In comparing the conformers of $N_2(CF_3)_4$ with N_2F_4, the electronegativity of the CF_3 group is somewhat less ($\sim$3.2) than that of the fluorine atom (4.0) which would favor the gauche conformer. In addition, the short N–N bond length of 1.40 Å in $N_2(CF_3)_4$ relative to the N–N bond length of 1.49 Å in N_2F_4 favors the gauche isomer. Thus, one can rationalize the 100% gauche conformer for $N_2(CF_3)_4$ compared to a 47% gauche in N_2F_4 on the basis of the electronegativity and the X–X bond lengths. Even though the CF_3 group is quite large and expected to lead to a large steric interaction, the exchange forces dominate in the $N_2(CF_3)_4$ molecule because of the short N–N bond length.

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Stereochemistry of Octahedral Titanium(IV) Complexes. II. The Titanium Tetrachloride–Titanium Tetrafluoride–1,2-Dimethoxyethane System

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Low-temperature fluorine-19 magnetic resonance spectra of solutions containing titanium tetrachloride, titanium tetrafluoride, and 1,2-dimethoxyethane (DME) have shown that halogen redistribution occurs to produce all possible octahedral mixed-halide complexes containing a single cis-chelated DME. Complexes containing more than one DME were not observed. Isomer ratios were determined and compared with those previously observed for similar complexes formed in the $TiCl_4$–TiF_4–tetrahydrofuran (THF) system. Isomers containing a minimum number of chlorine atoms oriented trans to the oxygen donor are favored in the DME system whereas isomers containing a maximum of this chlorine orientation are favored in the THF system. It is suggested that significant steric interaction between THF groups and cis-oriented chlorine atoms favors isomers with chlorine atoms oriented trans to THF. In the absence of such steric interaction, the preferred orientation is with fluorine atoms trans to the oxygen donor. This is presumably due to the enhanced π-bonding ability of a fluorine with this orientation. The following information was determined for each of the observed complexes at $-60°$ in excess DME: $TiF_4 \cdot DME$, only isomer I (Figure 2) was observed with δ_{FF} 74 ppm and J_{FF} = 40 Hz; $TiClF_3 \cdot DME$, isomer IV with fluorine trans to DME predominated with δ_{FF} 74 ppm and J_{FF} = 52 Hz, isomer III with chlorine trans to DME was present in much lower concentration with δ_{FF} 82 ppm and J_{FF} = 36 Hz; $TiCl_2F_2 \cdot DME$, isomer VI with both fluorines trans to DME predominated, isomer X with one fluorine and one chlorine oriented trans to DME was of intermediate concentration with δ_{FF} 83 ppm and J_{FF} = 48 Hz, isomer VII with both chlorines trans to DME was present in very low concentration; $TiClF_3 \cdot DME$, isomer XI with one fluorine and one chlorine trans to DME predominated, isomer XII with two chlorines trans to DME was present in low concentration.

Introduction

In a previous paper,[1] the stereochemistry of a new series of octahedral titanium(IV) complexes was discussed. These complexes were formed by halogen exchange between titanium tetrafluoride and titanium tetrachloride in excess tetrahydrofuran to give complexes of the type $TiCl_xF_{4-x} \cdot 2THF$. A total of 15 distinct octahedral species could exist for this system if all possible geometric isomers were formed. Fluorine-19 nmr spectroscopy could theoretically detect 13 of these species. The ^{19}F nmr spectra showed the presence of only five species. Of these the stereochemistry was ascertained for three, and certain structural limitations were suggested for the remaining two. In that paper it was suggested that fluorine and chlorine undergo a similar degree of π bonding to titanium, which is considerably greater than the π-bonding ability of a THF molecule.

In an attempt to obtain additional stereochemical information about similar complexes and to reduce the complexity of the system previously studied, a bidentate chelating agent, 1,2-dimethoxyethane (DME), has now been used in place of THF. Muetterties[2] and

Clark and Errington[3] have previously examined DME complexes of both TiF_4 and $TiCl_4$. Only 1:1 complexes were isolated. For the $TiCl_4 \cdot DME$ complex, the DME was shown to coordinate through both oxygens to form a cis-chelate complex.[3] If only cis-chelated structures are considered, the number of possible species for the $TiCl_4$–TiF_4–DME system is reduced to nine, eight of which contain fluorine. In this paper we present our interpretation of the ^{19}F nmr spectra obtained for the above system and the probable stereochemistry of the species observed.

Experimental Section

Reagents.—All liquid reagents were distilled under nitrogen from suitable drying agents into flame-dried storage ampoules. Titanium tetrafluoride (Ozark-Mahoning) was used as obtained. Titanium dichloride difluoride was prepared by the direct reaction of titanium tetrachloride and titanium tetrafluoride.[1,4] All reagents were stored in tightly sealed containers in a drybox under nitrogen and were used as soon as possible after their purification.

Preparation of Titanium Halide Complexes.—The $TiCl_4 \cdot DME$ complex was easily prepared by the combination of 1 M solutions of $TiCl_4$ and DME in benzene at room temperature. The bright yellow precipitate instantly formed and the solution was decanted. The crystals were washed with benzene and dried under

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(1) R. S. Borden and R. N. Hammer, *Inorg. Chem.*, **9**, 2004 (1970).

(2) E. L. Muetterties, *J. Amer. Chem. Soc.*, **82**, 1082 (1960).
(3) R. J. H. Clark and W. Errington, *Inorg. Chem.*, **5**, 650 (1966).
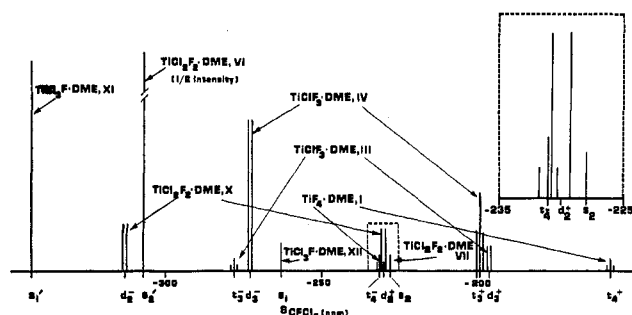(4) R. S. Borden, Ph.D. Thesis, Michigan State University, 1967.

Figure 1.—Fluorine-19 nmr spectrum of 2 M $TiCl_2F_2 \cdot DME$ at $-60°$. Chemical shift values are given in ppm from the external reference CCl_3F. The Roman numeral after each formula indicates the assigned structure from Figure 2.

a nitrogen stream. The analysis for $TiCl_4 \cdot DME$ follows. *Anal.* Calcd for $TiCl_4 \cdot C_4O_2H_{10}$: Ti, 17.12; Cl, 50.68; C, 17.17; H, 3.60. Found: Ti, 17.07; Cl, 50.75; C, 16.78; H, 3.58.

The $TiF_4 \cdot DME$ complex was rather difficult to isolate and often appeared as an oil which could not be crystallized. The following method has proved satisfactory. Titanium tetrafluoride is slowly added to DME at $-60°$ with stirring to prepare a 2 M solution. The exothermic process generally raises the solution temperature to near room temperature. In a good preparation the solution should be light pink to colorless. If the TiF_4 is added too quickly, the solution will become a darker red. The solution is then cooled to between -60 and $-80°$ where the $TiF_4 \cdot DME$ complex crystallizes out. Excess solution is decanted from the complex and the complex recrystallized from fresh DME until the supernatant liquid appears colorless. The complex is finally collected by filtering and drying under nitrogen. The analytical data for the complex $TiF_4 \cdot DME$ are as follows. *Anal.* Calcd for $TiF_4 \cdot C_4O_2H_{10}$: F, 35.51; C, 22.45; H, 4.71. Found: F, 34.86; C, 21.36; H, 4.81.

Preparation of Nmr Samples.—Solutions for the nmr study were prepared by slowly adding $TiCl_2F_2$ or known ratios of $TiCl_4$ and TiF_4 to an excess of DME at $-65°$ and allowing the mixture to warm to room temperature. Samples prepared with methylene chloride as the solvent were obtained by adding known ratios of the $TiCl_4 \cdot DME$ and $TiF_4 \cdot DME$ complexes to methylene chloride at room temperature. All operations were carried out in a drybox under a dry nitrogen atmosphere.

Fluorine-19 Magnetic Resonance Spectra.—Low-temperature ^{19}F nmr spectra were obtained with a Varian Associates A-56/60A spectrometer operating at 56.4 MHz. Chemical shift values are given in ppm downfield from the reference standard CCl_3F. The fluorine-19 magnetic resonance region from -350 to -100 ppm was investigated.

Results

Fluorine-19 Magnetic Resonance Spectra.—The low-temperature spectra obtained for samples prepared from $TiCl_2F_2$ or equimolar mixtures of $TiCl_4$ and TiF_4 were identical. The same fluorine magnetic resonances also were observed with either excess DME or CH_2Cl_2 as the solvent. A small difference was noted for the chemical shift for certain resonances and there also appeared to be a slight difference in peak intensities for the spectra obtained in the two solvents. Figure 1 represents the spectra obtained for 2 M $TiCl_2F_2$ in DME at $-60°$. These data are tabulated in Table I along with the structural assignments from Figure 2 which will be discussed in the next section. Table II gives a similar compilation of fluorine-19 nmr data for 2 M $TiCl_2F_2 \cdot DME$ in methylene chloride at $-60°$.

Several spectra were obtained for samples where the chlorine to fluorine ratio was varied. For a Cl:F ratio of 3:1 the resonances designated s_1 and s_1' were enhanced at the expense of the other resonances. For a Cl:F ratio of 1:3 the resonances designated t_4^+, t_4^-, d_3^+, t_3^-, t_3^+, and d_3^- were increased in intensity. The

TABLE I
^{19}F NMR ASSIGNMENTS, COUPLING CONSTANTS, AND CHEMICAL SHIFT VALUES FOR THE TITANIUM(IV) CHLORIDE FLUORIDE DME COMPLEXES IN DME AT $-60°$

Compd, assignment	Peak designation	Peak ratios	J_{FF}, Hz	δ_{FF}, ppm	$-\delta_{CCl_3F}$, ppm
$TiF_4 \cdot DME$, I	t_4^+	1	40	74	157
	t_4^-	1	40		231
$TiClF_3 \cdot DME$, III	d_3^+	2	36	82	196
	t_3^-	1	36		278
$TiClF_3 \cdot DME$, IV	t_3^+	1	52	74	199
	d_3^-	2	52		273
$TiCl_2F_2 \cdot DME$, VI	s_2'				307
$TiCl_2F_2 \cdot DME$, VII	s_2				228
$TiCl_2F_2 \cdot DME$, X	d_2^+	1	48	83	230
	d_2^-	1	48		313
$TiCl_3F \cdot DME$, XI	s_1'				343
$TiCl_3F \cdot DME$, XII	s_1				258

TABLE II
^{19}F NMR ASSIGNMENTS, COUPLING CONSTANTS, AND CHEMICAL SHIFT VALUES FOR THE TITANIUM(IV) CHLORIDE FLUORIDE DME COMPLEXES IN METHYLENE CHLORIDE AT $-60°$

Compd, assignment	Peak designation	Peak ratios	J_{FF}, Hz	δ_{FF}, ppm	$-\delta_{CCl_3F}$, ppm
$TiF_4 \cdot DME$, I	t_4^+	1	40	84	154
	t_4^-	1	40		238
$TiClF_3 \cdot DME$, III	d_3^+	2	36	89	192
	t_3^-	1	36		281
$TiClF_3 \cdot DME$, IV	t_3^+	1	52	81	196
	d_3^-	2	52		277
$TiCl_2F_2 \cdot DME$, VI	s_2'				311
$TiCl_2F_2 \cdot DME$, VII	s_2				222
$TiCl_2F_2 \cdot DME$, X	d_2^+	1	48	93	223
	d_2^-	1	48		316
$TiCl_3F \cdot DME$, XI	s_1'				344
$TiCl_3F \cdot DME$, XII	s_1				251

spectrum of the $TiF_4 \cdot DME$ complex was also obtained in both excess DME and in methylene chloride. In both spectra the only resonances observed were t_4^+ and t_4^-.

Discussion

Interpretation of Spectra and Structural Assignments. —Previous studies on the $TiCl_4$–TiF_4–tetrahydrofuran system[1] and on numerous complexes of the types $TiF_4 \cdot 2$(donor),[5-7] $TiF_5 \cdot$donor$^-$,[8] and $SnF_4 \cdot 2$(donor)[9] have indicated that fluorine chemical shift values are influenced to a considerable extent by the nature of the ligand trans to the fluorine under consideration. It appears that a fluorine trans to another fluorine or chlorine has a resonance at considerably higher field strength than a fluorine trans to an oxygen donor such as DME or tetrahydrofuran. This phenomenon has been tentatively attributed to the ability of the fluorine and the ligand trans to it to form π bonds with the ti-

(5) D. S. Dyer and R. O. Ragsdale, *Chem. Commun.*, 601 (1966).
(6) D. S. Dyer and R. O. Ragsdale, *Inorg. Chem.*, **6**, 8 (1967).
(7) D. S. Dyer and R. O. Ragsdale, *ibid.*, **8**, 1116 (1969).
(8) R. O. Ragsdale and B. B. Stewart, *ibid.*, **2**, 1002 (1963).
(9) R. O. Ragsdale and B. B. Stewart, *Proc. Chem. Soc., London*, 194 (1964).
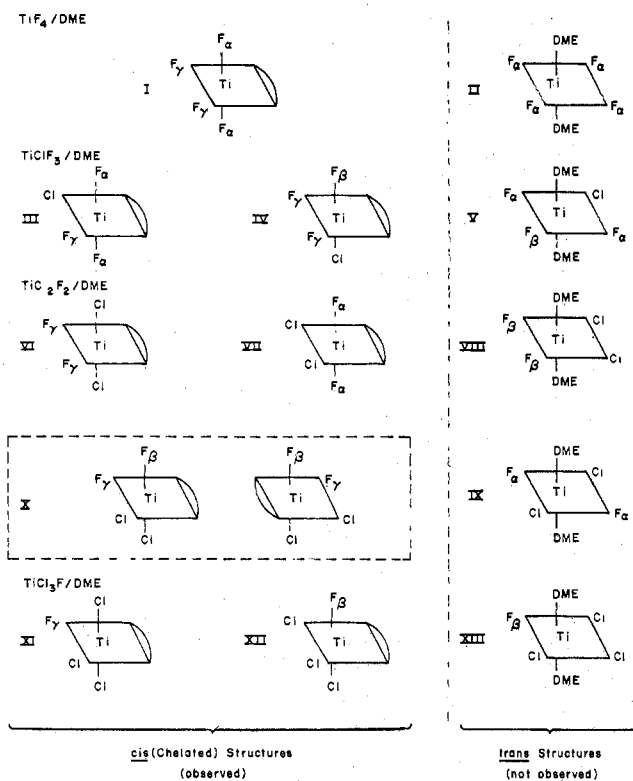
Figure 2.—Possible octahedral structures formed by halogen exchange in the $TiCl_4$–TiF_4–DME system.

tanium.[1,7] Presumably there is competition between the fluorine and the trans ligand for the same titanium d orbital. If the ligand is a weak π-bonding donor, the trans fluorine may undergo considerable π bonding, resulting in its being deshielded and in the appearance of its resonance at lower field strength. Whether or not this theory will adequately explain future experimental observations remains to be seen. For the present study there appears to be sufficient experimental evidence to suggest that for a given complex, the resonance of a fluorine trans to another fluorine or chlorine should appear at higher field strength than the resonance of a fluorine trans to a DME group. Previous studies[1] also suggest that as chlorine replaces fluorine in a series of mixed chloride fluoride titanium(IV) complexes, the resonance of a given fluorine type can be expected to move to lower field strength.

Figure 2 shows the possible octahedral structures for the compounds that could be formed by halogen exchange in the system under investigation. The various fluorine types are indicated by F_α, F_β, and F_γ corresponding to fluorines trans to fluorine, chlorine, and DME, respectively. There is considerable evidence to suggest that structures involving trans DME groups are not present and they are included in Figure 2 for reference only. Muetterties[2] was able to isolate only the TiF_4·DME complex and reported that it is monomeric. Clark and Errington[3] found from infrared studies that $TiCl_4$·DME involves chelation through both ether oxygens. Their attempts to coordinate a second DME group by reaction with excess DME proved unsuccessful. Our study also indicates that only 1:1 complexes are found with DME. The same

resonances were observed both in excess DME and in methylene chloride where the Ti:DME ratio was 1:1, which strongly supports this contention.

The possibility of binuclear complexes containing bridging DME groups, such as TiF_4·2DME·TiF_4, cannot be positively ruled out. Such complexes probably do exist but with half-lives too short to permit detection by nmr spectroscopy. If bridging complexes could be observed, it is reasonable to expect that additional resonances resulting from heterobinuclear complexes, such as TiF_4·2DME·$TiCl_4$ and the cis-chelated complexes, would be present. Such resonances are not observed. Since all resonances can be assigned to 1:1 cis-chelated complexes and since these complexes are expected to be inherently more stable than binuclear complexes or 1:2 complexes, these alternative structures will not be considered further.

From the spectral data, Figure 1 and Table I, the resonances designated $t_4{}^+$ and $t_4{}^-$ can be assigned to TiF_4·DME structure I. This structure is expected to give rise to two equal-intensity triplets with the higher field triplet, $t_4{}^+$, appearing at higher field than any other resonance. This assignment is confirmed by examining the spectra of the pure TiF_4·DME complex which shows only the presence of $t_4{}^+$ and $t_4{}^-$.

Both $TiClF_3$·DME isomers should give rise to a doublet–triplet combination in a 2:1 intensity ratio. In structure III, the γ fluorine gives rise to the triplet which is expected at lower field than the doublet arising from the α fluorines. The γ fluorines of structure IV, however, should appear as a low-field doublet with the higher field triplet being due to the β fluorine. If structure V were present, it would be expected to produce a doublet–triplet combination at relatively high field with a peak separation of only a few ppm. Since none of the other structures should give rise to a doublet–triplet combination, the resonances $d_3{}^+$ and $t_3{}^-$ can be assigned to structure III and the resonances $t_3{}^+$ and $d_3{}^-$ are assigned to structure IV. Structure V is not observed. The $TiCl_2F_2$·DME isomers VI and VII should give rise to a low-field and a high-field singlet, respectively, whereas isomer X should appear as a doublet–doublet combination with a 1:1 intensity ratio. The observed doublets $d_2{}^+$ and $d_2{}^-$ are ascribed to β- and γ-fluorine resonances of structure X. The singlet s_2' near the low-field doublet $d_2{}^-$ is ascribed to the γ fluorine of structure VI. The higher field singlet s_2 just above $d_2{}^+$ is attributed to the α fluorine of structure VII. The fact that the resonances s_2', s_2, $d_2{}^+$, and $d_2{}^-$ all arise from $TiCl_2F_2$·DME complexes is confirmed by the fact that their intensity ratios relative to one another remain fairly constant as the Cl:F ratio for the system is varied over a wide range. The two remaining singlets also have a constant ratio but achieve a maximum intensity for a Cl:F ratio of 3:1. These resonances are therefore attributed to isomers of $TiCl_3F$·DME. The lower field singlet s_1' is attributed to the γ-fluorine resonance of isomer XI and the higher field singlet s_1 to the β-fluorine resonance of isomer XII. The existence of the 1:2 complexes (structures VIII, IX, and XIII) is considered very unlikely. If these complexes were present, their fluorine resonance should be absent or at least less intense in methylene chloride than in excess DME. The spectra obtained in excess DME, however, show no additional resonances, and

TABLE III
OBSERVED ISOMER RATIOS AT $-60°$

Compd	Possible structures	Obsd[a] ratio	Compd[1]	Obsd structures	Obsd[a] ratio
TiF$_4$·DME	I		TiF$_4$·2THF	I	
TiClF$_3$·DME	III, IV	1:5	TiClF$_3$·2THF	III	
TiCl$_2$F$_2$·DME	VI, VII, X	25:1:8	TiCl$_2$F$_2$·2THF	VII,[b] X	9:2
TiCl$_3$F·DME	XI, XII	6:1	TiCl$_3$F·2THF	XII[b]	

[a] Observed ratios were estimated from peak height and should be considered as only approximate values. [b] In our earlier article[1] we indicated that one of the TiCl$_2$F$_2$·2THF isomers VII, VIII, or IX was present along with one of the TiCl$_3$F·2THF isomers XII or XIII. On the basis of the present study it now appears more reasonable to exclude the possibility of the trans structures VIII, IX, and XIII.

there does not appear to be a significant change in the ratio between s$_1'$ and s$_1$ or between d$_2^+$ and s$_2$ in the two solvents.

Stereochemical Preferences.—In the present study all possible 1:1 cis-chelated complexes have been observed. The absence of 1:2 complexes is presumably due to their lower stabilities and lower entropies than those of the chelated 1:1 complexes. The formation of the mixed-halide complexes from their parent compounds appears to be a fairly random process. The mole fraction for each of the five compounds was calculated from fluorine nmr intensity data and compared with values calculated assuming random ordering. These values agree within the limits of experimental error except for the TiCl$_3$F·DME complex which appears slightly less stable and the TiCl$_4$·DME complex which appears somewhat more stable than predicted for a randomly ordered system. Similar results were previously reported for the TiCl$_4$–TiF$_4$–THF system.[1] The ratio of the isomers observed for each compound, however, does not correspond to the ratio predicted for random ordering and does not agree with the corresponding ratio observed for isomers of compounds formed in the THF system. The data obtained in the present study are compared with those observed for the TiCl$_4$–TiF$_4$–THF system[1] and are listed in Table III.

It is of particular interest to note that structure IV strongly predominates over structure III for the TiClF$_3$·DME complex, whereas structure IV is not observed for the TiClF$_3$·2THF complex. A similar change in isomer stability is noted for the other complexes. It is observed that structures having a maximum number of γ fluorines are favored in the DME system whereas the THF system favors those cis structures containing a minimum number of γ fluorines. This situation could be due to a difference in the bond strength for the various fluorines in the two systems but most likely results from steric effects. Since γ fluorines can undergo the strongest pπ–dπ interactions, it is expected that structures involving a maximum number of γ fluorines should be the most stable. This is presumably the case for the DME system where little steric interaction is expected. The THF complexes, however, may involve significant steric repulsion between THF groups and chlorine atoms. The least repulsion would be observed for structures involving chlorine groups oriented trans to the THF groups. This arrangement would minimize the number of γ fluorines. Sufficient steric interaction between cis-oriented THF and chlorine could overpower the enhanced stability due to γ fluorines and result in structures involving a minimum number of γ fluorines as has been observed.