18-Crown-6 and Titanium Tetrafluoride − Preparation of the Ti^{IV} Fluoride Crown Ether Complexes $(TiF_4)_2$(18-Crown-6) and the Stabilization of *cis*-$TiF_4(H_2O)_2$ in [{*cis*-$TiF_4(H_2O)_2$}$_2$(18-Crown-6)]

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Reaction of TiF_4 and 18-crown-6 in MeCN affords the molecular complex [(*cis*-$TiF_4)_2$(18-crown-6)] (**1**) only. Water and THF displace the 18-crown-6 in the tetrafluoro complex **1**, with the formation of *cis*-TiF_4L_2. The complex *cis*-$TiF_4(H_2O)_2$ and 18-crown-6 form [{*cis*-$TiF_4(H_2O)_2$}$_2$(18-crown-6)] (**2**), in which *cis*-$TiF_4(H_2O)_2$ and 18-crown-6 are connected by hydrogen bonding through the protons of coordinated H_2O in $TiF_4(H_2O)_2$ and the oxygen atoms of the crown ether. Complexes **1** and **2** were characterized by X-ray single crystal analysis, elemental analysis, IR, NMR and Mass spectroscopy. The relative basicities of the 18-crown-6 and the molecular donor ligands MeCN, THF, H_2O toward Ti^{IV} fluoride were established by NMR spectroscopic investigations of the substitution reactions. 18-crown-6 is slightly more basic than MeCN, similar to that of Et_2O, and less basic than THF and H_2O.

Introduction

Crown ethers are known as variable multidentate ligands that act as macrocycles and chelate ligands,[1] and form a variety of host guest complexes with the neutral molecules.[2] Interest in the crown ethers stems in part from its ability to stabilize metal cations,[1,2] cationic complexes, and aqua complexes of the transition metals.[1−3] Interaction of the transition metal chloride salt, for example $FeCl_3$, $CoCl_2$, $CuCl_2$, VCl_4, with the crown ether in the acetonitrile solution spontaneously yields cationic transition-metal complexes.[4] The group IV chlorides $TiCl_4$, $SnCl_4$,[5] and $TiCl_3$[3e] in the presence of moisture and 18-crown-6 give molecular donor-acceptor adducts with a rare bidentate bonding mode for the 18-crown-6 molecule. The crown ether pillared α-zirconium phosphonate phosphate $Zr_2(L)_{1.17}(PO_4)(HPO_4)_{0.83}F_2Cl_{0.17}(H_2O)_{1.69}$ (L = 1-aza-15-crown-5), according to the solid state NMR spectroscopy, contains the fluorine atom bonded to Zr, and was found to have selective ion exchange properties.[6] However, to the best of our knowledge, no structurally characterized group IV crown ether fluoride complexes are found in the literature.'

Titanium fluoride complexes have been attracting considerable attention for use in several fields including synthetic methodology, catalysis and theoretical studies. $TiHal_4$ (Hal = F, Cl) was used as a reference Lewis acid for the theoretical investigation of the nature of donor−acceptor bond in complexes of the type $TiHal_4L_2$ [L= $C(NH_2)_2$, NH_3, CO].[7] The complex $CpTiF_3$ is active in syndiospecific styrene polymerization in the presence of methylaluminoxane (MAO),[8] and $[TiF_2(NMe_2)_2]_4$ was found to have a relatively modest activity for the catalysis of olefin polymerizations in the presence of MAO.[9] An equimolar mixture of TiF_4 and (*S*)-(−/)-1,1′-bi-2-naphthol treated with 2 equiv. of allylsilane is an effective catalyst for enantioselective addition of allylsilanes to aldehydes.[10] In addition, titanium fluoride complexes have been extensively employed as complexing agents for LiF, NaF, MgF_2, CaF_2, Li_2O, ZnF_2, and preparation of hot-guest compounds, e. g. (Cp*$TiF_3)_4CaF_2$, [$(Cp^*TiF_3)_8(ZnF_2)_3$] etc., which are soluble in organic solvents.[11]

Our interest in the chemistry of titanium fluoride complexes is focused on the structure and reactivity of the complexes, and on the development of a simple high yield synthesis of the Ti^{IV} non-metallocene fluoride complexes. In this paper, we report the preparation, characterization and stability of the titanium(IV) fluoride complex with 18-

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crown-6. In addition, 18-crown-6 was used to stabilize *cis*-$TiF_4(H_2O)_2$, which was found as an intermediate hydrolysis product of TiF_4.[12] The complex *cis*-$TiF_4(H_2O)_2$ was reported to be unstable to give $(H_3O)[TiF_4(OH)(H_2O)]$.[12]

Results and Discussion

Reaction of TiF_4 and Crown-6 in MeCN, Preparation of $[(TiF_4)_2(18\text{-Crown-6})]$ (1)

Interaction of 2 or 3 M TiF_4 and 1 M of 18-crown-6 in the MeCN led to the precipitation of crystalline $[(TiF_4)_2(18\text{-crown-6})]$ (**1**) with an isolated yield of approximately 50% (Scheme 1). Reaction of 1 M TiF_4 and 1 M 18-crown-6 in the same solvent led to the isolation of 18-crown-6 and complex **1**.

$$(2 \text{ or } 3)TiF_4 + [18\text{-Crown-6}] \xrightarrow{MeCN} [TiF_4]_2(18\text{-Crown-6}) \downarrow$$

Scheme 1

The structure of **1** consists of a discrete $[(TiF_4)(18\text{-crown-6})(TiF_4)]$ molecular complex (Figure 2),[13] with bidentate chelation by oxygen atoms of the crown ether to each titanium atom. The most related halogen containing complexes are $[PPh_4]_2[(VCl_4)_2(18\text{-crown-6})]$[3f] and $[TiCl_4(18\text{-crown-6})]$,[5] in which each metal atom is bidentately coordinated to oxygen atoms of 18-crown-6. Both M−O bond lengths in $[(VCl_4)_2(18\text{-crown-6})]$ [2.116(6) and 2.117(6) Å] and in $[TiCl_4(18\text{-crown-6})]$ [2.123(8) and 2.154(9) Å], and O−M−O angles 75.6(2)° and 75.5°, respectively, vary only slightly from those in **1** (Table 1). Complex **1** can also be compared with the binuclear anionic complex $[(TiF_4)(\mu\text{-}C_2O_4)(TiF_4)]^{2-}$,[14] in which each TiF_4 unit is coordinated to two oxygen atoms of the oxalato anion. The Ti−O bond lengths in **1** are similar to the corresponding bond lengths in the binuclear anion $[(TiF_4)(\mu\text{-}C_2O_4)(TiF_4)]^{2-}$.[14] The bidentate ligating mode of the crown ether is relatively rare and has been mostly observed for early transition metal chloride complexes of titanium and vanadium.[5,15]

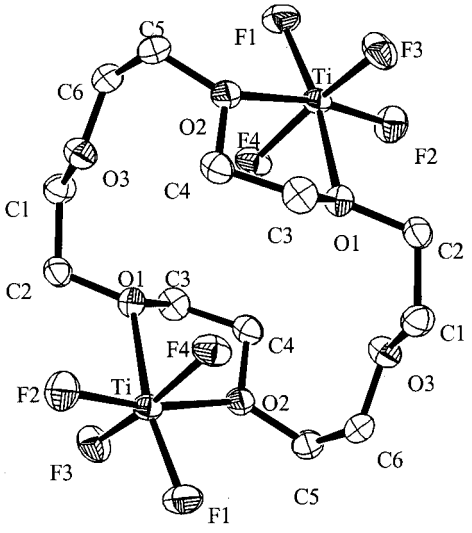

Figure 1. ORTEP drawing (50% thermal probability ellipsoids) of the crystal structure of $[(cis\text{-}TiF_4)_2(18\text{-crown-6})]$ (**1**) with atomic numbering scheme; hydrogen atoms are omitted for clarity

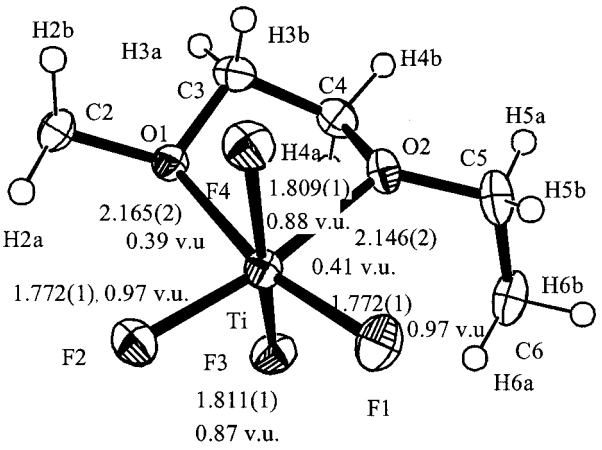

Figure 2. A portion of the $[(cis\text{-}TiF_4)_2(18\text{-crown-6})]$ (**1**) molecule showing the coordination sphere around titanium with the corresponding distances (Å) and bond valences (v.u.)[13]

Table 1. Selected bond lengths (Å) and angles (°) for **1** and **2**; symmetry transformations used to generate equivalent atoms in **1**: $1 - x + 1, -y + 1, -z + 2$; symmetry equivalent positions as x, y, z in **2**: $+x, +y, +z$; $1/2 - x, 1/2 + y, 1/2 - z$; $-x, -y, -z$; $1/2 + x, 1/2 - y, 1/2 + z$

Bond lengths (Å)		Angles (°)	
Complex **1**			
Ti−F(1)	1.772(2)	F(1)−Ti−F(2)	103.12(7)
Ti−F(2)	1.772(2)	F(1)−Ti−F(4)	94.61(6)
Ti−F(4)	1.809(2)	F(1)−Ti−O(1)	164.78(7)
Ti−F(3)	1.811(2)	F(1)−Ti−O(2)	88.95(6)
Ti−O(2)	2.146(2)	F(4)−Ti−F(3)	166.46(6)
Ti−O(1)	2.165(2)	O(2)−Ti−O(1)	75.86(6)
Complex **2**			
Ti−F(2)	1.831(3)	F(2)−Ti−F(3)	95.6(1)
Ti−F(3)	1.790(3)	F(2)−Ti−F(5)	93.4(1)
Ti−F(5)	1.808(3)	F(2)−Ti−O(4)	178.5(1)
Ti−F(6)	1.811(3)	F(2)−Ti−O(5)	92.7(1)
Ti−O(4)	2.087(3)	F(5)−Ti−F(6)	165.6(1)
Ti−O(5)	2.065(3)	O(4)−Ti−O(5)	86.0(1)

The Ti−F bonds of the *trans* F−Ti−O fragment of **1** are shorter than those of the ordinate F−Ti−F fragment due to the *trans* effect in octahedral Ti^{IV} complexes (Table 1). In previously reported *cis*-TiF_4L_2 (L=DMSO), Ph_3PO,[16,17] and $[(cis\text{-}TiF_4)(\mu\text{-}C_2O_4)(cis\text{-}TiF_4)]^{2-}$ [14] complexes, the *trans* effect was implied by the data, but the high Ti−F standard deviation and nonequivalence of all the Ti−F distances ruled out unambiguous interpretations. The Ti−F bond lengths for the F−Ti−F moiety in $[(TiF_4)(\mu\text{-}C_2O_4)(TiF_4)]^{2-}$ are 1.802(5) Å and 1.823(5) Å, and those for the F−Ti−O ordinate are 1.792(5) Å and 1.771(5) Å. In this work the standard deviation allows for the unambiguous observation of the *trans* effect in the titanium(IV) fluoride complex **1**. The average F−Ti−F angle of 96.0(1)°

in **1** is substantially greater than the O−Ti−O angle of 75.9(1)°, reflecting the much greater Ti−F bond order (0.92 v.u. av.) than that of Ti−O (0.40 v.u. av.) and the presence of $p_\pi-d_\pi$ back bonding to titanium.[18]

Elemental analysis shows that complex **1** corresponds to $[TiF_4]_2$(18-crown-6). The crystals of **1** do not change appearance on storage in sealed ampoules at room temperature for several months, but decompose at 141 °C. The heaviest particle detected by EI-MS corresponds to the $[TiF_3(18\text{-crown-6})^+]$ cation. The $[(18\text{-crown-6})^+]$ and $[TiF_3^+]$ ions are also detected. Analysis of the isotope distribution from the EI-MS data also shows ions that are formed by the subtraction of $(CH_2)_2O$ and $O(CH_2)_2O$ from the 18-crown-6.

The observed bands due to Ti−F absorption of **1** [581(m), 648 (vs), 670 (vs) cm^{-1} (IR) and 582 (vs), 672 (vs) cm^{-1} (Raman)] are located in the 400−700 cm^{-1} region for Ti−F vibrations for known TiF_4L_2 complexes. For comparison, these absorptions are located at 560 (vs, br.) for *trans*-$TiF_4(bfq)_2$ (bfq = 5,6 benzoquinoline),[19a] 610 (vs) and 550 (s) for *cis*-$TiF_4(Me_2SO)_2$,[19b] 670 (vs, br.) and 585 (vs, br.) for *cis*-$TiF_4(DME)_2$ (DME = dimethoxyethane),[19b] and 634 (vs, br.) and 562 (s) for *cis*-$TiF_4(bipy)_2$ (bipy = 2,2′-bipyridyl).[19c]

The ^{19}F NMR spectrum of **1** in acetonitrile shows resonances assigned to $TiF_4(MeCN)_2$, $[Ti_2F_9]^-$, oligomeric complexes with bridging fluorine atoms, and *face*-$[TiF_3(MeCN)_3]^+$.[20,21] Two broad resonances at 230−232 and 156−159 ppm (−40 °C) are assigned to the titanium tetrafluoride crown ether complex [*cis*-TiF_4(18-crown-6)] (Supporting Information, Figure S1). Therefore, in the acetonitrile solution of **1**, a complex equilibrium is observed between oligomeric fluoride complexes with bridging fluorides, monomeric complexes of TiF_4 with acetonitrile and TiF_4 complexes with crown ether, since the donor properties of acetonitrile and 18-crown-6 toward TiF_4 are similar.

Resonances assigned to [TiF_4(18-crown-6)] as well as $[Ti_2F_9]^-$ are detected in the ^{19}F NMR spectrum of **1** in $CDCl_3$, which is a very poor donor toward Ti^{IV} fluorides. The corresponding cationic complex is not detected, possibly due to a rapid exchange process involving this complex.

Reaction of Complex 1 with THF and H_2O, Stabilization of *cis*-$TiF_4(H_2O)_2$ by Coordination with the Crown Ether

Complex **1** is very soluble in THF and insoluble in Et_2O. The NMR spectrum of **2** and excess THF in MeCN and $CDCl_3$ at room temperature and at low temperatures show resonances for *cis*-$TiF_4(THF)_2$,[22] as well as a single resonance for 18-crown-6. Therefore, THF displaces MeCN and 18-crown-6 in the titanium(IV) tetrafluoro complexes.

Complex **1** readily reacts with water. The ^{19}F NMR spectrum of **1** and 1−4 equivalents of water in MeCN shows resonances for $[Ti_2F_9]^-$,[21] four resonances for the intermediate oligomeric titanium fluoride complex (A) and *cis*-$TiF_4(H_2O)_2$. The relative concentration of the species in solution depends on the amount of added H_2O (Supporting Information, Figures S11 and S12).

Complex [{*cis*-$TiF_4(H_2O)_2$}$_2$(18-crown-6)] (**2**), formed from *cis*-$TiF_4(H_2O)_2$ and 18-crown-6, precipitates quantitatively as a white insoluble powder on reaction with 4 equivalents of H_2O in acetonitrile. Colorless crystals of **2** are formed from the acetonitrile solution and contain 2.2 mol of water per one mol of complex **1** at −24 °C.

The structure of **2** consists of $TiF_4(H_2O)_2$ and 18-crown-6 units connected through hydrogen bonding (Figure 3) between the protons H(14), H(15), and H(16) of the coordinated H_2O in $TiF_4(H_2O)_2$ and O1, O2, and O3 oxygen atoms of the crown ether. The H(14−16)···O(1−3) distances (Figure 4) in **2** are similar to the corresponding H···O distances in $TiCl_3(H_2O)$[18-crown-6][3e] (1.8 Å) and close to those observed in known hydrogen-bonded complexes

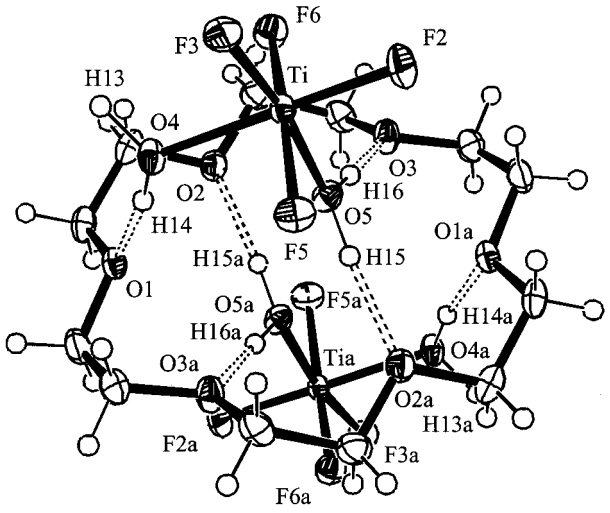

Figure 3. ORTEP drawing (50% thermal probability ellipsoids) of the crystal structure of [{*cis*-$TiF_4(H_2O)_2$}$_2$(18-crown-6)] (**2**) with atomic numbering scheme

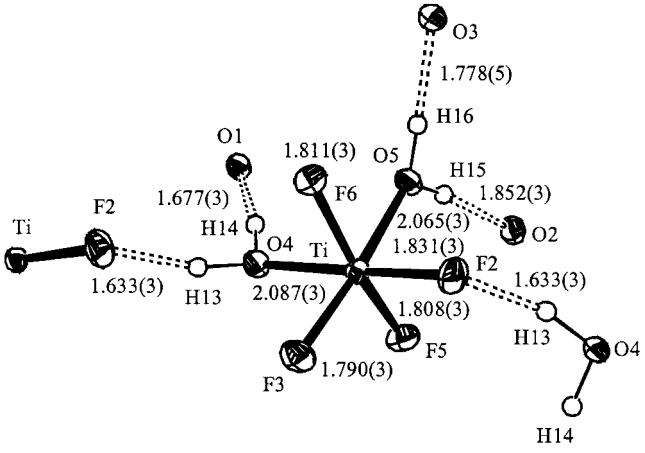

Figure 4. A portion of [{*cis*-$TiF_4(H_2O)_2$}$_2$(18-crown-6)] (**2**) showing the coordination sphere around titanium with the corresponding distances and hydrogen bonding between the protons H13−H16 of the coordinated H_2O and F2 of the neighboring $TiF_4(H_2O)_2$ unit and O1−O3 atoms of 18-crown-6

(1.7−1.9 Å).[23] The $TiF_4(H_2O)_2$ units are joined together through H(13)···F(2) contacts 1.633(3) Å (Figure 4), which are similar to the H···F distances in related compounds, e.g. $CuF_2{\cdot}2H_2O$ (1.69 Å)[24] and $FeSiF_6{\cdot}6H_2O$ (1.86 Å).[24c]

Each titanium atom in the *cis*-$TiF_4(H_2O)_2$ moiety is connected to four fluorine atoms and two oxygen atoms to form a distorted octahedral environment around the titanium center (Figure 4). The Ti−F bond lengths are nonequivalent. The shortest bond is Ti−F(3) [1.790(3) Å, 0.92 v.u.] and involves the fluorine *trans* to H_2O. The two distances Ti−F(5) and Ti−F(6) in the *trans* F(5)−Ti−F(6) fragment of **2** [1.808(3) Å 0.88 v.u. and 1.811(3) Å 0.87 v.u.] are slightly greater than Ti−F(3) due to the *trans* effect in octahedral Ti^{IV} complexes. The hydrogen bonding between F(2) and H(13) leads to the longer Ti−F(2) bond [1.831(3) Å, 0.83 v.u.]. The titanium−oxygen bond length lies in the range for normal Ti−O distances [1.985(7)−2.160 (6) Å] in known complexes with the oxygen donor ligands.[14,16,17,25] The F−Ti−F, F−Ti−O and O−Ti−O angles (Table 1) around titanium are in agreement with VSEPR theory.[18]

Crystals of **2** change appearance in air due to reaction with H_2O. On storage in sealed ampoules at room temperature they are stable for several months, and decomposition occurs above 200 °C in sealed melting point tubes.

The EI-MS of the hydrolysis product shows $[M^+ - 2HF - C_6H_{12}O_3]$ {252 (2)} and $[M^+ - 2H_2F - C_6H_{12}O_3]$, as well as the cations $[TiF_2O^+]$ and $[TiF_3^+]$, which are formed by the decomposition of **2** during the EI-MS experiment. The strongest signals are for $[C_4H_8O_2^+]$, $[C_3H_6O^+]$, and $[C_2H_5O^+]$, which correspond to fragments of 18-crown-6.

Formation of OH···O hydrogen bonds in **2** is reflected by the strong, broad H_2O IR absorption band at 3350−3150 cm^{-1} (maximum at 3295 cm^{-1}). For comparison, the IR absorption bands for H_2O in $TiCl_3(H_2O){\cdot}$(18-crown-6) occurs at 3380 and 3328 cm^{-1}.[3e] Three TiF_4 absorption bands are observed at 667, 607, and 559 cm^{-1}. The skeletal stretches for 18-crown-6 (839, 900, 962 cm^{-1}) are shifted to higher frequencies relative to those of 18-crown-6 (827, 858, 943 cm^{-1})[26] due to interaction of the oxygen atoms of 18-crown-6 with the protons of the $TiF_4(H_2O)_2$ moieties.

The ^{19}F NMR spectra of **2** in MeCN at room temperature shows resonances assigned to $[Ti_2F_9]^-$, oligomeric titanium complex (A) and *cis*-$TiF_4(H_2O)_2$. Lowering the temperature leads to the disappearance of the resonances assigned to $[Ti_2F_9]^-$, and at −35 °C the ^{19}F NMR spectrum shows resonances for (A) and *cis*-$TiF_4(H_2O)_2$, which is consistent with a temperature-dependent equilibrium between the titanium fluoride complexes in solution.

Interaction between 18-crown-6 and *cis*-$TiF_4(H_2O)_2$ leads to a downfield shift of the proton resonance for 18-crown-6 detected at δ_H = 5.1 ppm [δ_H(18-crown-6) 4.3 ppm]. The proton resonance for the *cis*-$TiF_4(H_2O)_2$ moiety (δ_H = 7.4 ppm) detected at −35 °C also shifts 0.5 ppm downfield relative to that of *cis*-$TiF_4(H_2O)_2$ in MeCN, due to interaction of the protons of coordinated water with 18-crown-6 in solution.

An Estimation of the Basic Properties of 18-Crown-6 Toward Titanium Tetrafluoride

In order to establish the relative stability of the [TiF_4(18-crown-6)] complex, the relative basicity of the commonly used donors and 18-crown-6 was compared.

Previous authors have reported a linear relationship between Δδ (H NMR and F NMR spectroscopy) and ΔH^0 values for adduct formation between a series of bases and substituted phenols,[27] and a linear correlation between Δδ (F NMR spectroscopy) in [*cis*-TiF_4(L1)(L2)] (L1 = *N*,*N*-dimethylacetamide, L2 = *p*-substituted pyridine I-oxide) and the appropriate Hammett substituent parameters[28] and also the electronegativity of the substituent R in L1, L2−R_3PO.[29] A linear relationship was also observed between Δδ (F NMR spectroscopy) in $[TiF_5L]^-$ (L − neutral Lewis bases) and pK_α values.[30] This allows us the opportunity to estimate the donor properties of 18-crown-6 toward TiF_4 with the correlation between Δδ (F NMR) in *cis*-TiF_4L_2 and the donor properties of ligand L. We have observed a linear correlation between Δδ (F NMR) of F_A and F_x in *cis*-TiF_4L_2 (Table 2, Figure 5), and the relative basicities of the molecular ligands L (V.Gutmann, G. Olofsson).[31] From this dependence it was concluded that the basic properties of the crown ether (Table 2, Figure 5) are slightly greater than those of acetonitrile and similar to that of Et_2O.

Table 2. Chemical shifts for the *cis*-TiF_4L_2 complexes

Complex	Solvent	Temp. (K)	δ (CCl_3F) (ppm)	*J* (Hz)	Donor number L	Ref.
$TiF_4(MeCN)_2$	50%MeCN, 50%CH_2Cl_2	182 220	252.4; 169.9 253.3; 171.9	31.3	14.1(MeCN)[a]	[20,35]
$TiF_4(Et_2O)_2$	20%Et_2O, 80% MeCN	203	227.2; 163.2	−	19.2(Et_2O)[a]	[35]
		220	228.6; 164.0	−		
$TiF_4\{(MeO)_3PO\}_2$	MeCN	240	214.0; 149.4	41.3	23.0[a]	[20,35]
$TiF_4(THF)_2$	MeCN	240	214.8; 160.4		20.0[a]	this work
$TiF_4(H_2O)_2$	MeCN	240	215.8; 146.1		24.3[b]	this work
$TiF_4(Ph_3PO)_2$	MeCN	240	197.2; 142.4	41.3	27.0[c]	[20]
$TiF_4(Me_2SO)_2$	MeCN	240	188.4; 137.6	37.1	29.8[a]	[20]
$[TiF_6]^{2-}$	MeCN	240	79.8		53(±5)[c]	[20,36c]
[TiF_4(18-crown-6)]	MeCN	240	230−232; 156−159	−	20(±2)	this work
$TiF_4(H_2O)$(THF)	THF	240	219.5;212.2; 150.3	−		this work

[a] Ref.[31] [b] Ref.[32] [c] Ref.[36c]

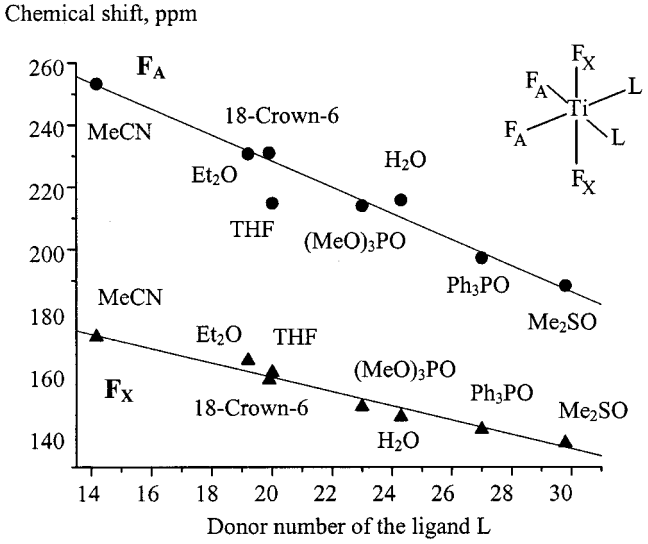

Figure 5. Relationship between the relative basicities of the ligands L (donor number) and chemical shifts of the ^{19}F resonances F_A and F_X in the *cis*-TiF_4L_2 complexes

The substitution reaction (Scheme 2) should proceed[32] if the donor strength of Base1 is greater than that of Base2. The displacement reactions involving TiF_4 and the above molecular donor ligands were studied[16,17,25,33–35] (this work, Supporting Information).

$$[TiF_4(\text{Base 1})] + (\text{Base 2}) \longrightarrow [TiF_4(\text{Base 2})] + (\text{Base 1})$$

Scheme 2

The 18-crown-6 displaces MeCN with the formation of complex **1** in acetonitrile, while THF and H_2O displace 18-crown-6 to give *cis*-TiF_4L_2 (L = THF, H_2O) in solution. Thus, 18-crown-6 is a stronger donor than MeCN, but weaker than THF and H_2O toward titanium tetrafluoride. The basicity of 18-crown-6 might be similar to that of Et_2O since the basic properties of the Et_2O are slightly weaker than those of THF and larger than that of MeCN. Our preliminary NMR spectroscopic study of TiF_4 in mixtures of MeCN and Et_2O show that the mixed complexes $[TiF_4(MeCN)_{2-x}(Et_2O)_x]$ and $[Ti_2F_9]^-$,oligomeric complexes with bridging fluoride atoms, are formed in solutions,[36] much like that in the solution of **1** in MeCN.

Finally, the order of the relative basicities of the ligands in the Ti^{IV} fluoride complexes was established to be MeCN $<$ Et_2O $\approx$ 18-crown-6 $<$ THF $<$ $(MeO)_3PO$ $<$ H_2O[37] $<$ Ph_3PO $<$ Me_2SO $<$ $[F]^-$.

Conclusions

Reaction of TiF_4 and 18-crown-6 in MeCN affords only one molecular complex [(*cis*-TiF_4)$_2$(18-crown-6)] (**1**). The crown ether 18-crown-6 bidentately coordinates through the oxygen atoms to titanium tetrafluoride in **1**, in a manner similar to that in the corresponding chloride complex [$TiCl_4$(18-crown-6)]. However, the stoichiometry of the fluoride and chloride complexes (2:1 and 1:1 respectively) differs from each other, and the complex [TiF_4(18-crown-6)] (1:1) was not isolated from the [TiF_4(18-crown-6)]/acetonitrile system.

Water and THF displaces 18-crown-6 in the tetrafluoro complex with the formation of *cis*-$TiF_4(L)_2$ (L= THF, H_2O) in solution. The complex *cis*-$TiF_4(H_2O)_2$ and 18-crown-6 form [{*cis*-$TiF_4(H_2O)_2$}$_2$(18-crown-6)] (**2**), in which *cis*-$TiF_4(H_2O)_2$ and 18-crown-6 are connected by hydrogen bonding through protons of coordinated H_2O in $TiF_4(H_2O)_2$ and oxygen atoms of the crown ether. Thus, reaction of TiF_4 and **2** with water yields the molecular adduct *cis*-$TiF_4(H_2O)_2$, which was observed in solution,[12] but has not hitherto been isolated and characterized.

The basic properties of 18-crown-6 toward TiF_4 were established from a linear correlation between $\Delta\delta$ (F NMR spectroscopy) of F_A and F_x in *cis*-TiF_4L_2 and the relative basicities of the molecular ligands L (V.Gutmann, G. Olofsson) as well as from the displacement reaction data involving complex **1**, MeCN, THF, and H_2O. The relative basicity of the ligands increase in the order MeCN $<$ Et_2O $\approx$ 18-crown-6 $<$ THF $<$ $(MeO)_3PO$ $<$ H_2O $<$ Ph_3PO $<$ Me_2SO $<$ $[F]^-$.

Thus the molecular donor ligands that have greater donor properties than Et_2O will displace 18-crown-6 in **1**, and THF, H_2O, Me_2SO, and other solvents cannot be used for the preparation and investigation of complex **1**.

Experimental Section

General Remarks: All operations were performed with standard Schlenk line techniques under a purified nitrogen atmosphere. Solid reagents and crystals were manipulated in a Vacuum Atmospheres Dri-Lab equipped with a Dri-Train (HE-493) and 1 kg of 3 Å molecular sieves contained in an internal circulating drying unit. Titanium tetrafluoride (99%, Across Organics) was purified by holding under 2.5 atm of F_2 for 4 days in the Monel metal vessel, 18-crown-6 (99.5%, Aldrich) was used as received, acetonitrile, THF, CH_2Cl_2, and $CDCl_3$ were dried over CaH_2 and degassed. NMR spectra were recorded with a Varian 400 NMR spectrometer. Proton shifts are reported in δ units downfield from Me_4Si, with the solvent as the reference signal. $CClF_3$ was used as a reference for the ^{19}F NMR spectra. NMR samples were prepared in 5 mm NMR tubes fitted with J. Young valves. Mass spectra were recorded on a KRATOS ms 50 TC mass spectrometer equipped with an EI source (30 eV), from samples sealed in dried glass m.p.t. tubes by the direct inlet method. FT-IR spectra were recorded on a Thermo Nicolet spectrometer (Nexus 470 FT-IR), and FT-Raman spectra were obtained from neat samples, sealed under a nitrogen atmosphere in glass capillaries, using an FT-IR spectrometer (Bruker IFS66)

equipped with an FT-Raman accessory (Bruker FRA 106), incorporating a Nd-YAG laser (emission wavelength: 1064 nm; maximum laser power: 300 mW). Melting points were measured in sealed capillary tubes under nitrogen and are not corrected. Elemental analysis was carried out by Galbraith Laboratories, Inc.

Preparation of [$(TiF_4)_2$(18-Crown-6)] (1): Acetonitrile (30 mL) was condensed into the mixture of TiF_4 (0.8 g, 6.5 mmol) and 18-crown-6 (0.8 g, 3.0 mmol) at −79 °C, and the solution was warmed to 50 °C to dissolve the reagents. The obtained solution was filtered, concentrated to ca. 10−15 mL, and left at room temperature for 5 days. Colorless crystals were separated by filtration, washed three times with cold (−20 to −40 °C) CH_2Cl_2 (5 mL). Yield 0.8 g (50% based on 18-crown-6). M.p. 141−143 °C decomposition. $C_{12}H_{24}F_8O_6Ti_2$ (512.1): calcd. C 28.12, H 4.69, F 29.68; found C 28.00, H 4.55, F 29.20. EI-MS (30 eV, heating room temperature −170 °C): *m/z* = 368 (0.2) [TiF_3(18-crown-6)$^+$], 264 (5) [(18-crown-6)$^+$], 221 (8) [(18-crown-6)−$C_2H_4O^+$], 204 (1) [$TiF_2C_5O_3H_{10}^+$], 188 (3) [$TiF_2C_5H_{10}O_2^+$], 177 (50) [(18-crown-6)−$C_4H_8O_2^+$], 174 (12) [$TiF_2C_4H_8O_2^+$], 161 (3) [(18-crown-6)−$C_4H_8O_3^+$], 159 (3) [$TiF_2C_3H_5O_2^+$], 146 (4) [$TiF_2C_2H_4O_2^+$], 132 (65) [(18-crown-6)−$C_6H_{12}O_3^+$], 116 (35) [$TiF_2CH_2O^+$], 105 (90) [TiF_3^+], 88 (100) [$C_4H_8O_2^+$], calculated theoretical isotops distribution matched that experimentally observed for all peaks. ^{1}H NMR (400 MHz, $CDCl_3$, −60 °C, undissolved solid is present in the NMR ampoule): δ_H = 3.59 (br., 4 H, 7%), 3.64 (s, 4 H), 3.70 (s, 4 H), 3.73 (s, 4 H), sum of the relative intensities of the resonances 3.64, 3.70, 3.73 is 68%, 3.76 (s, 4 H, 2%), 3.80 (s, 4 H, 2%), 3.92 (br., 4 H, 7%), 4.36 (br., 4 H, 7%), 4.57 (br., 4 H, 7%) ppm. ^{19}F NMR (376.3 MHz, $CDCl_3$, −60 °C, undissolved solid is present in the NMR ampoule): δ_F = 260.1 (m, 6F, *face*-[TiF_3(μ-F)$_3$TiF_3]$^-$, 32%), 236.4 (br., [TiF_4(18-crown-6)], 26%), 149.7 (br., [TiF_4(18-crown-6)], 26%), −17.8 (br., 3F, *face*-[TiF$_3$(μ-*F*)$_3$TiF$_3$]$^-$, 16%), −51.3 (C−F), −69.1 (CDF_3), −73.8 (CDF_2Cl), −75.1 (CD*F*Cl$_2$) ppm. ^{19}F NMR (MeCN, room temperature): δ_F = 324 [*face*-TiF_3(MeCN)$_3$], 306 to −260 [{*face*-TiF_3(MeCN)$_x$(μ-F)$_{3-x}$}$_y$, *x* = 0−2], 263.5 (*face*-[TiF_3(μ-F)$_3$TiF_3]$^-$), 232 (br., [TiF_4(18-crown-6)]), 230.3 (br), 215 (br., *cis*-TiF_4-(MeCN)$_2$], 158 (br. [TiF_4(18-crown-6)]), 0 to −20 [{*face*-TiF$_3$(MeCN)$_x$(μ-*F*)$_{3-x}$}$_y$, *x* = 0−2], −20.7 (*face*-[TiF$_3$(μ-*F*)$_3$TiF$_3$]$^-$), (MeCN, −40 °C), 321 [*face*-TiF_3(MeCN)$_3$], 306−260 [{*face*-TiF_3(MeCN)$_x$(μ-F)$_{3-x}$}$_y$, *x* = 0−2], 264.5 (*face*-[TiF_3(μ-F)$_3$TiF_3]$^-$), 254 (m) 231 (br., [TiF_4(18-crown-6)]), 226.8 (br.), 228−202 (overlapped resonances of *cis*-TiF_4(MeCN)$_2$ and mixed monomeric complexes containing MeCN and 18-crown-6), 158 (br. [TiF_4(18-crown-6)]), 0 to −20 [{*face*-TiF$_3$(MeCN)$_x$(μ-*F*)$_{3-x}$}$_y$, *x* = 0−2], −21.6 (*face*-[TiF$_3$(μ-*F*)$_3$TiF$_3$]$^-$) ppm. IR (AgCl, Perflouroalkyl ether, Fluorolube mull): $\tilde{\nu}$ = 1363 (m), 1355 (m), 1305 (m), 1288 (w), 1276 (w), 1264 (m), 1247 (w), 1236 (m), 1142 (s), 1121 (w), 1107 (m), 1066 (s), 1040 (s), 1015 (m), 928 (s), 920 (s), 909 (s), 855 (s), 813 (w) 793 (m), 670 (vs, TiF_4), 648 (vs, TiF_4), 581 (m, TiF_4), 550 (w), 516 (m) cm^{-1}. Raman (solid): $\tilde{\nu}$ = 3026 (s), 3011 (s), 2965 (vs), 2932 (w), 2902 (m), 2874 (s), 2860 (m), 2826 (m), 2743 (w), 1473 (m), 1455 (s), 1425 (w), 1394 (w), 1378 (w), 1352(w), 1295 (m), 1268 (m), 1249 (m), 1236 (w), 1159 (w), 1139 (w), 1117 (w), 1098 (w), 1076 (w), 1060 (w), 1028 (w), 954 (w), 929 (m), 836 (m), 788 (m), 673 (vs, TiF_4), 589 (vs, TiF_4), 558 (w), 505 (w), 422 (w), 354 (w), 336 (w), 284 (m), 265 (m), 245 (m), 229 (w), 209 (w), 179 (w), 108 (w) cm^{-1}. Raman (160−4000 cm^{-1}) spectrum of the compound **1** is given in the Supporting Information (Figure S4).

Interaction of Complex 1 with H_2O: Complex **1** (0.1 g, 0.2 mmol) was loaded into a 5 mm NMR tube, and MeCN (0.7 mL) was added. Four aliquots of H_2O (4 × 0.003.510^{-3} mL) were added by means of a micro syringe. Addition of 3 or 4 equivalents of H_2O (0.6, 0.8 mmol of H_2O) to the solution of **1** leads to precipitation of the white product **2**. Finally, MeCN was removed by decantation, and the resulting solid dried under dynamic vacuum for 1 hour. Recovered 0.11 g of the solid **2**. Yield of **2** 95% (based on **1**). All NMR spectroscopic data are given in the Supporting Information. M.p. 205−207 °C decomposition. $C_{12}H_{32}O_{10}Ti_2F_8$ (584.2): calcd. Ti 16.43; found Ti 16.50. EI-MS (30 eV, heating room temperature −170 °C): *m/z* = 264 (1) [(18-crown-6)$^+$], 254 (2) [M^+ − 2HF − $C_6H_{12}O_3$], 252 (2) [M^+ − $2H_2F$ − $C_6H_{12}O_3$], 221 (1) [(18-crown-6)−$C_2H_4O^+$], 177 (6) [(18-crown-6)−$C_4H_8O_2^+$], 175 (2) [$TiF_2C_4H_9O_2^+$], 133 (10) [$TiFO_4H_2^+$], 117 (6) [$TiFO_3H_2^+$], 101 (20) [TiF_2O^+], 105 (15) [TiF_3^+], 88 (100) [$C_4H_8O_2^+$], 72 (30) [$C_4H_8O^+$], 58 (50) [$C_3H_6O^+$], 45 (100) [$C_2H_5O^+$], calculated theoretical isotope distribution matched that experimentally observed for all peaks. ^{1}H NMR (400 MHz, MeCN, room temperature): δ_H = 5.0 (br), 4.3 (18-crown-6) ppm. ^{1}H NMR (400 MHz, MeCN, −35 °C): δ_H = 7.5 (*H*$_2$O), 5.2 (br), 4.2 (18-crown-6) ppm. ^{19}F NMR (MeCN, room temperature): δ_F = 262.1 (m, 6F, *face*-[TiF_3(μ-F)$_3$TiF_3]$^-$, 10%), 233.0 (m, nF, 6%), 220.7 (m, 2nF, 12%), 214.5 (br., *cis*-TiF_4(H$_2$O)$_2$, 21%), 153.3 (br., *cis*-TiF_4(H$_2$O)$_2$, 21%), −11.7 (m, 2nF, 12%), −19.70 (m, 2nF, 12%), −21.6 (br., 3F, *face*-[TiF$_3$(μ-*F*)$_3$TiF$_3$]$^-$, 5%) ppm. ^{19}F NMR (MeCN, −35 °C): δ_F = 233.0 (m, nF, 7%), 220.7 (m, 2nF, 14%), 210.7 (*cis*-TiF_4(H$_2$O)$_2$, 24%), 148.3 (*cis*-TiF_4(H$_2$O)$_2$, 24%), −11.7 (m, 2nF, 14%), −19.70 (m, 2nF, 14%) ppm. IR (KBr, Perflouroalkyl ether, Fluorolube mull): $\tilde{\nu}$ = 3350−3150 [maximum 3295] (br., vs, H−O stretches), 2408 (w, H_2O), 1352 (s), 1298 (w), 1282 (m), 1269 (w) 1254 (m), 1244 (w), 1234 (w), 1197 (s), 1155 (m), 1124 (s), 1096 (vs), 962 (vs), 900 (s), 839 (s), 745 (m), 667 (s, TiF_4), 607 (s, TiF_4), 559 (s, TiF_4), 522 (m), 439 (w) cm^{-1}.

Reactions between TiF_4 and THF, and H_2O, leading to $TiF_4(THF)_2$ and $TiF_4(H_2O)_2$, respectively are described in the Supporting Information.

Crystal Growth and X-ray Crystallography: Crystals of **1** were grown by slow cooling of a saturated solution in acetonitrile from room temperature to +5 °C. Crystals of **2** were grown by slow diffusion of water vapor into a saturated solution of **1** at +5 °C. Single crystals were coated with Paratone-N oil, mounted using a glass fiber, and frozen in cold nitrogen and mounted on the goniometer. The structure of **1** was measured on a Bruker AXS P4/SMART 1000 diffractometer and that of **2** was measured on a Rigaku AFC5R diffractometer. The data of the major component of **1** and **2** were reduced (SAINT)[38] and corrected for absorption (SADABS).[39] The structures of **1** and **2** were solved by and expanded with Fourier techniques.[40] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in Fourier difference maps and refined isotropically. All calculations were performed with the SHELXTL[41a] (**1**) and teXsan[41] crystallographic software package of Molecular Structure Corporation (**2**). For the structure of **2**, neutral atom scattering factors were taken from Cromer and Waber.[42] Anomalous dispersion effects were included in $F_{calcd.}$;[43] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[44] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[45]

CCDC-35610 and CCDC-235611 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystallographic data of the X-ray diffraction studies of **1** and **2**

	1	**2**
Empirical formula	$C_{12}H_{24}F_8O_6Ti_2$	$C_{12}H_{32}F_8O_{10}Ti_2$
M_r	512.11	584.16
Temperature (K)	198(1)	133(1)
Radiation used [λ (Å)]	Mo-K_α (0.71073)	Mo-K_α (0.71073)
Crystal description	Colorless, plate	colorless, block
Crystal size (mm)	0.075 × 0.1 × 0.25	0.22 × 0.20 × 0.42
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	7.3481(12)	8.975(4)
b (Å)	7.8660(13)	12.830(6)
c (Å)	8.9165(14)	11.024(4)
α (°)	111.851(2)	90
β (°)	96.136(2)	111.13(3)
γ (°)	95.348(2)	90
V (Å^3)	470.64(13)	1184.1(9)
Z	1	4
F (000)	260	600.00
$\rho_{calcd.}$ (g cm^{-3})	1.807	1.638
μ (mm^{-1})	0.952	0.780
Total reflections	2386	3832
Unique reflections	1548	3628
R(int)	0.0237	0.040
Scan range θ (°)	2.49 to 24.99	1.00 to 30.1
Completeness to θ_{max} (%)	93.5	100
Index ranges	$-8 \le h \le 7$	$0 \le h \le 12$
	$-8 \le k \le 9$	$0 \le k \le 18$
	$-10 \le l \le 10$	$-9 \le l \le 14$
Data/restrains/parameters	1548/0/175	3476/0/161
$R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0302, 0.0896	0.045, 0.1275
$R1$, $wR2$ (all data)[a]	0.0343, 0.0923	0.045, 0.1275
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F
Goodness-of-fit on F^2	1.064	1.07
Max./min. el. dens. (e·Å^{-3})	0.451, −0.293	0.78, −0.76

[a] $wR2 = ([w(F_o^2 - F_c^2)2]/[F_o^4])1/2$, $R1 = ||F_o| - |F_c||/|F_o|$, Weight = $1/[\sigma^2(F_o^2) + (0{\cdot}0745P)^2]$, where $P = (\max [F_o^2] + 2F_c^2)/3$.

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