most intense band in the spectra indicates that a strict center of inversion is destroyed in the site symmetry. The presence of the rare earth ions in the B site of the pyrochlore ($A_2B_2X_7$) structure in $Gd_2GdSbO_7$ creates a local distortion due to the considerable difference in the ionic radii of $Gd^{3+}$ (0.97 Å) and $Sb^{5+}$ (0.62 Å). The rare earth ion at the A site is coordinated to a regular framework of oxygen octahedra and two other oxygen atoms linearly at a shorter distance. The lowering of site symmetry at the B site will cause a distortion of the ($GdO_8$) polyhedra at the A site. Although the degree of distortion may be negligibly small to retain the basic pyrochlore structure, the highly sensitive $Eu^{3+}$ emissions will respond to such a deviation from the strict center of symmetry. Blasse, *et al.*,[14] observed the same kind of phenomenon in the fluorescence spectrum of $LaTiSbO_6$–Eu (site symmetry, $D_{3d}$) where the forbidden electric dipole transition $^5D_0 \rightarrow {}^7F_2$ was found to be stronger than the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$.

The transition $^5D_0 \rightarrow {}^7F_1$ split up into two crystal field components at 17,020 and 16,978 $cm^{-1}$ corresponding to a nondegenerate ($A_{2g}$) and a doubly degenerate ($E_g$) level as expected for $D_{3d}$ symmetry. The intensity of these bands was very similar to that of the transition $^5D_1 \rightarrow {}^7F_3$.

Four well-resolved band areas at 16,807, 16,639, 16,507, and 16,460 $cm^{-1}$ could be observed for the transition $^5D_2 \rightarrow {}^7F_6$. The broken nature of the bands indicates mixing of the closely situated other crystal field components. The transition $^5D_0 \rightarrow {}^7F_2$ appeared as a narrow band at 16,260 $cm^{-1}$ and did not show any crystal field splitting. The weak intensity of this band suggests that the distorted site symmetry will be very close to $D_{3d}$.

The weak band at 15,971 $cm^{-1}$ was assigned to the transition $^5D_1 \rightarrow {}^7F_4$. The broad weak band at 16,026 $cm^{-1}$ was most probably due to the noncentrosymmetric vibrational modes of the surroundings of the rare earth ion. Weber and Schaufele[15] reported this kind of transition with $SrTiO_3$–Eu.

The reflectance spectrum (Figure 3) showed three weak and sharp bands at 17,256, 18,774, and 21,523 $cm^{-1}$ corresponding to the transitions $^7F_0 \rightarrow {}^5D_0$, $^7F_0 \rightarrow {}^5D_1$, and $^7F_0 \rightarrow {}^5D_2$, respectively.

The effect of distortion of the $D_{3d}$ site on the cathode ray spectra of $3Gd_2O_3 \cdot Sb_2O_5$(3.5% Eu) was further studied by fluxing with $KSbO_3$ which has a pyrochlore structure. A mixture of $3Gd_2O_3 \cdot Sb_2O_5$(3.5% Eu)–$KSbO_3$ in a molar ratio of 1:1 was heated in air at 1300° for 16 hr. The sample was washed in boiling water. The X-ray diffraction pattern of this sample showed a single phase $3Gd_2O_3 \cdot Sb_2O_5$ with a slight change in the *d* values suggesting a solid solution. The cathode ray spectrum of this sample (Figure 2) showed the electric dipole transition $^5D_0 \rightarrow {}^7F_2$ and $^5D_1 \rightarrow {}^7F_3$ to be the strongest ones although the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ appeared as a pair of fairly weak bands. Obviously the presence of large $K^+$ (1.33 Å) ions in the lattice of $3Gd_2O_3 \cdot Sb_2O_5$ caused further distortion of $D_{3d}$ site symmetry.

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# A Fluorine-19 Nuclear Magnetic Resonance Study of Tin Tetrafluoride Diadducts of Various Aromatic Amine Oxides

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An $^{19}F$ nmr study of diadducts of $SnF_4$ with 19 aromatic amine oxides is reported. The results indicate that the steric nature of the ligand is probably more important than the base strength in determining the relative chemical shifts. The trans isomer is identified in all of the complexes whereas the cis isomer is present only with the less bulky ligands.

## Introduction

The donor properties of various aromatic amine oxide systems have been reviewed recently.[2,3] It has been shown that in most cases there is a linear correlation between some observable property such as an infrared stretching frequency or a $^{19}F$ chemical shift and a suit-

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able substituent constant for the 4-substituted pyridine 1-oxides[3] and 4-substituted quinoline 1-oxides.[4,5] Tin tetrahalides have been shown to form 2:1 addition compounds with many different Lewis bases. In general most of the studies have been with the chlorides, bromides, and iodides.[6]

The 2:1 addition compounds of titanium tetrafluoride with many aromatic amine oxides have been prepared and studied. A linear correlation between the $^{19}F$ chemical shift and $\sigma_{pyNO}$ substituent constants has been demonstrated.[7,8] Fluorine-to-titanium $\pi$ bonding has been proposed as a reason for the sensitivity of the $^{19}F$ chemical shift to changing ligand basicity.[7] Two geometrical isomers were observed for some of the 4- and 6-substituted quinoline 1-oxides and 2-substituted pyridine 1-oxides with titanium tetrafluoride.[8,9]

One objective of this 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 $SnF_4 \cdot 2D$ 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.

## Experimental Section

The various aromatic amine oxide ligands used in this work were prepared as previously reported.[4] 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*.

Some of the compounds were analyzed by using excess Ti(III) to reduce the amine oxide to the amine. The excess Ti(III) is destroyed with excess $Cr_2O_7^{2-}$ which is then back-titrated with Ti(III).[12] These analyses confirmed the formation of 2:1 adducts. The similarity of the $^{19}F$ nmr spectra of all the complexes supports a 2:1 stoichiometry. These results are in agreement with those of Muetterites[13] where 2:1 adducts of $SnF_4$ were formed with oxygen donors.

The $^{19}F$ nmr studies were carried out on a Varian A-56/60 operating at 56.4 MHz. The instrument was fitted with a variable-temperature probe. All spectra were run at −40° except where noted. Freshly distilled chloroacetonitrile was used as a solvent and $CFCl_3$ was used as an internal reference in all samples.

## Results and Discussion

Since each tin atom 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 $TiF_4 \cdot 2D$ complexes where both isomers are present a first-order spectrum was obtained.[9] In the case of $SnF_4 \cdot 2C_2H_5OH$, however, a singlet due to the trans isomer and an unresolved multiplet identified as a second-order spectrum of the cis isomer were observed.[11] The dimethyl sulfoxide complex $SnF_4 \cdot 2DMSO$ shows a first-order spectrum for the cis isomer, but the trans isomer was not detected.[10] In our preliminary results, we have found both the cis and trans dimethyl sulfoxide complexes in chloroacetonitrile. However, at room temperature only two "triplets" are observed since the singlet resonance for the trans isomer has the same chemical shift as the center member of the downfield triplet, whereas at −40° separate signals are recorded for the singlet and the two triplets.

TABLE I

$^{19}F$ 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 |  |
|---|---|---|
|  | Trans | Cis |
|  | 4-ZpyNO |  |
| $CH_3$ | 162.4 | 165.2 |
| H | 162.4 | 165.2 |
| Cl | 162.6 | 166.0 |
|  | 4-ZQNO |  |
| $OCH_3$ | 160.5 |  |
| $CH_3$ | 161.3 |  |
| H | 160.9 |  |
| Cl | 161.5 |  |
|  | 6-ZQNO |  |
| $OCH_3$ | 161.3 |  |
| $CH_3$ | 161.4 |  |
| Cl | 161.4 |  |

[a] Spectra were measured in $ClCH_2CN$ solutions at −40 ± 1°. [b] Chemical shifts are relative to internal $CFCl_3$ as a reference, ±0.5 ppm.

TABLE II

$^{19}F$ NMR DATA[a] FOR SOME VARIOUS SUBSTITUTED PYRIDINE 1-OXIDE DIADDUCTS OF $SnF_4$

| Donor molecule | Chemical shift,[b] ppm |  | Coupling constant ($^{119}Sn-^{19}F$),[d] 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-$C_2H_5$ | 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 $ClCH_2CN$ solutions at −40 ± 1°. [b] Chemical shifts are relative to internal reference $CFCl_3$, ±0.5 ppm. [c] Room temperature. [d] ±5 cps.

In Tables I and II are listed the $^{19}F$ chemical shifts

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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 $SnF_4 \cdot 2D$ compounds generally appear to be less soluble than the corresponding $TiF_4 \cdot 2D$ 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.

In this study both the cis isomer and the trans isomer were observed with the substituted pyridine 1-oxides as long as neither the 2 nor the 6 position was substituted. The resonance due to the cis isomer in these compounds was an unresolved multiplet (see Figure 1) indicative of a second-order spectrum. A second-order spectrum occurs when the coupling constant and the chemical shift differences between the two types of fluorines are of the same order of magnitude. Using the coupling constants for some other $SnF_4X_2^{2-}$ [10] complexes, from 30 to 60 cps the two types of fluorines are probably not separated by more than 1 ppm. The complexes with the other substituted pyridine 1-oxides and the quinoline 1-oxides showed only the trans isomer. Comparing these data with the titanium tetrafluoride complexes with the same ligands one finds that with substituted pyridine 1-oxides where the substitution is in positions 3, 4, and 5 or any combination thereof only the cis isomer is observed. The titanium complexes with 2-substituted pyridine 1-oxides and some 4- and 6-substituted quinoline 1-oxides show both the cis and trans isomers. Only the trans isomer is observed in the $TiF_4 \cdot 2(2,6\text{-}(CH_3)_2C_5H_3NO)$. In the cases where both isomers are observed there is a significant difference in the amount of the trans present between the tin complexes and the titanium complexes. The isomer distribution has been determined under equilibrium conditions. In the tin complexes the trans present is about 20% at +30° and 30% at −40°. This is in reasonable agreement with statistical considerations. With the titanium complexes only about 3–17% trans is observed at −40°, and at 0° there is no detectable amount of the trans isomer present. There is much less trans present than statistical considerations would predict. This supports the previously suggested stabilization of cis-$TiF_4 \cdot 2D$ by π bonding.[9]

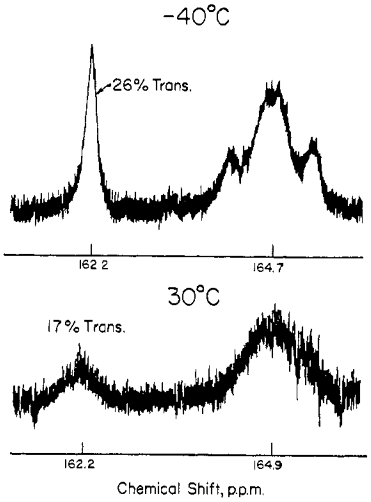

Figure 1.—The $^{19}F$ nmr spectra of *cis*- and *trans*-$SnF_4 \cdot 2(3,4\text{-}(CH_3)_2C_5H_3NO)$ at two temperatures.

The results in Tables I and II seem to fall into two separate groups. The 4-substituted pyridine 1-oxides together with 3-$CH_3$-, 3,4-$(CH_3)_2$-, and 3,5-$(CH_3)_2$pyO 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 $2\text{-}CH_3C_5H_4NO$ to the $2,6\text{-}(CH_3)_2C_5H_3NO$. 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 $TiF_4$ compound was attributed to a steric interaction with bulky ligands.[9]

The $^{119}Sn-^{19}F$ coupling constants were measured where observable. These values are helpful in determining what tin–fluorine type of 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 $SnF_6^{2-}$ on the basis of their chemical shift values. However, the $^{119}Sn-^{19}F$ coupling constant for $SnF_6^{2-}$ is about 1570–1600 cps while the values for $SnF_4 \cdot 2D$ complexes are much higher.[10,11] There is not much variation in the values reported in Table II. The coupling constant does appear to increase as the bulkiness of the ligand increases.

In Figure 1 is a representative spectrum of both the cis and trans isomers. Spectra at both −40 and +30° are given. It is of interest to note (see Table II) that there is almost no change in chemical shift with temperature. 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 $TiF_4\cdot 2D$ compounds.[14] The half-height width of the trans peak for the spectra shown is 10 Hz at $-40°$ and 32 Hz at $+30°$, while for the $TiF_4\cdot 2D$ complexes, where D represents the 2-$CH_3$-, 2,4-$(CH_3)_2$-, and 2-$C_2H_5$-substituted pyridine 1-oxides, the values at $-40°$ are 18, 46, and 29 Hz, respectively. At $+30°$ there are no measurable spectra for these titanium complexes indicating that exchange has made the signals unobservable. Comparison of the data indicates the exchange processes for the $SnF_4\cdot 2D$ molecules are slower.

The difference in the above exchange can be explained by considering that the mechanism of exchange proposed for the $TiF_4\cdot 2D$ adducts[14] is applicable to tin. The first step involves dissociation followed by intra-

$$MF_4\cdot 2D \rightleftharpoons MF_4\cdot D + D$$

molecular rearrangement in the $MF_4\cdot D$ species and then recombination with a base molecule. The difference can then be rationalized if stronger bonds are formed between tin and the oxygen donor than those formed with titanium. Infrared studies have indicated that the metal–oxygen stretching frequency for $TiF_4$ diadducts with pyridine 1-oxides[15] is probably in the region below 300 $cm^{-1}$ while the $SnF_4$ diadducts[16,17] are 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.

The previous discussion here suggests several hypotheses. First, in the $SnF_4\cdot 2D$ complexes the steric nature of the ligand seems 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-oxides are the same, yet the $pK_a$ values are quite different. Second, previous studies have suggested strongly that fluorine-to-metal $\pi$ bonding is important in $TiF_4\cdot 2D$ type complexes and explains the sensitivity of the $^{19}F$ chemical shifts to changing substitutents and also the lack of formation of the trans isomer with many ligands.[8,9] One would expect in the case of tin that fluorine-to-tin $\pi$ bonding would be unimportant since the 2p fluorine orbital would have to overlap with appropriate 5d tin orbitals, and the two sets of orbitals are poorly matched energetically. If there is little fluorine-to-tin $\pi$ bonding and some fluorine-to-titanium $\pi$ bonding, one would expect the $SnF_4\cdot 2D$ resonances to occur upfield from the $TiF_4\cdot 2D$ resonances. Increased fluorine-to-metal $\pi$ bonding will increase the paramagnetic contribution to the chemical shift and cause a downfield shift.[18] Fluorine shielding is very sensitive to small intramolecular perturbations in the fluorine atom $\pi$-charge density produced by para substituents.[19] The resonances for the $TiF_4\cdot 2D$ complexes appear in the region below $-120$ ppm[9] whereas the $SnF_4\cdot 2D$ complexes are in the region above $+150$ 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. Further support for the $\pi$-bonding interpretation comes from a consideration of some preliminary work with $BF_3\cdot$4-ZpyNO adducts.[20] The chemical shifts for this series occur in the range 154.3–153.5 ppm. In four-coordinate complexes boron does not have available any empty low-energy orbitals with which the fluorines can $\pi$ bond. A difference in $\pi$ bonding between tin and titanium also explains the stereochemical data. The cis isomer would be stabilized more for the titanium complexes than for complexes with tin. Where both cis and trans isomers occur with titanium, only the trans isomer occurs with tin; where only the cis isomer is observed with titanium, both isomers are observed with tin.

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