stants have been attributed to rehybridization at the carbon atom,[29,30] although with a highly electronegative Y atom in CH_3Y, the effect of changes in the effective nuclear charge of carbon on the 2s orbital appears to make a substantial contribution.[31] The data for the six dimethylmetal ions and molecules are illustrated in Figure 7 which shows that an increase in $^1J(^{13}C\text{–}H)$ is paralleled by an increase in $K(C\text{–}H)$, the valance stretching force constant. There is no obvious correlation with what would be expected for the orbital electronegativities of the metals; *e.g.*, the coupling constant is greater with lead than with tin and greater with thallium than with indium. Because the largest coupling constant within an isoelectronic sequence occurs with the dipositive cation, it seems likely that these variations may arise from contraction of the carbon 2s orbital. The charge also would tend to lead to increased ionic character in the C–H bonds, and Brown and Puckett[28] have suggested that this is the primary cause for increase in C–H stretching force constants. As a result of these factors, there is no simple correlation between the metal–carbon bond strengths and the carbon-13–proton–coupling constants or the C–H stretching force constants. The low values for the (C–H) stretching force constants for $(CH_3)_2Cd$ and $(CH_3)_2Hg$ may reflect the fact that they were measured under different conditions than the ions. The relative values for the cations are probably significant to ±0.01 mdyn/Å.

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Stereochemistry of Octahedral Titanium(IV) Complexes. I. The Titanium Tetrachloride–Titanium Tetrafluoride–Tetrahydrofuran System[1]

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Tetrahydrofuran (THF) complexes of titanium tetrachloride and titanium tetrafluoride have been found to undergo a redistribution reaction in excess THF to produce the mixed-halogen complexes. Fluorine-19 magnetic resonance spectra obtained at −60° have been used to establish both the presence of the mixed complexes and in most cases the specific isomer(s) present for each complex. Comparison of rough equilibrium constants calculated from the nmr spectral intensities with those calculated statistically for random ordering shows that the formation of the mixed-halogen complexes is nearly a random process whereas the formation of the specific isomers for a given complex is apparently controlled by other factors. The following information was determined for each of the observed species. $TiF_4\cdot 2THF$: Only the *cis* isomer (I) was observed, with δ_{FF} 60 ppm and $J_{FF} = 38$ Hz. $TiClF_3\cdot 2THF$: Only one isomer was observed with *cis* THF and *trans* fluorine groups (III), with δ_{FF} 67 ppm and $J_{FF} = 33$ Hz. $TiCl_2F_2\cdot 2THF$: Two isomers were observed. One contains similar ligands *cis* (X), with δ_{FF} 76 ppm and $J_{FF} = 45$ Hz. The structure of the second isomer remains in doubt. $TiCl_3F\cdot 2THF$: The only isomer observed for this compound is believed to contain the fluorine *trans* to a chlorine (XII or XIII).

Introduction

The stereochemistry of a number of titanium(IV) octahedral complexes has been previously examined. A number of titanium tetrafluoride complexes have been studied by low-temperature fluorine-19 magnetic resonance.[3-9] In a recent article by Dyer and Ragsdale[9] the factors responsible for the *cis* or *trans* orientation of the donor molecules for complexes of the type $TiF_4\cdot 2$(donor) are summarized. They suggested that the *cis* isomer is favored by the tendency to maximize pπ–dπ bonding and symmetry effects and that the *trans* isomer only exists when these factors can be overcome by steric interactions (bulky donor groups). A number of dihalobis(β-diketonato)titanium(IV) complexes also have been studied by Fay, *et al.*,[10,11] and were found to contain *cis* halides. The factors responsible for the preference of *cis* halides were not discussed.

We have prepared a series of mixed-halide complexes which may provide additional insight into the nature of

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[1] Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.
[2] (a) Taken in part from the Ph.D. Thesis of Robert S. Borden, Michigan State University, 1967. (b) Wittenberg University. (c) Michigan State University.
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[10] R. C. Fay and R. N. Lowry, *ibid.*, **6**, 1512 (1967).
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octahedral stereochemistry. Halogen exchange has been observed between titanium tetrafluoride and other titanium tetrahalides in suitable donor solvents such as tetrahydrofuran (THF). The resulting solutions contain in addition to the parent complexes the three possible mixed-halide complexes. Fifteen distinct geometric forms could exist for these octahedral complexes containing two donor molecules if geometric isomers are considered. Fluorine-19 nmr spectroscopy could conceivably detect 13 of these species and provide some knowledge of the geometric form of each species. We have found that it is generally possible to identify each mixed-halide complex and in most cases to ascertain the actual stereochemistry of each isomer observed. It is also possible to obtain from the nmr data equilibrium constants which, when compared with those calculated statistically for random ordering, give useful information about the preferred geometries of the resulting species. In this paper we report our findings for the $TiCl_4$–TiF_4–THF system.

Experimental Section

Reagents.—Titanium tetrachloride (J. T. Baker, Purified) was distilled under nitrogen into a flamed-out storage ampoule. Titanium tetrafluoride (Alfa Inorganics, 97% purity) was sublimed into a stream of dry nitrogen (80 ml/min) in a flamed-out Pyrex tube at 200–250°.[12] Titanium chloride trifluoride, $TiClF_3$, and titanium dichloride difluoride, $TiCl_2F_2$, were prepared by the direct reaction of titanium tetrachloride and titanium tetrafluoride. The preparation and properties of these substances are described elsewhere.[13] Tetrahydrofuran (reagent grade) was distilled under nitrogen from lithium aluminum hydride into a flamed-out glass ampoule. All reagents were stored in tightly sealed containers in a drybox under dry nitrogen and were used as soon as possible after their purification.

Preparation of Nmr Samples.—Solutions for the nmr study were prepared by slowly adding to a known volume of tetrahydrofuran at −65° either a known amount of titanium tetrachloride or titanium tetrafluoride or a known weight of titanium dichloride difluoride or titanium chloride trifluoride.[14]

Preparation of solutions and loading of the standard thin-wall 5-mm nmr sample tubes was accomplished in a drybox under nitrogen sufficiently dry that titanium tetrachloride could be handled for prolonged periods without observable fuming. The low solubility of $TiCl_4 \cdot 2THF$ in tetrahydrofuran limited work to moderately dilute solutions. With less than rigorously anhydrous conditions, samples decomposed slowly to produce a brown-black precipitate, whereas those prepared under the most anhydross conditions appeared to be stable indefinitely.

Fluorine-19 Magnetic Resonance Spectra.—Fluorine-19 magnetic resonance spectra were obtained with a Varian Associates HA-100 high-resolution spectrometer operating at 94.1 MHz. Trichlorofluoromethane was employed both as internal and as external reference standard. Chemical shift values are given in ppm from the reference standard and are considered to be negative in sign when the indicated resonance appears at lower field than the reference standard. The fluorine-19 magnetic resonance region from −430 ppm to +355 ppm from trichlorofluoromethane was investigated. All observed fluorine-19 magnetic resonances were downfield from trichlorofluoromethane in the region between −310 and −160 ppm.

Results and Discussion

Interpretation of Spectra. Titanium Tetrafluoride–Tetrahydrofuran.—At room temperature the fluorine-19 magnetic resonance spectrum showed a single broad resonance peak at about −197 ppm from the external reference CCl_3F. As the sample temperature was reduced, this peak first broadened and then separated into two singlets. At −50° the singlets began to split into triplets and at −60° these were well resolved. Chemical shift and coupling constant data at −60° are shown in Table I. In addition to this pair of equal-intensity triplets, a small peak was observed ~12 ppm upfield from the high-field triplet.

TABLE I

^{19}F NMR PEAK ASSIGNMENTS, COUPLING CONSTANTS, AND CHEMICAL SHIFT VALUES FOR THE TITANIUM(IV) CHLORIDE FLUORIDE–TETRAHYDROFURAN COMPLEXES AT −60°

Compd	Peak designation	Compd intens ratios	J_{FF}, Hz	δ_{FF}, ppm	δ_{CCl_3F}, ppm
$TiF_4 \cdot 2THF$	t_4^-	1	37.6	60	−223
	t_4^+	1	37.7		−163
$TiClF_3 \cdot 2THF$	t_3^-	1	33.1	67	−267
	d_3^+	2	33.1		−200
$TiCl_2F_2 \cdot 2THF$	s_2	. . .	. . .	. . .	−232
$TiCl_2F_2 \cdot 2THF$	d_2^-	1	45	76	−304
	d_2^+	1	45		−228
$TiCl_3F \cdot 2THF$	s_1	. . .	. . .	. . .	−253

The two possible octahedral $TiF_4 \cdot 2THF$ isomers are shown in Figure 1. The two triplets are ascribed to the *cis*-$TiF_4 \cdot 2THF$ isomer (I). This assignment is in agreement with the previous work of Muetterties.[3] We originally attributed the small peak to the *trans* isomer II, but subsequent work has shown that this peak is due to very slight hydrolysis of the *cis*-$TiF_4 \cdot 2THF$ complex.[15]

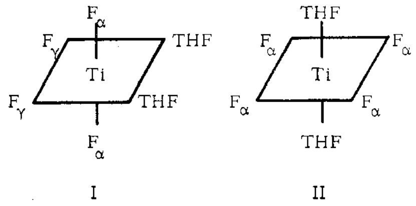

Figure 1.—Possible octahedral isomers for $TiF_4 \cdot 2THF$.

Interpretation of Spectra. Titanium Tetrachloride–Titanium Tetrafluoride–Tetrahydrofuran.—The low-temperature spectra obtained for tetrahydrofuran solutions prepared from either titanium(IV) chloride fluorides or mixtures of titanium tetrachloride and titanium tetrafluoride showed the same fluorine-19 resonances. The intensity of these resonances varied depending upon the chlorine to fluorine ratio of the sample. Figure 2 shows the resonances observed for 1.0 *M* $TiCl_2F_2$–THF. At room temperature these samples showed only a rough base line. At −60° all the samples gave a

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[12] Attempts to purify titanium tetrafluoride by vacuum sublimation proved unsatisfactory because the sublimate formed a glassy solid which could not be removed conveniently from the cold finger.

[13] R. S. Borden, Ph.D. Thesis, Michigan State University, 1967.

[14] Addition of any of the titanium halides to tetrahydrofuran even at −65° resulted in a vigorous reaction. At room temperature the quick addition of titanium tetrafluoride to tetrahydrofuran produced a dark red solution.

[15] D. S. Dyer, R. S. Borden, and P. A. Loeffler, unpublished study.

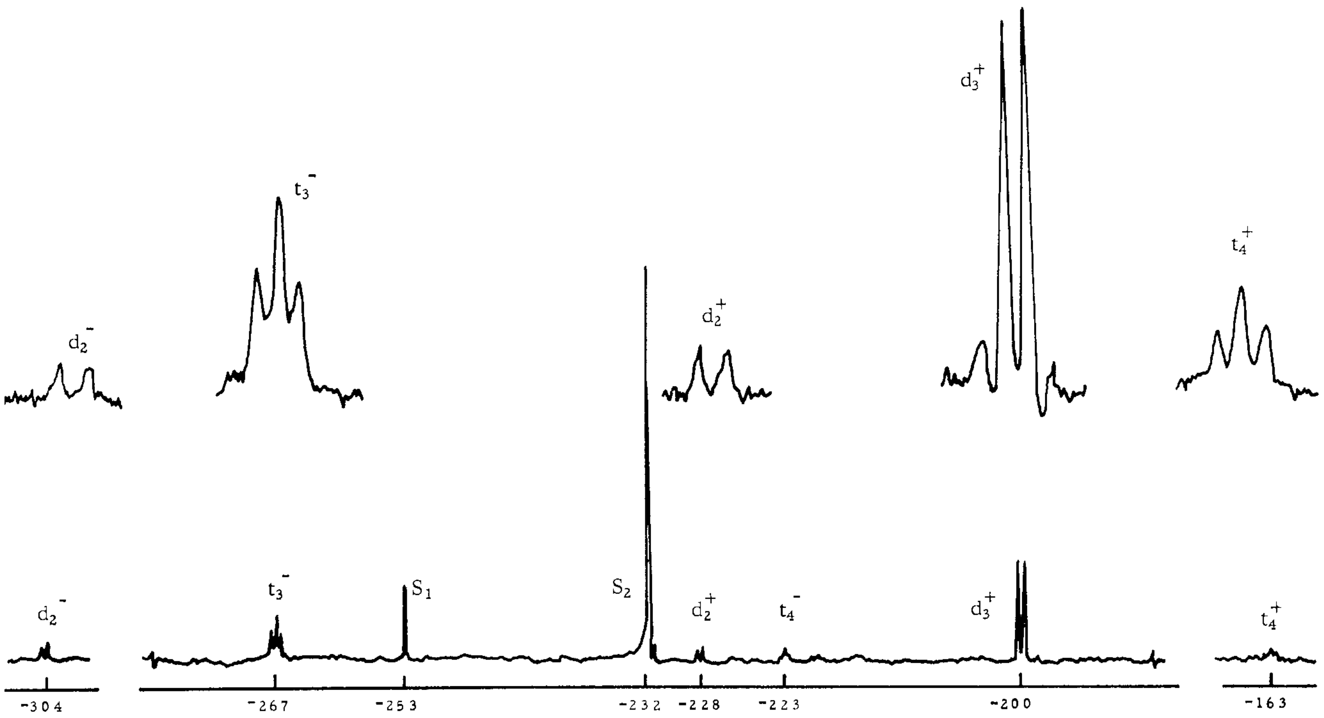
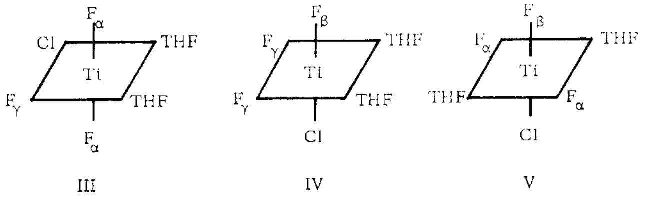


Figure 2.—Fluorine-19 nmr spectrum of 1.0 *M* TiF_2Cl_2–THF at −60°. Chemical shift values are given in ppm from the external reference CCl_3F.

nicely resolved spectrum which indicated the presence of the titanium(IV) chloride fluoride–tetrahydrofuran complexes as well as the titanium tetrafluoride–tetrahydrofuran complex. Table I gives the resonance peak assignments, coupling constants, and chemical shift data for these complexes.

The fluorine-19 resonance assignments were made on the basis of the expected FF coupling pattern and the intensity ratio of the resulting fluorine-19 resonances for each compound. The possible octahedral isomers which could arise for the mixed halide complexes are shown in Figures 3–5.

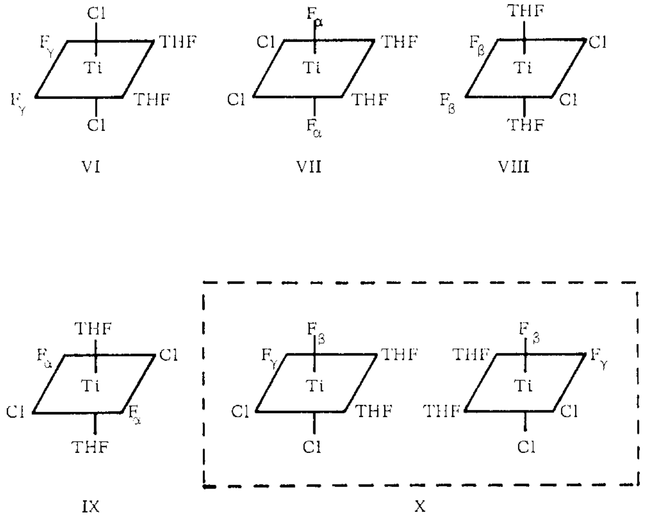


III IV V

Figure 3.—Possible octahedral isomers for $TiClF_3 \cdot 2THF$.

A fluorine atom is designated by F_α if it is *trans* to another fluorine, F_β if *trans* to a chlorine, and F_γ if *trans* to a THF group. These three types of fluorine atoms constitute those in any given isomer that can be distinguished from each other by fluorine-19 magnetic resonance.

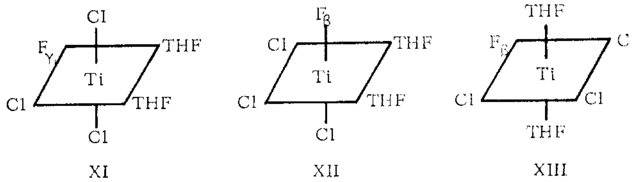
The *cis* isomer of $TiF_4 \cdot 2THF$ (I) contains two pairs of equivalent fluorine atoms, F_α and F_γ. The first-order fluorine-19 magnetic resonance spectrum for this isomer should consist of two equal-intensity triplets. This isomer is identified by the presence of t_4^- and t_4^+ in the spectrum. *trans*-$TiF_4 \cdot 2THF$ (II), which would give rise to a single fluorine-19 resonance, is not observed.



VI VII VIII

IX X

Figure 4.—Possible octahedral isomers for $TiCl_2F_2 \cdot 2THF$.



XI XII XIII

Figure 5.—Possible octahedral isomers for $TiCl_3F \cdot 2THF$.

The first-order spectrum for each $TiClF_3 . 2THF$ isomer should consist of a triplet and a doublet in a 1:2 intensity ratio. The spectrum shows the presence of a triplet, t_3^-, and a doublet, d_3^+, with the same coupling constants and in a 1:2 intensity ratio. Since no other

TABLE II

FLUORINE-19 CHEMICAL SHIFT AND COUPLING CONSTANTS FOR THE $TiCl_xF_{4-x} \cdot 2THF$ ISOMERS PROPOSED FROM A π-BONDING ORDER F $\sim$ Cl > THF

Isomer	$\delta_{F\gamma}$,[a] ppm	$\delta_{F\beta}$,[a] ppm	$\delta_{F\alpha}$,[a] ppm	δ_{FF}, ppm	$J_{F\alpha,F\gamma}$ Hz	$J_{F\beta F\gamma}$, Hz	$\Delta\delta$, ppm
$TiF_4 \cdot 2THF$ (I)	$-223\ t_4^-$	...	$-163\ t_4^+$	60	37.7	...	...
$TiClF_3 \cdot 2THF$ (III)	$-267\ t_3^-$	...	$-200\ d_3^+$	67	33.1	...	44–37
$TiCl_2F_2 \cdot 2THF$ (X)	$-304\ d_2^-$	$-228\ d_2^+$	...	76	...	45	37–27
$TiCl_2F_2 \cdot 2THF$ (VII, VIII, IX)?	...	$-232\ s_2$	...	...	...	...	32
$TiCl_3F \cdot 2THF$ (XII, XIII)?	...	$-253\ s_1$	...	...	...	...	~24

[a] Fluorine-19 chemical shifts measured from $CClF_3$ as external reference at −60°.

compound should give rise to an A_2X pattern, t_3^- and d_3^+ are ascribed to an isomer of $TiClF_3 \cdot 2THF$.

The isomers VI, VII, VIII, and IX of $TiCl_2F_2 \cdot 2THF$ contain two equivalent fluorine atoms and should give rise to a single fluorine-19 resonance. The enantiomorphs Xa and Xb have two dissimilar fluorine atoms and should produce a pair of equal-intensity doublets. Two equal-intensity doublets, d_2^- and d_2^+, with the same coupling constants are observed. The splitting pattern for isomer X is unique among those considered, and d_2^- and d_2^+ are ascribed to this isomer.

Each isomer of $TiCl_3F \cdot 2THF$ could give only a single fluorine-19 resonance. Two single fluorine-19 resonances are observed. The assignment of these was based on intensity measurements obtained for samples where the chlorine to fluorine ratio was varied. From the spectra for these samples it was possible to ascribe the higher field singlet, s_2, to an isomer of $TiCl_2F_2 \cdot 2THF$ and the lower field singlet, s_1, to an isomer of $TiCl_3F \cdot 2THF$. As the ratio of $TiCl_4$ to TiF_4 in the samples increases, the relative intensity of the s_1 resonance, attributed to $TiCl_3F \cdot 2THF$, also increases. The s_2 resonance is observed in all the spectra examined, but its maximum intensity is found for a 1:1 molar ratio of $TiCl_4$ to TiF_4. As the $TiCl_4$ to TiF_4 ratio changes, the expected variation in intensity of the other resonances is observed, thus confirming their previous assignments.

Stereochemistry.—Previous work on titanium and tin tetrafluoride complexes by Ragsdale, Dyer, and Stewart[4–6] suggests that the observed fluorine-19 chemical shifts are dependent upon the degree of fluorine to titanium $p\pi \rightarrow d\pi$ bonding. Titanium(IV) has a $3d^0$ configuration. In octahedral complexes, the d_{xy}, d_{yz}, and d_{xz} orbitals are available for π bonding along the x, y, and z axes. Weak π-bonding groups *trans* to a fluorine would allow for strong $p\pi \rightarrow d\pi$ bonding from fluorine to titanium. This should decrease the fluorine shielding constant and cause a downfield shift in the fluorine-19 magnetic resonance. Fluorines *trans* to a strong π-bonding donor should appear at higher field strength than fluorines *trans* to a weak π-bonding donor.[16]

If one assumes a π-bonding order of F > THF, then for the *cis*-$TiF_4 \cdot 2THF$ isomer (I) the low-field triplet t_4^- would arise from γ fluorine and the high-field triplet t_4^+ from α fluorine. Since the *trans* isomer contains only α fluorine, it should give rise to a single resonance near t_4^+. Where both *cis*- and *trans*-$TiF_4 \cdot 2$(donor) isomers have been observed, the *trans* isomer is found to give a single resonance very near the high-field triplet of the *cis* isomer.[4] For this system the *trans* isomer is not observed.

The other compounds observed all involve three ligands. The π-bonding orders F > Cl > THF and Cl > F > THF both can be used to give a reasonable interpretation of the spectra. Other π-bonding orders cannot be justified on the basis of the observed spectra.[17] It appears from our data that the chemical shift for a fluorine *trans* to another fluorine is about the same as the chemical shift for a fluorine *trans* to a chlorine for the same compound type. This can be seen in Table II where the δ_{FF} value observed for $TiCl_2F_2 \cdot 2THF$, X, with F_β and F_γ fluorines is approximately that which would be expected if the compound contained F_α and F_γ fluorines. The π-bonding order therefore is presumed to be F $\sim$ Cl > THF. For such a π-bonding order and for a given type of compound, fluorine resonances for F_α and F_β would be expected to occur within a few parts per million of each other and considerably upfield from the F_γ resonance.

Only one of the $TiClF_3 \cdot 2THF$ isomers, III, should give the observed low-field triplet and high-field doublet. Isomer IV should give a low-field doublet and high-field triplet and can therefore be eliminated from consideration. Isomer V should show the doublet and triplet very near one another with perhaps second-order effects. The $\delta_{F_\alpha F_\gamma}$ value expected for isomer III should be similar to that observed for *cis*-$TiF_4 \cdot 2THF$ (I) with α and γ fluorines and $\delta_{F_\alpha F_\gamma}$ 60 ppm, whereas the $\delta_{F_\alpha F_\beta}$ value expected for isomer V should be a few parts per million. The observed δ_{FF} value of 67 ppm supports the selection of isomer III.

Two isomers are observed for $TiCl_2F_2 \cdot 2THF$. Isomer X is confirmed by virtue of its unique splitting pattern. The low-field doublet d_2^- should arise from a γ fluorine and the high-field doublet d_2^+ from a β fluorine. The occurrence of the strong singlet s_2 just 4

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[16] The terms "π-bonding order" and "π-bonding strength" actually refer in this paper to the ability of a ligand *trans* to a fluorine to affect the position of that fluorine's magnetic resonance. A strong π-bonding donor is defined for the purpose of this paper as a ligand that will cause a smaller downfield shift in the resonance of a *trans* fluorine than a weak π-bonding donor. It is very convenient to visualize this phenomenon as described in the text, but whether or not π bonding is actually the primary factor responsible for the effect is a consideration beyond the scope of this paper.

[17] The π-bonding order F > THF > Cl was initially used in an attempt to interpret the fluorine-19 spectra. For this π-bonding order the existence of $TiClF_3 \cdot 2THF$, III, $TiCl_2F_2 \cdot 2THF$, VI and X, and $TiCl_3F \cdot 2THF$, XI, is suggested. These assignments and this π-bonding order are, however, rejected because of the inconsistency in the observed chemical shift for fluorines of the same type for the series $TiCl_xF_{4-x} \cdot 2THF$.

ppm downfield from d_2^+ indicates that s_2 arises from either α or β fluorines. To make a finer distinction than this would require a more accurate knowledge of the π-bonding strength of the ligands. For a π-bonding order of $F > Cl \gg THF$, it would be expected that an F_α resonance should appear upfield from d_2^+. The s_2 peak slightly downfield from d_2^+ could then be assigned to the F_β resonance of isomer VIII. If, on the other hand, the π-bonding order were $Cl > F \gg THF$, the F_α resonance would be expected to be downfield from d_2^+, and s_2 could be assigned to an F_α resonance of isomer VII or IX. Reasoning of this type is tenuous since distortions from pure octahedral symmetry undoubtedly cause certain anomalies from that theoretically predicted. It should be noted that the structures which have been established all contain *cis* THF groups. This fact alone is, however, not sufficient to rule out those structures with *trans* THF groups. It does appear safe to rule out the existence of isomer VI.

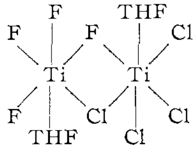
Isomers of $TiCl_3F \cdot 2THF$ give only a single resonance. In systems where π-bonding is possible, fluorine-19 resonances generally shift to lower field strengths as fluorine atoms are replaced with less electronegative atoms. This has been observed for boron fluoride halides,[18] carbon chloride fluorides,[19] and phosphorus(V) chloride fluorides.[20] As fluorine atoms are replaced with chlorine atoms in the series $TiCl_xF_{4-x} \cdot 2THF$, the fluorine-19 resonances for fluorines of the same type also appear to move to lower field strengths. If the observed resonance s_1 for $TiCl_3F \cdot 2THF$ resulted from a β fluorine, a reasonable decrease of approximately 24 ppm is observed for the chemical shift between the β fluorines of $TiCl_2F_2 \cdot 2THF$, X, and $TiCl_3F \cdot 2THF$. If, however, s_1 arose from a γ fluorine, s_1 would appear at approximately 50 ppm upfield from the γ-fluorine resonance of $TiCl_2F_2 \cdot 2THF$, X. The expected decrease in the chemical shift as fluorines are replaced with chlorines in the series $TiCl_xF_{4-x} \cdot 2THF$ is only maintained by ascribing the s_1 resonance to a β fluorine of isomer XII or XIII. If isomer XI were present, it would be expected to exhibit a single resonance approximately 85 ppm downfield from the s_1 resonance observed. No resonance is, however, observed in this region and isomer XI is therefore ruled out. Table II lists the $TiCl_xF_{4-x} \cdot 2THF$ isomers which are believed to be present on the basis of the observed fluorine-19 magnetic resonance and for a π-bonding order of $F \sim Cl > THF$.

Halogen Exchange.—Donor molecule exchange in $TiF_4 \cdot 2$(donor) complexes has been known for some time.[3,6,7] Halogen exchange, however, has not been extensively studied. Fay and Lowry[10] have shown that halogen exchange takes place for dihalobis(acetylacetonato)titanium(IV) compounds. Their work indicates that halogen exchange is slower than the rate of exchange of methyl groups between nonequivalent environments. In our study we made no attempt to measure exchange rates but we can report that an equilibrium condition appeared to exist by the time the solutions for the nmr study were prepared.

There are a number of possible mechanisms by which halogen exchange can take place in octahedral complexes. The bridging mechanism

$$TiF_4 \cdot 2THF \xrightleftharpoons[+THF]{-THF} TiF_4 \cdot THF$$

$$TiF_4 \cdot THF + TiCl_4 \cdot 2THF \xrightleftharpoons[+THF]{-THF}$$



$$\xrightleftharpoons[-THF]{+THF} TiClF_3 \cdot 2THF + TiClF_3 \cdot THF$$

$$TiCl_3F \cdot THF \xrightleftharpoons[-THF]{+THF} TiCl_3F \cdot 2THF$$

is favored.[21] Six equilibrium equations are required to describe all the ways that two components can react by the above mechanism to produce new compounds.

Equilibrium Constants.—Equilibrium constants for the formation of the mixed-halide complexes from their parent halides have been calculated from fluorine-19 nmr intensity data. Difficulties encountered in preparing nmr samples with accurately known chlorine to fluorine ratios, coupled with the problem of obtaining accurate nmr intensity data for widely separated peaks, resulted in average values that were subject to considerable error. The difference in the free energy of reaction calculated from these equilibrium constants and the free energy changes expected for random ordering was found in each case to be less than 0.4 kcal/mol for each of the mixed-halide complexes. It therefore appears that the formation of the mixed-halide complexes from their parent compounds is very nearly that expected for a randomly ordered system; the formation of the isomers for each of the complexes, however, is clearly not a random process. Table III lists the isomer ratios expected for random ordering and those actually observed.

TABLE III

STATISTICAL[a] AND EXPERIMENTAL ISOMER RATIOS

Compound	Possible structures	Statistical[a] ratio	Obsd structures	Obsd ratio
$TiF_4 \cdot 2THF$	I, II	4:1	I	. . .
$TiClF_3 \cdot 2THF$	III, IV, V	2:2:1	III	. . .
$TiCl_2F_2 \cdot 2THF$	VI, VII, VIII, IX, X	2:2:1:8	(VII, VIII, IX)[b]:X	9:2
$TiCl_3F \cdot 2THF$	XI, XII, XIII	2:2:1	XII or XIII	. . .

[a] Calculated on the basis of a random distribution of ligands around a single titanium atom. [b] Only one of the isomers VII, VIII, and IX was present. The actual structure of the isomer present has not been determined.

The factors responsible for stereochemical preferences in octahedral complexes are at present not clear. It is

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(18) T. D. Coyle and F. G. A. Stone, *J. Chem. Phys.*, **32**, 1892 (1960).

(19) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

(20) R. R. Holmes, R. P. Carter, and G. E. Peterson, *Inorg. Chem.*, **3**, 1748 (1964); R. P. Carter and R. R. Holmes, *ibid.*, **4**, 738 (1965).

(21) A second plausible mechanism involves acid-catalyzed halide exchange. Attempts were made to exclude this possibility, but because of the nature of the reactants, elimination of catalytic amounts of acid is nearly impossible. The presence of HF was not observed by ^{19}F nmr for any of the samples investigated, but the observation of very small amounts would not be expected. E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **81**, 1084 (1959), have suggested that acid-catalyzed fluoride exchange may be responsible for the line broadening of the ^{19}F resonance observed for some fluoro anions.

expected that when additional data are obtained for systems similar to those described in this paper, these factors will become more evident.

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Heteropolyvanadomanganates(IV) with Mn:V = 1:11 and 1:4

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Two new vanadomanganate(IV) heteropoly complexes have been prepared by reaction of manganese(II), peroxydisulfate, and isopolyvanadate(V) ions. One complex, isolated as $K_5MnV_{11}O_{32} \cdot 10H_2O$, $Cs_{4.5}H_{0.5}MnV_{11}O_{32} \cdot 7H_2O$, and $(NH_4)_{4.5}H_{0.5}MnV_{11}O_{32} \cdot 12H_2O$ (all red to dark red crystals) is moderately stable in solutions of pH 2–3. In the pH range 4–6 it reacts to give high yields of 13-vanadomanganate(IV), accompanied by some amorphous precipitate and at least one other complex in low yields. The second complex, isolated as $K_5HMn_3V_{12}O_{39} \cdot 10H_2O$ and $(NH_4)_5HMn_3V_{12}O_{39} \cdot 15H_2O$ (black crystals), is also obtained in the pH range 2–3 and apparently exists up to a pH near 6. It is formulated as a trimeric species on the basis of the chemical analyses and single-crystal X-ray data. The 3:12 complex is unexpectedly inert to reaction with excess vanadium(V) to give 1:11 or 1:13 complexes. No visual evidence for heteropoly "blue" species was observed on reduction of the complexes. The 1:13 complex was found to be slightly photosensitive, the decomposition products apparently including the green reduced species. The acid decomposition of vanadomanganates(IV) leads to formation of small quantities of permanganate; similar behavior was noted for 12-niobomanganate(IV).

Introduction

We have recently reported the synthesis and characterization of 13-vanadomanganate(IV) heteropoly complexes, *e.g.*, $K_7MnV_{13}O_{38} \cdot (16\text{–}18)H_2O$.[1] During that investigation it was found that a species with Mn:V = 1:11 is formed on suitable adjustment of the reaction stoichiometry and that this species can be isolated in good yield. It could also be obtained by acidification of solutions of the 1:13 complex, in which vanadium(V) oxide forms as a by-product. A second complex with Mn:V = 1:4 is also obtained along with the 1:11 species. We report here the synthesis and characterization of these complexes. Photosensitivity of the 1:13 complex is also described.

Experimental Section

Reagents.—The preparation of reagents not obtained commercially (potassium metavanadate, sodium pyrovanadate) has been described.[1]

Potassium 11-Vanadomanganate(IV), $K_5MnV_{11}O_{32} \cdot (10\text{–}12)H_2O$.—A hot solution of 7.6 g (55 mmol) of KVO_3 in *ca.* 200 ml of water was treated with 5 ml of 1 *F* HNO_3 followed by 5.0 ml of 1.0 *F* $MnSO_4$ and 2.7 g (10 mmol) of $K_2S_2O_8$. The mixture was stirred and kept at 70–90°. A brown precipitate which formed during the first 10 min (probably $MnV_2O_6 \cdot 4H_2O$) redissolved in 0.5–1 hr. The deep red solution was heated for a further 4–6 hr and allowed to evaporate to a final volume of 30–50 ml. During the final 2-hr period some red-brown precipitate, mainly V_2O_5, separated. The solution was filtered and allowed to cool. After 1 day, dark red crystals mixed with oxide precipitate were obtained. The crude product was recrystallized from a solution 0.3 *F* in K_2SO_4 and 0.2 *F* in $KHSO_4$ to give dark red parallelepiped crystals. The crystals were washed with ethanol–water followed by 95% ethanol and were then air dried. The yield was about 50%. The compound is not efflorescent at moderate humidity. Room-temperature evaporation of the recrystallization solution gave more dark red crystals accompanied by black parallelepiped crystals of a second compound which proved to be the 3:12 compound described below.

The potassium 1:11 salt could also be obtained by treatment of the 1:13 compound with acids. Two grams (*ca.* 1 mmol) of $K_7MnV_{13}O_{38} \cdot 18H_2O$ was dissolved in a mixture of 10 ml of water and 10 ml of 0.3 *F* K_2SO_4–0.2 *F* $KHSO_4$ by heating the mixture nearly to boiling. When the solution was allowed to cool, much starting material recrystallized, indicating that insufficient acid was added. Addition of 0.7 g (5 mmol) of $KHSO_4$ and reheating of the solution led to further reaction. After filtration, the solution was allowed to stand for a few days so that large (3-mm) crystals could be obtained. Since more vanadium(V) oxide also precipitated at this stage, the mixture was reheated and filtered. Pure product subsequently crystallized. The yield was 1.6 g, nearly quantitative based on the reaction

$$MnV_{13}O_{38}^{7-} + 2H^+ \longrightarrow MnV_{11}O_{32}^{5-} + V_2O_5 + H_2O$$

In another experiment (3.708 g of potassium 13-vanadomanganate, 5 mmol of K_2SO_4, 10 mmol of $KHSO_4$, 40 ml of water, heated for 1 hr) the yield of 1:11 compound was 2.160 g, corresponding to 76% of the manganese taken. The solution was still orange red. Further evaporation led to crystallization of K_2SO_4 and decomposition to insoluble orange brown solids. Analytical data for this and most of the following compounds are given in Table I.

Ammonium 11-Vanadomanganate(IV), $(NH_4)_{4.5}H_{0.5}MnV_{11}O_{32} \cdot 12H_2O$.—Synthesis was carried out as above, but with the substitution of the corresponding ammonium compounds for potassium compounds. The product was recrystallized from a solution 0.6 *F* in ammonium sulfate and 0.4 *F* in ammonium bisulfate. Dark red prismatic crystals (up to 1 cm long) were obtained when the solution was evaporated at room temperature. The crystals were washed with ethanol–water containing not more than *ca.*

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[1] C. M. Flynn, Jr., and M. T. Pope, *J. Amer. Chem. Soc.*, **92**, 85 (1970).