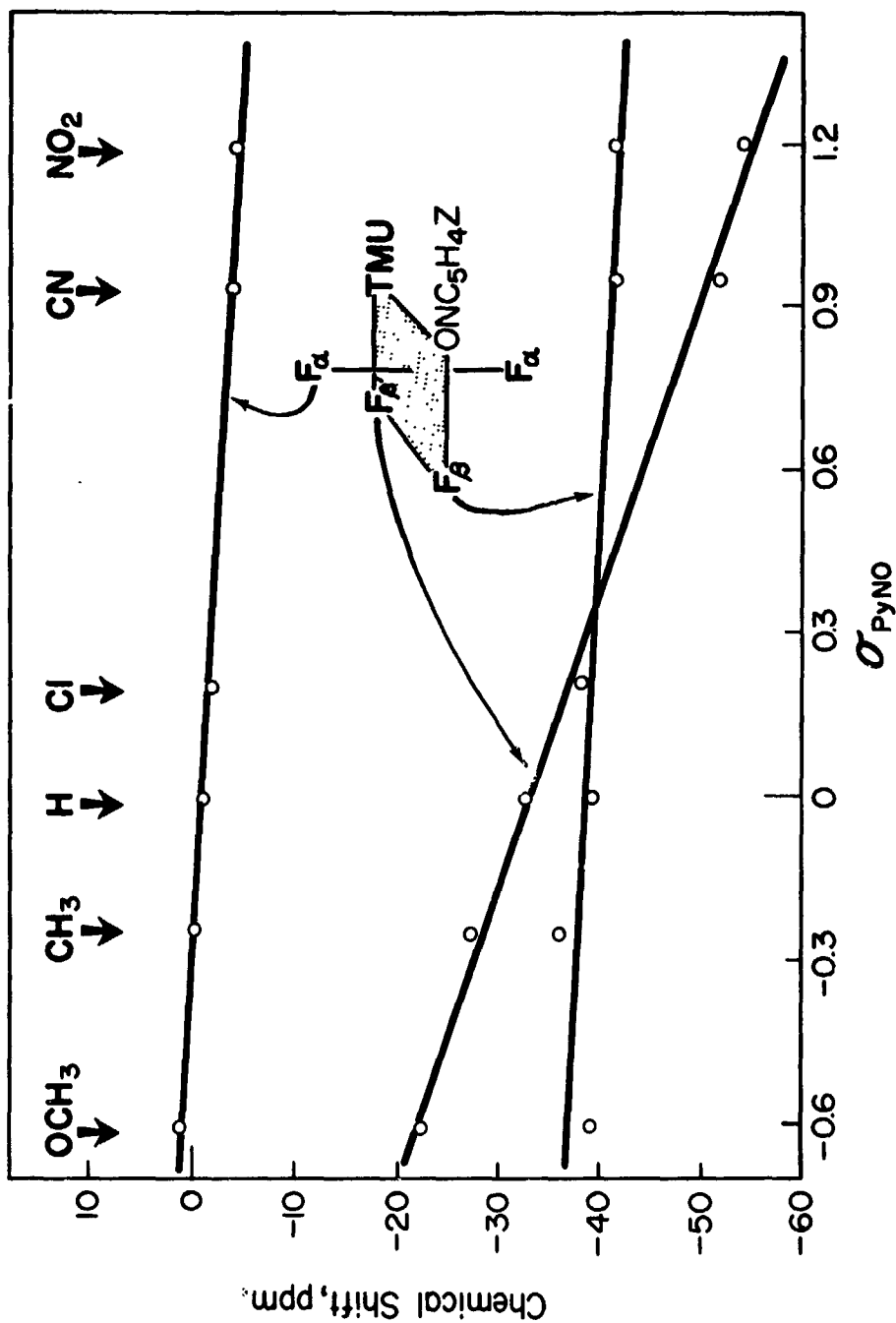


TABLE IV

 ^{19}F Chemical Shifts for $\text{TiF}_4 \cdot (\text{TMU})(\text{Z}-\text{C}_5\text{H}_4\text{NO})$ Complexes^a

Z	F _{α}	F _{β}	F _{β'}
-CN	-4.3	-41.7	-49.5
-Cl	-2.3	-38.3	-38.3
-2CH ₃	+0.4	-40.4	-29.9
-4CH ₃	-0.4	-36.1	-27.4
-2,4(CH ₃) ₂	+1.6	-39.8	-25.9
-OCH ₃	+1.1	-39.1	-22.7
-2,6(CH ₃) ₂	-1.5 ^b	None	None
-NO ₂	-4.6	-41.8	-51.9
-H	-1.3	-39.3	-33.0

^a Chemical shifts are all relative to the upfield triplet of $\text{TiF}_4 \cdot 2\text{-TMU}$ in chloroacetonitrile at -30°C ; accuracy is $\pm .5\text{ppm}$.

^b Chemical shift for the fluorines in trans- $\text{TiF}_4 \cdot \text{TMU}$, $2,6(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NO}$.

TABLE V

The ^{19}F Spin-Spin Coupling Constants for $\text{TiF}_4 \cdot \text{TMU ZC}_5\text{H}_4\text{NO}$ Complexes^a

Z	$J_{\alpha\beta}^b$	$J_{\alpha\beta'}^b$	$J_{\beta\beta'}^b$
-CN	42	36	50
-Cl	42 ^c	37 ^c	47 ^c
-2CH ₃	44	36	50
-4CH ₃	43	37	47
-2,4(CH ₃) ₂	44	36	48
-OCH ₃	41	35	49
-2,6(CH ₃) ₂	None	None	None
-NO ₂	43	36	50
-H	43	36	50

^a Measured in Chloroacetonitrile at -30°.^b ± 1 cps^c The spectra are approaching second order, therefore the coupling constants are only approximate.

A similar argument is applicable for the results reported here.

In comparing the lines for F_β and $F_{\beta'}$ in Figure 5 with a similar plot made for $TiF_4 \cdot (DMA)(4ZC_5H_4NO)^3$, a striking feature may be noted. In the mixed system with DMA, the spectra approach second order when $Z = NO_2$, while with TMU, the spectra approach second order when $Z = Cl$. A second order spectrum will be obtained when the relative basicity of D and D' towards TiF_4 is the same. One would expect TMU to be a stronger base than DMA because of its two strong electron donating groups, $(CH_3)_2N$, vs one for DMA. Our data suggest that the basicity of $TMU \approx 4-ClC_5H_4NO$ and $DMA \approx 4-NO_2C_5H_4NO$ with TiF_4 as a reference acid.

It is interesting to compare the results of the addition of 2,6-dimethylpyridine 1-oxide to $TiF_4 \cdot 2TMU$ in chloroacetonitrile with those reported for a similar experiment with $TiF_4 \cdot 2DMA$.⁹ The $TiF_4 \cdot DMA$, 2,6- $(CH_3)_2C_5H_3NO$ adduct consisted of both the cis and trans isomers. Whereas with $TiF_4 \cdot TMU$, 2,6- $(CH_3)_2C_5H_3NO$ only the trans isomer was detected. (Figure 4) This difference can be explained by the increase in bulkiness of TMU as compared to DMA. In fact with TMU both the cis and trans isomers ($TiF_4 \cdot 2TMU$) are formed as noted in Figures 2-4. The trans- $TiF_4 \cdot 2D$ complex is formed only when there is sufficient steric interaction to overcome symmetry effects and the tendency to maximize $p\pi-d\pi$ bonding.⁹

The values found for the three types of coupling constants are given in Table V. Two aspects of this data should be noted: (1) comparison of the F-F coupling constants of the $TiF_4 \cdot DD'$ complexes shows that the spin-spin interactions are insensitive to the nature of Z and (2) the three coupling constants for each complex are quite different

from each other. As noted earlier⁶ the best rationale (and as also supported by this data) for explaining the fluorine -19 spin-spin interaction is by a through-space mechanism. The largest coupling constant is found for $J_{\beta\beta'}$, and the angle $F_{\beta}TiF_{\beta'}$, would be decreased by both donor-fluorine interactions and would be expected to be the smallest FTiF angle in the complex.

SECTION IV

COMPLEXES OF TIN TETRAFLUORIDE

1. COMPLEXES WITH AROMATIC AMINE OXIDES

Tin tetrahalides have been shown to form two to one addition compounds with many different Lewis bases. In general most of the studies have been with the chlorides, bromides and iodides,²⁸ although some adducts have been reported with SnF_4 .^{1,10,11}

The two to one addition compounds of titanium tetrafluoride with many aromatic amine oxides, amides and sulfoxides have been prepared and studied as noted in Section III. A linear correlation between the ^{19}F chemical shift and σ_{PyNO} substituent constants has been demonstrated with the pyridine 1-oxides. Fluorine-to-titanium π bonding has been proposed as a reason for the sensitivity of the ^{19}F chemical shift to changing ligand basicity. Two geometrical isomers were observed for the bulky ligands which were coordinated to titanium tetrafluoride.

One objective of this phase of the research was to study the ^{19}F nmr spectra of various aromatic amine oxide diadducts of tin tetrafluoride since chemical shift values have been reported for only two neutral $\text{SnF}_4 \cdot 2\text{D}$ compounds.^{10,11} It was also of interest to compare the ^{19}F chemical shifts, ^{19}F - ^{19}F coupling constants, and the stereochemistry of the tin tetrafluoride complexes with the data which have been obtained with the titanium tetrafluoride diadducts.

Since each tin atom as was the case with titanium is bonded to four fluorines and two ligand molecules, there may be two geometrical

isomers formed, a cis isomer and a trans isomer. In the trans isomer all fluorines are equivalent while in the cis isomer there are two fluorine environments each containing two fluorines. Thus the ^{19}F nmr spectra should contain a singlet in the former case and two equal intensity triplets in the latter case if first order spectra are obtained. In all $\text{TiF}_4 \cdot 2\text{D}$ complexes where both isomers are present a first order spectrum was obtained. In the case of $\text{SnF}_4 \cdot 2\text{C}_2\text{H}_5\text{OH}$ however, a singlet due to the trans isomer and an unresolved multiplet identified as a second order spectrum of the cis isomer were observed.¹⁰ The dimethylsulfoxide complex, $\text{SnF}_4 \cdot 2\text{DMSO}$ shows a first order spectrum for the cis isomer. The trans isomer was not detected.¹¹

In Tables VI and VII are listed the ^{19}F chemical shifts and the ^{119}Sn - ^{19}F coupling constants where measurable for the compounds studied. In addition the diadducts with 4-methoxy, 4-cyano and 4-nitropyridine 1-oxides and 4-cyano and 4-nitroquinoline 1-oxides were prepared but were insufficiently soluble for any ^{19}F resonance to be observed. The $\text{SnF}_4 \cdot 2\text{D}$ compounds generally appear to be less soluble than the corresponding $\text{TiF}_4 \cdot 2\text{D}$ compounds. It should also be noted that in some of the spectra there were some small peaks (less than 10% of the total intensity) in the region of ~ 158 ppm. Because of the low intensity, it was not possible to identify these species.

The results in Tables VI and VII seem to fall into two separate groups. The 4-substituted pyridine 1-oxides together with the 3- CH_3 -, 3,4- $(\text{CH}_3)_2$ - and 3,5- $(\text{CH}_3)_2$ -substituted pyridine 1-oxides form one group in which both isomers are present and for which the chemical shifts are nearly the same. The 4- and 6-substituted quinoline 1-oxides together with the other substituted pyridine 1-oxides form a group in which only the trans isomer is observed

and in which the chemical shift seems to be related to the bulkiness of the ligand. Comparing the chemical shift values with the analogous titanium compounds shows several differences. The total range of chemical shifts is only 14 ppm in tin and about 28 ppm in titanium. In the tin compounds there is no variation in the chemical shift values with changing substituent for either the 4-substituted pyridine 1-oxides or quinoline 1-oxides. In contrast the titanium complexes show a linear correlation between the substituent constant and chemical shift for these ligands. The tin complexes with the 2-substituted pyridine 1-oxides all have the same chemical shift. The complexes with the 2,6- and 2,4,6-substituted pyridine 1-oxides are also the same but shifted downfield about 6 ppm from the 2-substituted compounds. In the titanium compounds with these same ligands a similar effect is noted. The chemical shift of the trans peak is downfield about 5.5 ppm in going from the 2-CH₃C₅H₄NO to the 2,6-(CH₃)₂C₅H₃NO. We account for the downfield shift of 6 ppm for the tin complexes with the 2,6-substituted ligands as due to a steric interaction between the ligands and fluorines since no change in chemical shift was observed for the 4-substituted adducts. Also the formation of only a trans TiF₄ compound was attributed to a steric interaction with bulky ligands.⁹

The ¹¹⁹Sn-¹⁹F coupling constants were measured where observable. These values are helpful in determining what tin-fluorine type compound is present. Singlets observed for the 2-substituted pyridine 1-oxides and 2,6-substituted pyridine 1-oxides could be assigned as being due to SnF₆⁼ on the basis of their chemical shift values. However, the ¹¹⁹Sn-¹⁹F coupling constant for SnF₆⁼ is about 1570-1600 cps while the values for SnF₄·2D complexes are much higher.^{10,11} There is not

TABLE VI

^{19}F NMR Data,^a For Some 4-Substituted Pyridine 1-Oxide And 4-And 6-Substituted Quinoline 1-Oxide Diadducts Of SnF_4

Donor Molecule	Chemical Shift ^b ppm	
	<u>Trans</u>	<u>Cis</u>
4Z-PyNO		
CH ₃	162.4	165.2
H	162.4	165.2
Cl	162.6	166.0
4Z-QNO		
OCH ₃	160.5	
CH ₃	161.3	
H	160.9	
Cl	161.5	
6Z-QNO		
OCH ₃	161.3	
CH ₃	161.4	
Cl	161.4	

^a Spectra were measured in ClCH_2CN solutions at -40°C , $\pm 1^\circ\text{C}$.

^b Chemical shifts are relative to internal CFCl_3 as a reference, ± 0.5 ppm.

TABLE VII

¹⁹F nmr Data^a For Some Various Substituted Pyridine1-oxide Diadducts of SnF₄.

Donor Molecule	Chemical Shift ^b (ppm)		Coupling Constant ^d ¹¹⁹ F-Sn- ¹⁹ F, (cps)
	Trans	Cis	
2-CH ₃	158.8		
2,3-(CH ₃) ₂	158.7		1992
2,4-(CH ₃) ₂	158.6		1989
2-C ₂ H ₅	158.4		2002
2,6-(CH ₃) ₂	152.2		
2,4,6-(CH ₃) ₂	152.2		2056
3-CH ₃	161.1		1964
		163.9	1965
3,5-(CH ₃) ₂	161.0		1972
		163.7	1956
3,4-(CH ₃) ₂	162.2		1977
		164.7	1978
3,4-(CH ₃) ₂ ^c	162.2		
		164.9	

^a Spectra were measured in ClCH₂CN solutions at -40°C, ± 1°C^b Chemical shifts are relative to internal reference CFCl₃, ± 0.5 ppm^c Room temperature^d ± 5 cps

much variation in the values reported in Table VII. The coupling constant does appear to increase as the bulkiness of the ligand increases.

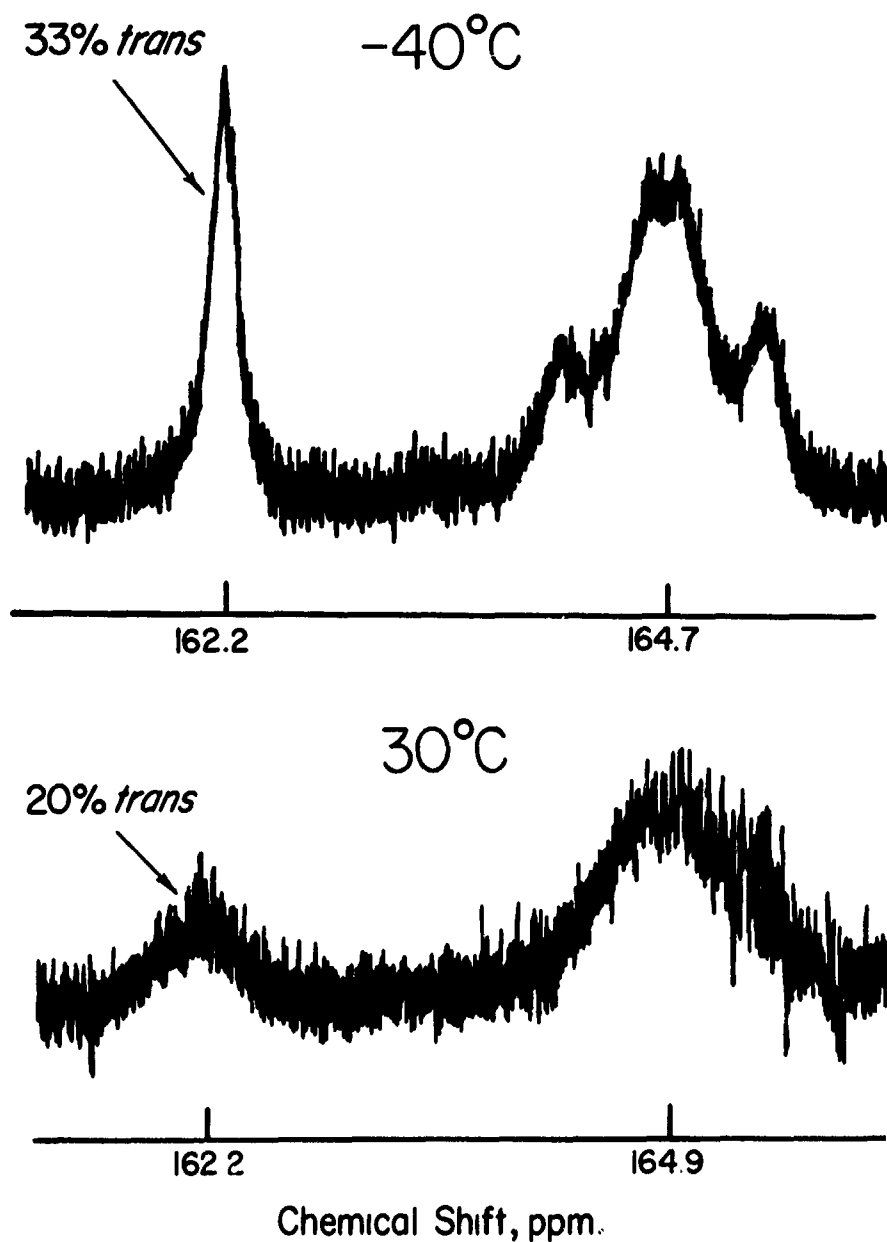
In Figure 6 is a representative spectrum of both the cis and trans isomers. Spectra at both -40°C and $+30^{\circ}\text{C}$ are given. It is of interest to note (see Table VII) that there is almost no change in chemical shift in going from one temperature to the other. The peaks become broader at the higher temperature and there is no resolution of the multiplet. This is indicative of an exchange process. This is not unreasonable since exchange processes have been observed with the $\text{TiF}_4 \cdot 2\text{D}$ compounds.⁵ The half-height width of the trans peak for the spectra shown is 10 cps at -40° and 32 cps at $+30^{\circ}$, while for the $\text{TiF}_4 \cdot 2\text{D}$ ($\text{D} = 2\text{-CH}_3, 2,4(\text{CH}_3)_2$, and $2\text{-C}_2\text{H}_5$ substituted pyridine 1-oxides) the values at -40° are 18 cps, 46 cps, and 29 cps, respectively. At $+30^{\circ}\text{C}$ there is no measureable spectra for these titanium complexes indicating that exchange has made the signals unobservable. Comparison of the data indicate the exchange processes for the $\text{SnF}_4 \cdot 2\text{D}$ molecules are slower.

The difference in the above exchange can be explained by considering that the mechanism of exchange proposed for the $\text{TiF}_4 \cdot 2\text{D}$ adducts⁵ is applicable to tin. The first step involves dissociation,



followed by intramolecular rearrangement in the $\text{MF}_4 \cdot \text{D}$ species and then recombination with a base molecule. The difference can then be rationalized if stronger bonds are formed between tin and the oxygen

Figure 5. ^{19}F nmr spectrum of cis and trans $\text{SnF}_4 \cdot 2(3,4-(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NO})$ at -40° and 30° in chloroacetonitrile.



donor than those formed with titanium. Infrared studies have shown that the metal-oxygen stretching frequency for TiF_4 diadducts with pyridine 1-oxides²⁵ is in the region below 300 cm^{-1} while for the corresponding SnF_4 diadducts²⁶ it is in the region of 400 cm^{-1} . This indicates that the metal oxygen bond is stronger in the latter case. Since the proposed mechanism for exchange requires the breaking of the metal oxygen bond as a first step one would expect the SnF_4 diadducts to exchange more slowly.

All of the previous discussion here seems to point out several facts. First, in the $\text{SnF}_4 \cdot 2\text{D}$ complexes the steric nature of the ligand seems to be the most important factor in accounting for the range in chemical shift values for the aromatic amine oxide compounds. The base strength of the ligand does not seem to be important; e.g., the chemical shift values of 4-methoxy- and 4-chloroquinoline 1-oxide are the same yet the pK_a values are quite different. Secondly, previous studies have suggested strongly that fluorine-to-metal π -bonding is important in $\text{TiF}_4 \cdot 2\text{D}$ type complexes and explains the sensitivity of the ^{19}F chemical shifts with changing substituent constant and also the lack of formation of the trans isomer with many ligands (Section III). One would expect in the case of tin that fluorine-to-tin π -bonding would be less favorable than that with titanium since the 2p fluorine orbitals would have to overlap with appropriate 5d tin orbitals which is energetically less favorable. If there is little fluorine-to-tin π -bonding and some fluorine-to-titanium π -bonding one would expect the $\text{SnF}_4 \cdot 2\text{D}$ resonances to occur upfield from the $\text{TiF}_4 \cdot 2\text{D}$ resonances. The resonances for the $\text{TiF}_4 \cdot 2\text{D}$ complexes appear in the region below -120 ppm^9 whereas the $\text{SnF}_4 \cdot 2\text{D}$ complexes are in the region above $+150\text{ ppm}$. This is a shift of over 270 ppm upfield. This

is interesting when one considers the fact that the range of all fluorine resonances is only about 800 ppm. A difference in π -bonding between tin and titanium also explains the stereochemical data. The cis isomer would be stabilized more for the titanium complexes than for complexes in the tin. Where both cis and trans isomers occur with titanium only the trans isomer occurs with tin and where only the cis isomer is observed with titanium both isomers are observed with tin.

2. COMPLEXES WITH SULFOXIDES

The diadduct of tin tetrafluoride with dimethylsulfoxide was prepared by Muetterties.¹ The chemical shifts for a cis diadduct were reported.¹¹ No resonance attributable to the trans isomer was observed.¹¹

Here we report a nmr study of four sulfoxide complexes of SnF_4 . The chemical shifts and fluorine-19 spin-spin coupling constants are given in Table VIII. The ^{19}F nmr spectrum of the dimethylsulfoxide complex at 30° and -40° is shown in Figure 7. In the spectrum at 30° , it appears that there are two triplets of unequal intensity. The dilemma is resolved by considering the spectrum at -40° . At this temperature two 1:2:1 triplets of equal intensity are observed as well as a singlet. In the room temperature spectrum the singlet has the same chemical shift as the middle member of the downfield triplet. As already noted with the aromatic amine oxide complexes of SnF_4 the cis - trans ratio is temperature dependent. This can also be seen in Figure 7. The chemical shifts depend upon the temperature, since the chemical shift of the singlet is different

TABLE VIII

^{19}F NMR Data For Some Sulfoxide Diadducts
of SnF_4 in Chloroacetonitrile at 30°

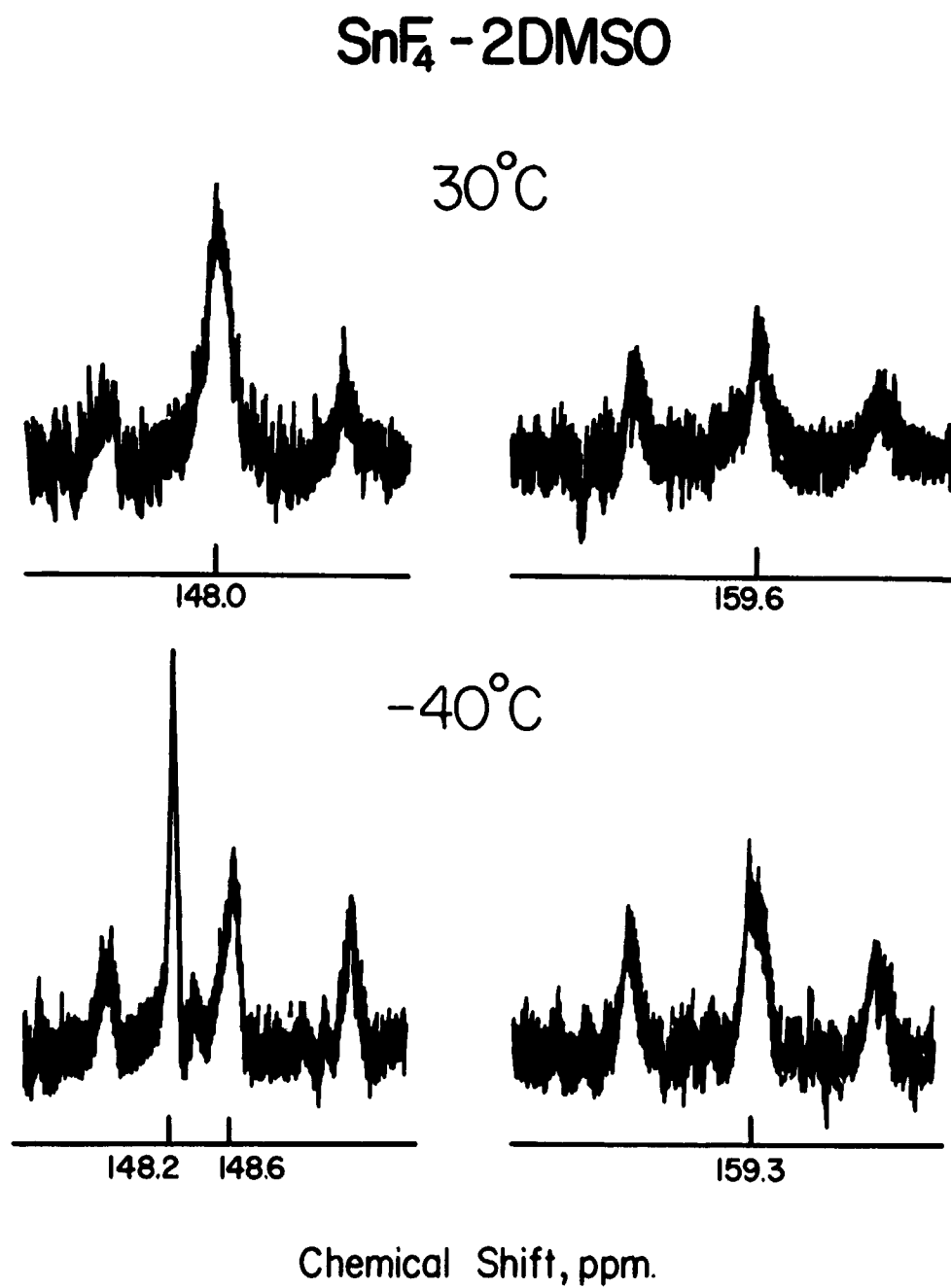
Donor Molecule	Chemical Shift ^a			^{19}F - ^{19}F Coupling Constant, cps ^b
	<u>trans</u> singlet	downfield triplet	<u>cis</u> upfield triplet	
Dimethylsulfoxide	148.0	148.0	159.6	53
Dimethylsulfoxide ^c	148.2	148.6	159.3	53
Di-n-propylsulfoxide	151.0	150.9	160.1	52
Di-n-butylsulfoxide	150.5	150.8	160.1	55
Tetramethylenesulfoxide	149.9	149.9	160.4	52

^a Chemical shifts are all relative to internal CFCl_3 , ± 0.5 ppm.

^b ± 1 cps.

^c Measured at -40° .

Figure 7. ^{19}F nmr spectrum of cis and trans $\text{SnF}_4 \cdot 2\text{DMSO}$ at -40° and 30° .

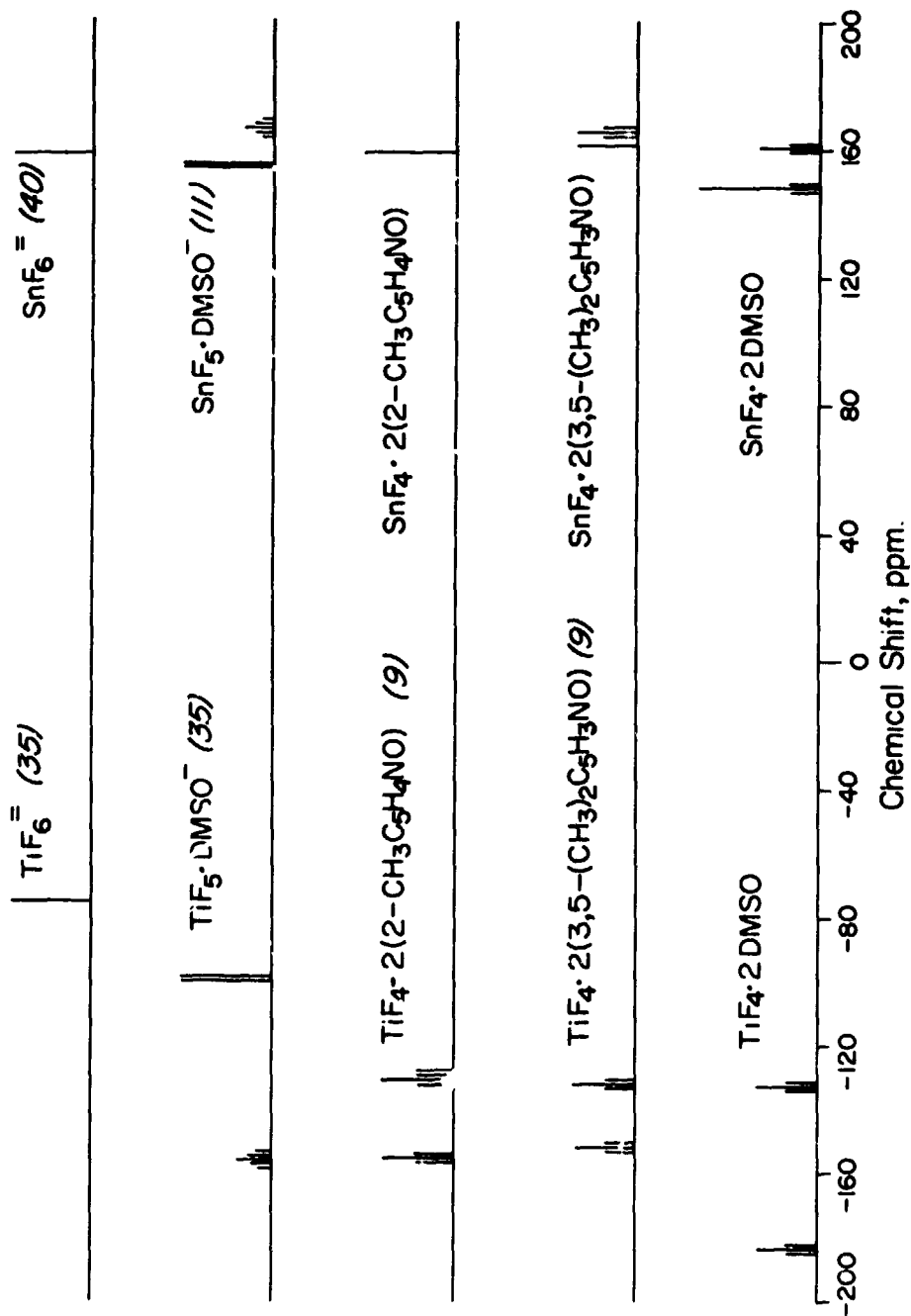


than the triplet at -40° . In all probability Dean and Evans¹¹ who measured the spectrum of $\text{SnF}_4 \cdot 2\text{DMSO}$ at room temperature did not detect the difference in the intensity of the "two triplets." As in the case with the cis - trans isomers of TiF_4 , we assign the two triplets to the cis - adduct and the singlet to the trans - adduct.

It is interesting to note the differences between the spectra of the fluoro complexes of tin and titanium. A schematic diagram illustrating the chemical shifts and the multiplets for several complexes of tin and titanium is given in Figure 8. First the ^{19}F chemical shifts for all the tin complexes are very similar to that for the hexfluorostannate ion. In contrast the chemical shifts of the titanium fluorine complexes are all much further downfield than the resonance of TiF_6^{-2} . Also the chemical shifts for the tin complexes fall in a very narrow range whereas those for titanium cover a large range. The data in Table VIII indicate that the chemical shifts for all the sulfoxide adducts of tin are nearly the same. The chemical shifts for the same sulfoxide complexes with titanium cover a larger range (Table III). Another difference is in the location of chemical shifts for the trans fluorines. With titanium the resonances for the trans fluorines are downfield whereas they are upfield resonances for the tin adducts.

Earlier in this report we rationalized the difference between the ability of SnF_4 and TiF_4 to form cis and trans adducts as due to the difference in π -bonding of the fluorines with the metal ion. The chemical shifts of the titanium tetrafluoride adducts have also been explained on the basis of π -bonding.^{3,9,38} There is a decrease in the π -bonding capacity of fluorine with tin since the appropriate 5d orbitals are of high energy. The narrow chemical shift range for

Figure 8. A schematic diagram showing the ^{19}F nmr chemical shifts and multiplets for some tin and titanium fluorine compounds. The data for complexes studied previously are designated by the appropriate reference.



the tin-fluorine complexes also suggest minimal π -bonding of the fluorines with tin. The lack of change in the chemical shifts with a change in the para-substituent of an aromatic amine oxide reflects the lack of significant π -bonding.

Finally from Figure 8 it can be seen that the trans complex is formed in each case with tin. When the donor is bulky enough to cause both cis and trans adducts with titanium, only the trans complex is found with tin. Second order spectra are found with the SnF_4 when it is coordinated with the stronger bases. Weak bases like the sulfoxides form adducts with tin tetrafluoride which have first order spectra. A method which can be used in predicting whether first or second order spectra will be observed for SnF_4 adducts is to observe the $\Delta\delta$ values for the same complex with TiF_4 . When there is a large difference one would predict that a first order spectrum would be found.

3. COMPLEXES WITH AMIDES

Muetterties¹ reported the preparation of the N,N,-dimethylformamide complex with SnF_4 . Elemental analyses and a molecular weight determination showed that a 2:1 adduct was formed. In Table IX the ^{19}F nmr data are presented for 13 amides with tin tetrafluoride. A typical ^{19}F spectrum for the amide complexes is shown in Figure 9 for the N,N-diethylbutyramide compound in excess ligand as the solvent. This spectrum is quite similar to the one for the dimethylsulfoxide complex (Figure 7).

Both the cis and trans complexes are found with the amides. First order 1:2:1 triplets are observed for the cis adducts. From the data in Table IX, one can note that there is not much change in chemical

TABLE IX

 ^{19}F NMR Data For Some Amide Diadducts of SnF_4 at 30°

Donor Molecule	Chemical Shift ^a		Coupling Constants ^b , cps	
	<u>Trans</u>	<u>Cis</u>	<u>$^{119}\text{Sn}-^{19}\text{F}$</u> ^b	<u>$^{19}\text{F}-^{19}\text{F}$</u>
N,N-dimethylacetamide ^{c,e}	147.9	147.6 154.8		56
N,N-diethylacetamide ^c	149.8	148.7 156.9		52
N,N-diethylacetamide ^d	150.5	148.9 159.7	1792	50
N,N-di-n-propylacetamide ^c	150.2	148.8 157.1		52
N,N-di-n-propylacetamide ^d	150.5	148.6 159.8	1806 1796 1974	54
N,N-di-n-butylacetamide ^d	151.2	149.0 159.8	1806	56
Propionamide ^{c,e}	146.4	143.7 155.4		50
N,N-dimethylpropionamide ^c	150.1	149.0 157.7		53
N,N-dimethylpropionamide ^d	151.0	149.2 159.7		53
N,N-diethylpropionamide ^d	152.1	150.2 160.7	1790 1798 1900	55
N,N-di-n-propylpropionamide ^d	152.5	150.0 161.0	1808	55

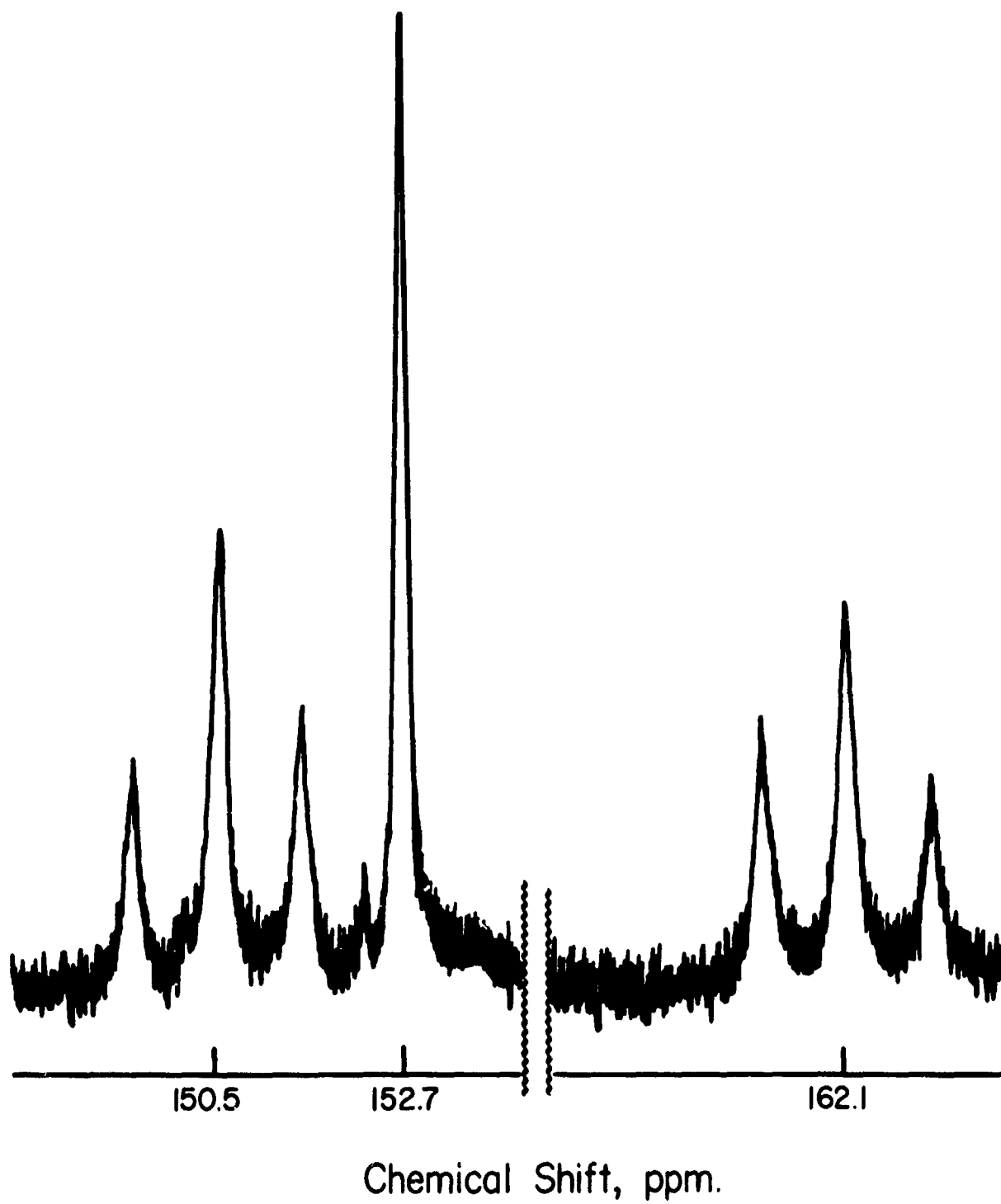
TABLE IX (Cont'd.)

 ^{19}F NMR Data For Some Amide Diadducts of SnF_4 at 30°

Donor Molecule	Chemical Shift ^a		Coupling Constants ^b , cps	
	Trans	Cis	$^{119}\text{Sn}-^{19}\text{F}^b$	$^{19}\text{F}-^{19}\text{F}$
N,N-diisopropylpropionamide ^d	151.0	147.4 160.8	1790	56
N,N-di-n-butylpropionamide ^d	152.1	149.7 160.7		59
N,N-diisobutylpropionamide ^d	152.1	148.9 160.8		57
N,N-dimethylbutyramide ^c	150.1	148.9 157.6		57
N,N-dimethylbutyramide ^d	151.0	149.5 159.6	1792	53
N,N-diethylbutyramide ^d	152.7	150.5 162.1	1813	57

^a Relative to internal CFCl_3 , ± 0.5 ppm.^b $^{119}\text{Sn}-^{19}\text{F}$ coupling constants, ± 5 cps, were not measurable in all cases due to low solubility; $^{19}\text{F}-^{19}\text{F}$ coupling constants, ± 1 cps.^c Spectrum obtained in ClCH_2CN as a solvent.^d Spectrum obtained in excess donor as a solvent.^e Spectrum measured at -40°C .

Figure 9. ^{19}F nmr spectrum of N,N-diethylbutyramide diadduct of SnF_4 in excess amide as the solvent.



shift for the complexes in various solvents. Many of the adducts were prepared in excess ligand and the ligand was used as the solvent since the complexes had a very limited solubility. Because of the low solubility it was not possible to measure the ^{119}Sn - ^{19}F coupling constants for all the complexes. In most of the spectra some resonances of low intensity appeared in the range 150-160 ppm. It was not possible to identify the species giving rise to these resonances (usually < 5% of the fluorine species). We would suggest that this may be due to polymeric species.

The range in chemical shifts for the trans compounds was 6.3 ppm. For the cis complex the downfield triplet had a chemical shift range of 6.8 ppm and 7.3 ppm for the upfield triplet. Here as with the amide complexes of titanium tetrafluoride there is not much of a change in the chemical shift values with the different amides. This suggests that there is not much of a difference in the relative basicity of the amide, although as pointed out in the work with the aromatic amine oxide adducts, the fluorine resonances in tin complexes are not sensitive to basicity. Ligand-fluorine interactions appear to have the largest effect on the fluorine chemical shifts.

The ^{19}F - ^{19}F coupling constants are similar to those measured for the tin-sulfoxide compounds. In general the values increase with an increase in the size of the amide. This conclusion is similar to that found for ^{19}F - ^{19}F coupling constants in TiF_4 complexes.⁶ The ^{119}Sn - ^{19}F coupling constants are quite similar. At this point there are not enough data for these constants to make any definite conclusions.

One of the interesting facets is that first order spectra were obtained as with the sulfoxide compounds. To a large extent the

basicity of the ligands seem to determine whether first or second order spectra will be obtained with the SnF_4 diadducts. One would predict that with very weak bases like the amides or sulfoxides first order spectra will be found for the cis complex and SnF_4 complexes with relatively strong bases like the aromatic amine oxides second order ^{19}F spectra will be measured. More systems need to be investigated since one would predict a first order spectrum for the $\text{SnF}_4 \cdot 2(\text{C}_2\text{H}_5\text{OH})$ complex and a second order spectrum was observed.¹⁰ In agreement with our conclusions above a first order spectrum was found with the acetone adduct of SnF_4 .⁴¹

SECTION V

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