Eur. J. Inorg. Chem. **2004** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2004 · ISSN 1434–1948

SUPPORTING INFORMATION

Title: 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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Ref. No.: I040310

Interaction of one and three equivalent TiF_4 and one equivalent of 18-Crown-6

Acetonitrile 30 mL was condensed on to the mixture of TiF_4 (0.8 g, 6.5 mmol) and 18-crown-6 (1.73 g, 6.5 mmol) at –79 ºC. Then reaction mixture was warmed to 50 ºC to dissolve the reagents. The obtained solution was filtered, concentrated to *ca.* 10-15 mL and left undisturbed at +5 ºC. While the large block colourless crystals (A) (about 5 x 5 x 3 mm) formed in a period of one day, small colourless crystals (0.8 x 0.5 x 0.25 mm) (B) with the characteristic shape formed after 5- 7 days. The crystals that formed were separated by filtration from the mother liquid and separated manually from each other in the glove box. Raman, IR, proton NMR spectra of the large crystals (A) were identical to that of 18-crown-6 [1] and the {18-Crown-6} · MeCN adduct,[2, 3, 4] no ^{19}F resonance was detected at low and at r.t. Raman, IR, ^{1}H, ^{19}F NMR spectra of the small crystals (B) were identical to that of $[TiF_4]_2$(18-Crown-6).

Reaction of 3 moles of TiF_4 with 1 mol of 18-crown-6 yields crystals of $[TiF_4]_2$(18-Crown-6) **1** (IR, NMR, parameters of the unit cell of the crystals) that deposits from the syupernatant solution. Under the same conditions $TiF_4(MeCN)_2$ is much more soluble in MeCN than **1** and therefore can be separated by crystallization. Evaporation of supernatant yields a solid that contains **1** and $TiF_4(MeCN)_2$.[5]

Low temperature NMR spectra of 1 in MeCN (Figure 1) and $CDCl_3$ (Figures 2,3)

Complex **1** exhibit broad resonances at r.t. in the ^{19}F NMR spectrum in $CDCl_3$ due to rapid exchange process in solution. Lowering the temperature lead to narrowing the resonances and at the temperatures below –40 °C the ^{19}F NMR spectrum of **1** contains Two ^{19}F resonances $\delta^{19}F$ 237 and 151 ppm of equal intensity assigned to the titanium tetrafluoride complex with crown ether {TiF_4(18-Crown-6)} (Fig.2). Fine structure of two resonances was not observed even at -70 °C due to rapid exchange processes. The available data does not allow to determine ratio of TiF_4 and 18-Crown-6 in the specie in solution. The ^{19}F NMR spectrum of **1** also contains resonances of $[Ti_2F_9]^-$ anion and weak signals of $CDCl_{3-n}F_n$,[6] the cationic complex was not detected possibly due to rapid exchange process including this complex.

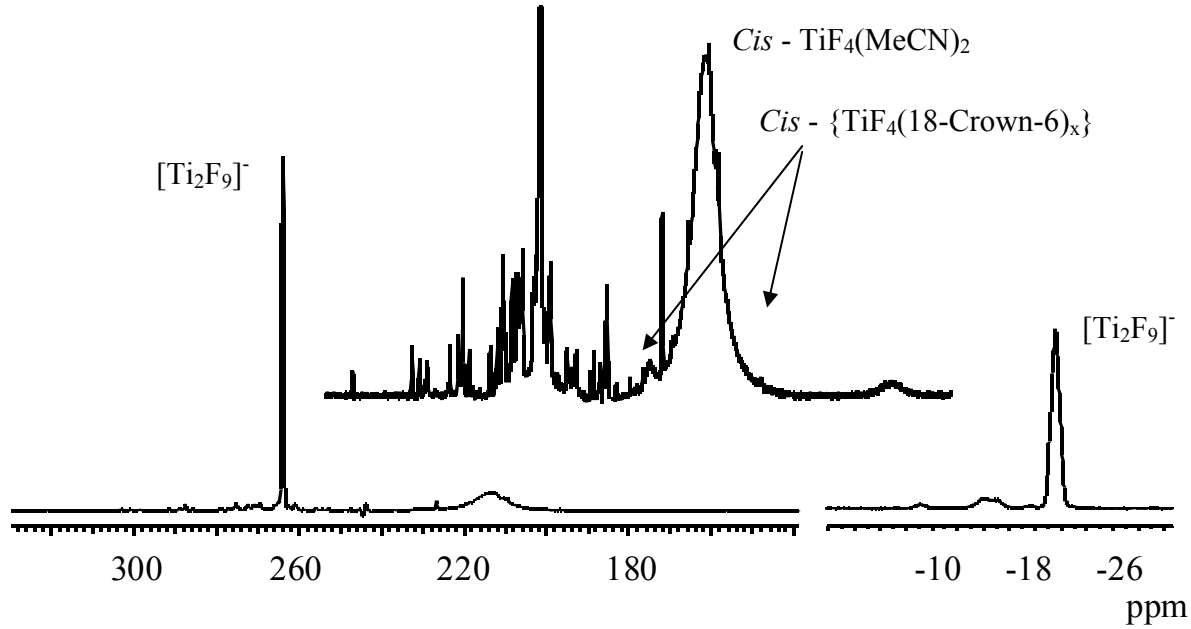

Figure 1.

^{19}F NMR spectrum of **1** in MeCN, -30 ºC. Spectrum is measured 1 day after preparation of solution.

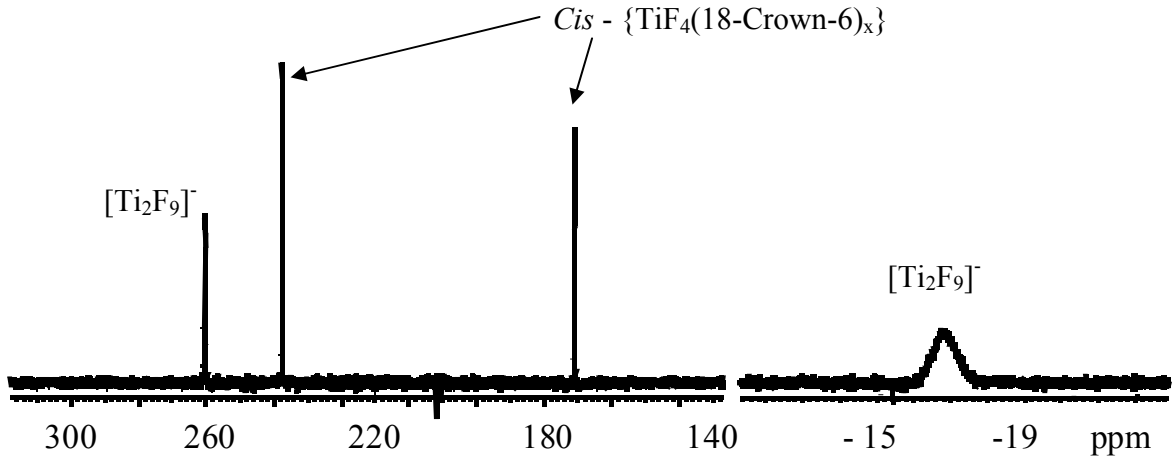

Figure 2.

^{19}F NMR spectrum of **1** in $CDCl_3$, -60 ºC. Spectrum is measured 1 day after preparation of solution.

The proton spectrum of **1** in $CDCl_3$ at r.t. contains single resonance, close to the signal of pure crown ether. At –60 °C proton spectrum shows one major resonance of 18-Crown-6, overlapped with the several less intensive resonances of $(MeCN)_x$[18-Crown-6], and broad resonances 4.6-3.8 ppm assigned to the crown ether coordinated to titanium (Fig.3).

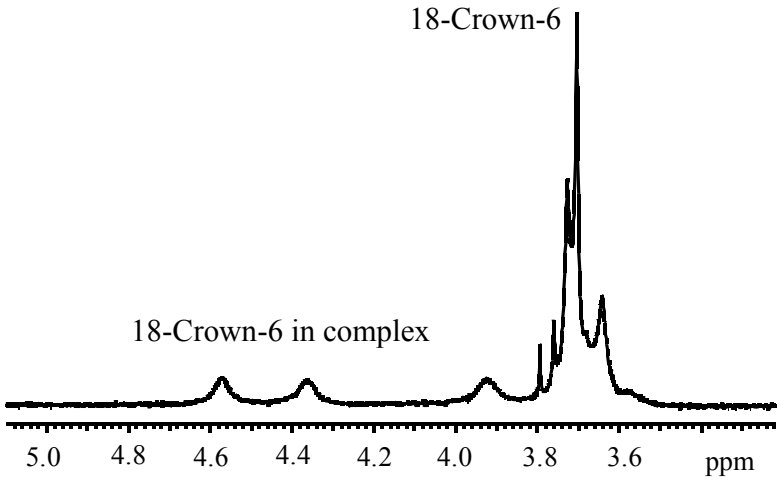

Figure 3

Proton NMR spectrum of **1** in $CDCl_3$, -70 ºC. Spectrum is measured 1 day after preparation of solution.

4. The complete range Raman spectrum of 1

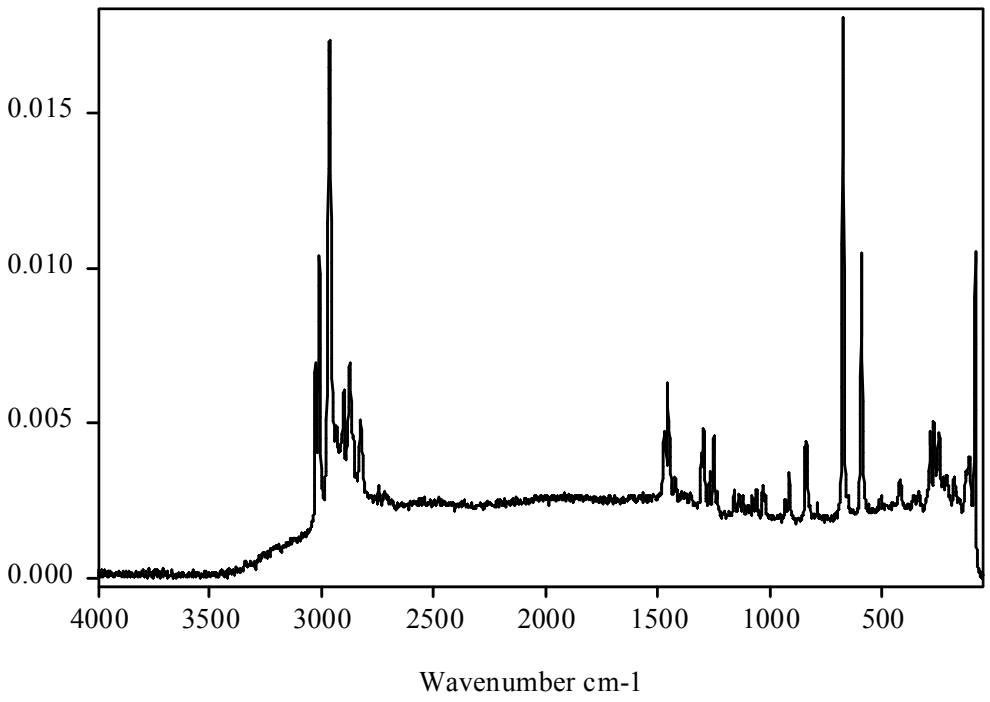

Figure 4.

Raman spectrum 4000 - 140 cm^{-1} of $(TiF_4)_2$(18-Crown-6) **1**.

The absorption band at 422 cm^{-1} (Raman, Fig.4) was assigned to the Ti-O stretching vibration, based on the assignment made for the $TiF_4(Z\text{-}C_5H_4NO)_2$ complexes Z = H, CH_3, OCH_3, NO_2, Cl.[7]

NMR reactions *in situ*.

The NMR study of interaction of TiF_4 and THF, H_2O in MeCN was carried out in order to assign the resonances in the spectra of **1** and THF, H_2O in the MeCN.

Interaction of TiF_4 and THF in MeCN

The ^{19}F NMR spectrum of the *cis*-$TiF_4(THF)_2$ was measured in the THF at -60ºC by the previous authors.[8] In this work, comparison of the ^{19}F NMR chemical shifts of the *cis*-TiF_4L_2 is carrying out in MeCN and $CDCl_3$ at -33ºC and -60º C, therefore solutions of the TiF_4 in THF and MeCN and TiF_4 in THF and $CDCl_3$ were studied by means of the NMR spectroscopy.

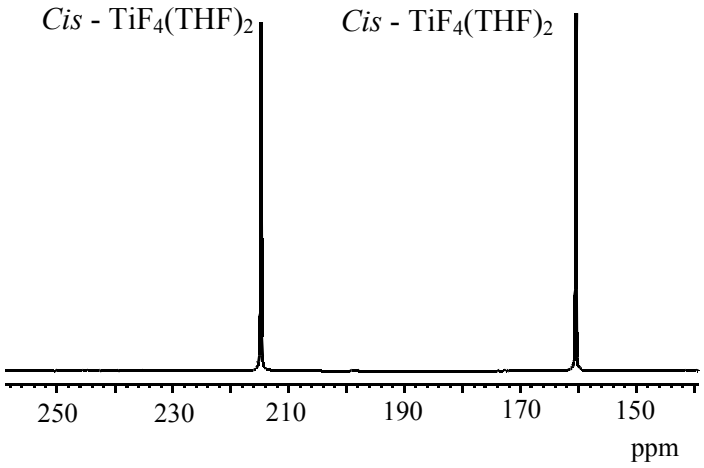

Figure 5

^{19}F NMR spectrum of TiF_4 and 4 equivalents of THF in MeCN, -40 ºC.

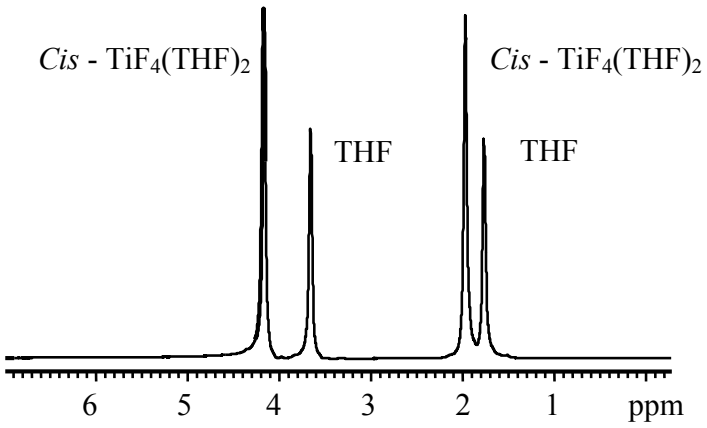

Figure 6

Proton NMR spectrum of TiF_4 and 4 moles of THF in $CDCl_3$, -40 ºC.

The ^{19}F NMR spectrum of the TiF_4 and 6 equivalents of the THF in MeCN, $CDCl_3$ show two resonances of equal intensity of the *cis*-$TiF_4(THF)_2$ (Fig.5). The proton resonances of the *cis*-$TiF_4(THF)_2$ are shifted downfield from the THF, the resonances of the coordinated and non coordinated THF are clearly distinguishable in the NMR spectra of the *cis*-$TiF_4(THF)_2$ in MeCN, $CDCl_3$, THF at -33ºC (Fig.6).

It is possible to conclude that the THF displaces the MeCN in the titanium (IV) fluoride complexes with formation of *cis*-$TiF_4(THF)_2$.

NMR scale Experiment. Interaction of TiF_4 and THF in $CDCl_3$, MeCN, THF: TiF_4 (0.05 g, 0.4 mmol) was loaded in the 5 mm NMR tube and 0.13 ml (0.12 g, 1.6 mmol) of THF added. Then 0.7 ml of the solvent MeCN, $CDCl_3$, THF was added and the clear colorless solution obtained. The NMR spectra were measured the next day after preparation. ^1H NMR (400 MHz, $CDCl_3$, -60 ºC), δ_H (ppm) = 4.2 (br, 4H, *cis*-$TiF_4(THF)_2$), 3.7 (br, 4H, THF), 2.0 (br, 4H, *cis*-$TiF_4(THF)_2$), 1.8 (br, 4H, THF); ^1H NMR (400 MHz, MeCN, -33 ºC), δ_H (ppm) = 4.4 (br, 4H, *cis*-$TiF_4(THF)_2$), 3.9 (br, 4H, THF), 2.3 (br, 3H, MeCN solvent), 1.8 (br, 4H, THF); ^1H NMR (400 MHz, THF, -40 ºC), δ_H (ppm) = 4.0 (br, 4H, *cis*-$TiF_4(THF)_2$), 3.5 (br, 4H, THF solvent), 1.8 (br, 4H, *cis*-$TiF_4(THF)_2$), 1.6 (br, 4H, THF solvent); ^{19}F NMR ($CDCl_3$, -60 ºC), δ_F (ppm) = 214.0 (br, 2F, *cis*-Ti$F_4(THF)_2$), 158.0 (br, 2F, *cis*-Ti$F_4(THF)_2$), ^{19}F NMR ($CDCl_3$, -33 ºC), δ_F (ppm) = 219.0 (br, 2F, *cis*-Ti$F_4(THF)_2$), 159.6 (br, 2F, *cis*-Ti$F_4(THF)_2$); ^{19}F

NMR (MeCN, -33 ºC), δ_F (ppm) = 214.8 (br, 2F, *cis*-TiF_4(THF)$_2$), 160.4 (br, 2F, *cis*-TiF_4(THF)$_2$); ^{19}F NMR (THF, -40 ºC), δ_F (ppm) = 221.9 (br, 2F, *cis*-TiF_4(THF)$_2$), 162.3 (br, 2F, *cis*-TiF_4(THF)$_2$).

Interaction of 1 and THF in MeCN.

Complex **1** is soluble in the THF. The ^{19}F NMR spectrum of **1** and 8 equivalents of the THF in $CDCl_3$ exhibits two resonances of the *cis*-$TiF_4(THF)_2$ (Fig.7) The proton spectrum contains signals of the *cis*-$TiF_4(THF)_2$, THF and 18-Crown-6 at –35ºC to -70ºC (Fig.8). Therefore, THF displaces 18-Crown-6 in the titanium tetrafluoride complex, forming the *cis*-$TiF_4(THF)_2$.

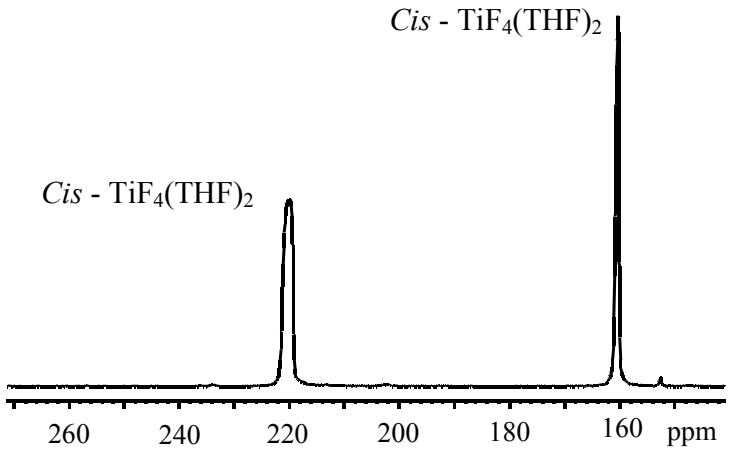

Figure 7

^{19}F NMR spectrum of **1** and 8 moles of THF in the MeCN, -40 ºC.

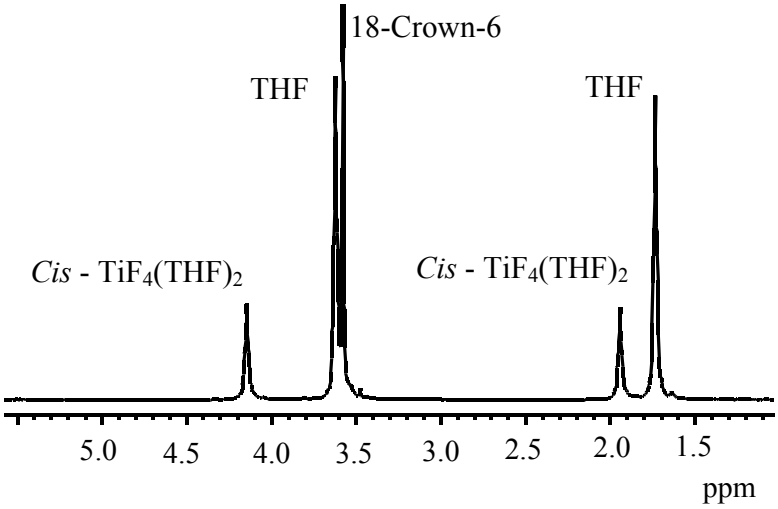

Figure 8

Proton NMR spectrum of **1** and the 8 moles of THF in the $CDCl_3$, -60 ºC.

*NMR scale Experiment. Interaction of $\{TiF_4\}_2$(18-Crown-6) (**1**) and THF in $CDCl_3$:* Complex **1** 0.05 g, (0.1 mmol) was placed in to the 5 mm NMR tube and 0.07 ml (0.06 g, 0.8 mmol) of the THF added. Then 0.7 ml of $CDCl_3$ was condensed in to the NMR ampoule *via* vacuum line. The clear colorless solution was obtained by warming. ^{1}H NMR (400 MHz, $CDCl_3$, -60 ºC), δ_H (ppm) = 4.2 (br, 4H, *cis*-$TiF_4(THF)_2$), 3.7 (br, 4H, THF), 3.6 (18-Crown-6), 1.9 (br, 4H, *cis*-$TiF_4(THF)_2$), 1.7 (br, 4H, THF); ^{19}F NMR ($CDCl_3$, -60 ºC), δ_F (ppm) = 216.2 (br, 2F, *cis*-Ti$F_4(THF)_2$), 158.7 (br, 2F, *cis*-Ti$F_4(THF)_2$).

Interaction of TiF_4 and H_2O in MeCN.

By means of the NMR spectroscopy were studied solutions of TiF_4 and 1, 2 equivalent of H_2O.

The ^{19}F NMR spectrum of TiF_4 and the 1 equivalent of the H_2O in MeCN contained resonances of the $[Ti_2F_9]^-$ anion, two broad exchange signals assigned to the *cis*-$TiF_4(H_2O)(MeCN)$ and two resonances of equal intensity attributed to the *cis*-$TiF_4(H_2O)_2$ (Fig.9). The proton spectrum of solution at the same temperature shows several signals in the area 8.7 to 7.0 ppm, showing formation of the different complexes containing coordinated $\{H_2O\}$. The major broad proton resonance δ_H 7.5 ppm was assigned to the *cis*-$TiF_4(H_2O)(MeCN)$.

The ^{19}F NMR spectrum of the TiF_4 and 2 equivalents of the H_2O in MeCN at -40ºC contains major resonances of the *cis*-$TiF_4(H_2O)_2$ and the minor ^{19}F resonances of the $[Ti_2F_9]^-$ and the *cis*-$TiF_4(H_2O)(MeCN)$ (Fig.9). The proton spectrum contains major broad signal at 7.0 ppm assigned to the *cis*-$TiF_4(H_2O)_2$ and minor resonance of the *cis*-$TiF_4(H_2O)(MeCN)$ (Fig.10).

Thus, water displaces MeCN in the titanium (IV) fluoride complexes with the formation of the *cis*-$TiF_4(H_2O)_2$ major product detected by means of the NMR in the MeCN solution.

It should be point out, that the water displaces also THF in the titanium (IV) fluoride complexes, since the ^{19}F NMR spectrum of the TiF_4 in the moist THF contains resonances of the mixed complex *cis*-$TiF_4(H_2O)(THF)$ δ_F 150.3, 212.2, 219.5 ppm, relative intensity of the signals is 2 : 1 : 1 correspondingly and the *cis*-$TiF_4(H_2O)_2$.

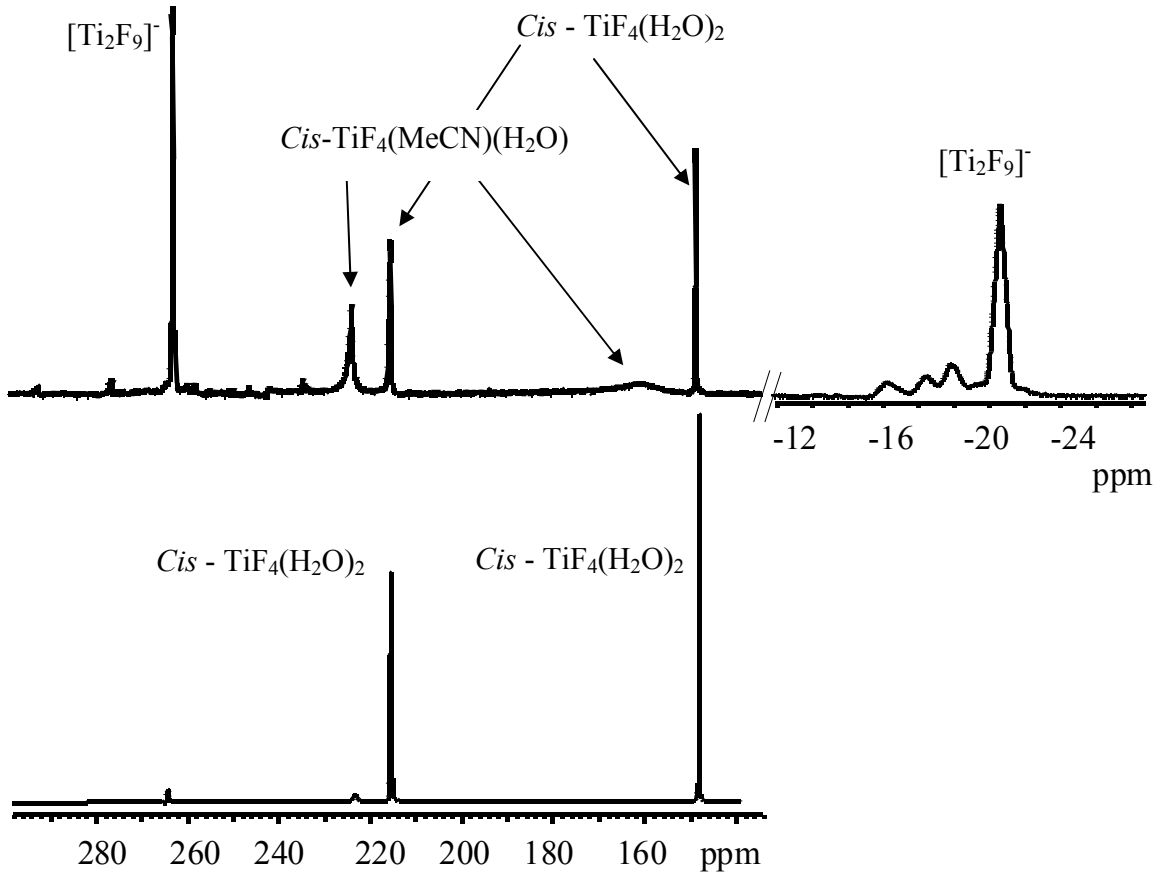

Figure 9.

^{19}F NMR spectra of the TiF_4 and 1, 2 equivalents of the H_2O in MeCN, -40 ºC.

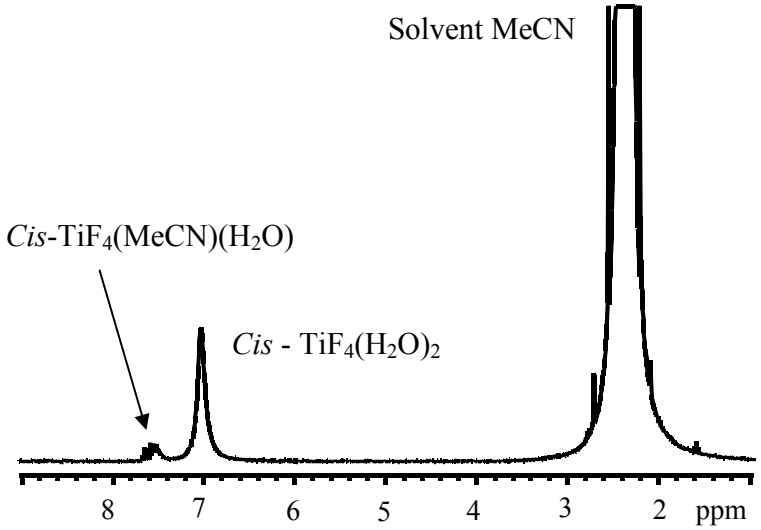

Figure 10.

Proton NMR spectrum of the TiF_4 and 2 equivalents of the H_2O in MeCN, -40 ºC.

NMR scale Experiments: TiF_4 (0.1 g, 0.8 mmol) was loaded in the 5 mm NMR tube and 0.7 ml of MeCN added. Two aliquots of H_2O $14.5 \cdot 10^{-3}$ ml (0.8 mmol) were added by means of the micro syringe to the obtained solution. The NMR spectra were measured in a period of 3 hours after preparation of solutions.

TiF_4 and 1 equivalent of H_2O in MeCN: ^{1}H NMR (400 MHz, MeCN, -40 ºC), δ_H (ppm) = 8.7 (br), 8.4 (br), 7.7 (br), 7.6 (br), 7.5 (br), 7.0 (br); ^{19}F NMR (MeCN, -40 ºC), δ_F (ppm) = 262.8 (m, 6F, *face*-[TiF_3(μ-F)$_3$TiF_3]$^-$, 31%), 223.6 (br, 2F, *cis*-TiF_4(H_2O)(MeCN), 14%), 215.0 (br, 2F, *cis* - TiF_4(H_2O)$_2$, 13%), 161 (br, *cis*-TiF_4(H_2O)(MeCN), 14%), 148.3 (br, *cis* - TiF_4(H_2O)$_2$, 13%), -14 (br), -22.7 (br, 3F, *face*-[TiF_3(μ-F)$_3$TiF_3]$^-$, 15%).

TiF_4 and 2 equivalents of H_2O in MeCN: ^{1}H NMR (400 MHz, MeCN, -40 ºC), δ_H (ppm) = 7.7 (br), 7.6 (br), 7.5 (br, 2H, *cis*-TiF_4(H_2O)(MeCN)), 7.0 (br, 4H *cis* - TiF_4(H_2O)$_2$); ^{19}F NMR (MeCN, -40 ºC), δ_F (ppm) = 262.8 (m, 6F, *face*-[TiF_3(μ-F)$_3$TiF_3]$^-$, 3%), 223.6 (br, 2F, *cis*-TiF_4(H_2O)(MeCN), 3%),

215.0 (br, 2F, *cis* - Ti$F_4(H_2O)_2$, 45%), 161 (br, *cis*-Ti$F_4(H_2O)$(MeCN), 3%), 148.3 (br, *cis* - Ti$F_4(H_2O)_2$, 45%), -14 (br, 0.5%), -22.7 (br, 3F, *face*-$[TiF_3(\mu\text{-}F)_3TiF_3]^-$, 1.5%).

Interaction of 1 and H_2O in MeCN.

The ^{19}F NMR spectrum of **1** and 1 equivalent of water show resonances of the $[Ti_2F_9]^-$ anion and four resonances assigned to the intermediate oligomeric titanium fluoride complex (A) containing coordinated water molecules (Fig.11). The relative intensities of the terminal and bridging fluorine atoms (1 : 2) : (2 : 2), sum 3 : 4 allow us to propose that the intermediate complex (A) could be al least tetrameric (hexameric, octameric, *ets.*). The NMR data does not allow to establish exactly the structure of complex (A) and the kind of the ligand L – H_2O or 18-Crown-6, however, one of the possible model could be the tetrameric cationic complex $\{[TiFL](\mu\text{-}F)_2[TiF_2](\mu\text{-}F)_2\}_2$ where each titanium atom is connected with the neighbouring atom *via* two bridging fluorine atoms.

The ^{19}F NMR spectra of one equivalent of **1** and 2 – 3.9 equivalent of H_2O in MeCN show resonances of $[Ti_2F_9]^-$ anion, complex (A) and *cis*-$TiF_4(H_2O)_2$ (Fig.11).

The relative intensities of the ^{19}F resonances in the spectrum of of **1** and 3.9 equivalent of H_2O differs by different temperatures: $[Ti_2F_9]^-$ 15%, complex (A) 43%, *cis*-$TiF_4(H_2O)_2$ 42% at r.t. and at -35 °C (A) 50%, *cis*-$TiF_4(H_2O)_2$ 50%. This is consistent with the temperature dependent equilibrium between in solution.

The proton spectrum of **1** and 3.9 equivalents of H_2O in MeCN, -40 ºC contains resonances of 18-Crown-6, 18-Crown-6 in complex and coordinated $\{H_2O\}$ in the c*is* - $TiF_4(H_2O)_2$ (Fig.12). The proton resonance of the c*is* - $TiF_4(H_2O)_2$ is shifted 0.5 ppm downfield in comparisson with that of the

c*is* - $TiF_4(H_2O)_2$ in MeCN due to interaction of protons of coordinated water with the 18-Crown-6 in solution at low temperature.

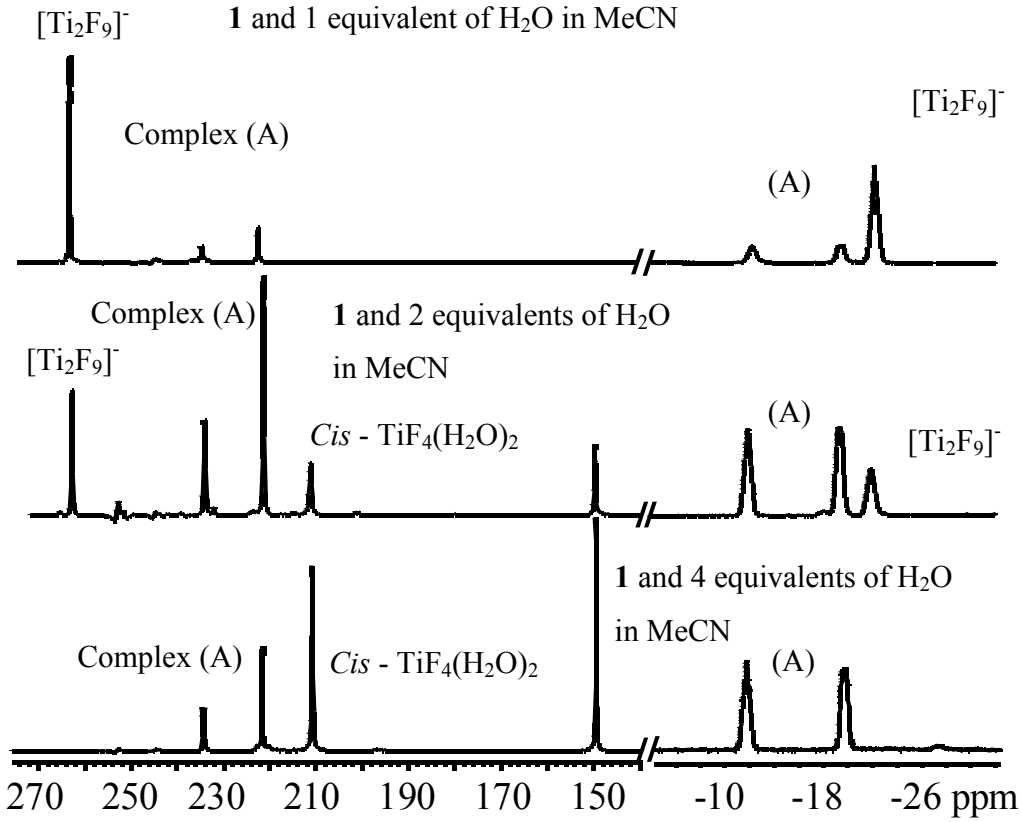

Figure 11.

^{19}F NMR spectra of **1** and 1-3.9 equivalents of the H_2O in MeCN, -30 ºC. Spectra are measured 3 hours after preparation of solution.

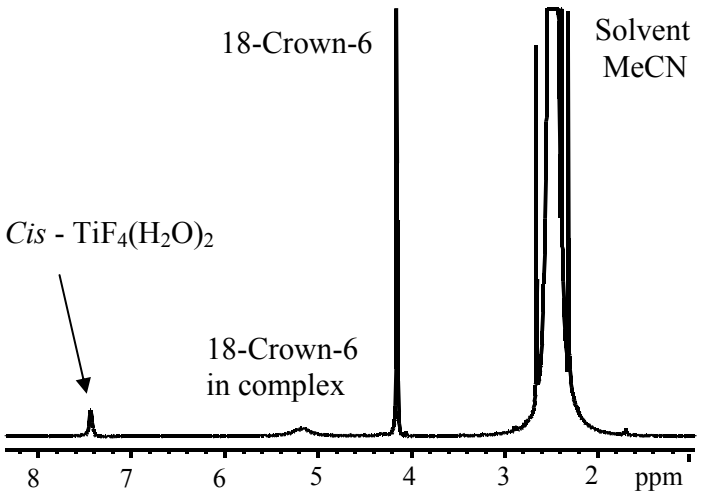

Figure 12.

Proton NMR spectrum of **1** and 3.9 equivalents of H_2O in MeCN, -40 ºC.

NMR scale Experiment: Complex **1** (0.1 g, 0.2 mmol) was loaded in the 5 mm NMR tube and 0.7 ml of MeCN added. Four aliquots of H_2O 4 x $3.5 \cdot 10^{-3}$ ml were added by means of a micro syringe. After adding of each aliquot a ^{19}F NMR spectra at r.t. and -35 ºC were measured.

*Complex **1** and 2 equivalents of H_2O in MeCN:* ^{19}F NMR (MeCN, r.t.), δ_F (ppm) = 262.3 (m, 6F, *face*-[TiF_3(μ-F)$_3$TiF_3]$^-$, 16%), 233.0 (m, nF, 10%), 220.8 (m, 2nF, 20%), 214.3 (br, *cis* - TiF_4(H_2O)$_2$, 7%), 153.0 (br, *cis* - TiF_4(H_2O)$_2$, 7%), -10.0 (m, 2nF, 20%), -17.6 (m, 2nF, 20%), -20.7 (br, 3F, *face*-[TiF_3(μ-*F*)$_3$TiF_3]$^-$, 3%); ^{19}F NMR (MeCN, -35 C), δ_F (ppm) = 262.7 (m, 6F, *face*-[TiF_3(μ-F)$_3$TiF_3]$^-$, 16%), 233.6 (m, nF, 10%), 221.3 (m, 2nF, 20%), 212.6 (br, *cis* - TiF_4(H_2O)$_2$, 7%), 151.4 (br, *cis* - TiF_4(H_2O)$_2$, 7%), -10.8 (m, 2nF, 20%), -18.7 (m, 2nF, 20%), -21.5 (br, 3F, *face*-[TiF_3(μ-*F*)$_3$TiF_3]$^-$, 3%).

*Complex **2** and 3.9 equivalents of H_2O in MeCN:* ^1H NMR (400 MHz, MeCN, r.t.), δ_H (ppm) = 5.0 (br), 4.3 (18-crown-6); ^1H NMR (400 MHz, MeCN, -35 ºC), δ_H (ppm) = 7.5 (*cis* - TiF_4(H_2O)$_2$), 5.2

(br), 4.2 (18-crown-6); ^{19}F NMR (MeCN, r.t.), δ_F (ppm) = 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_2O)$_2$, 21%), 153.3 (br, *cis* - TiF_4(H_2O)$_2$, 21%), -11.7 (m, 2nF, 12%), -19.70 (m, 2nF, 12%), -21.6 (br, 3F, *face*-[TiF$_3$(μ-*F*)$_3$TiF$_3$]$^-$, 5%); ^{19}F NMR (MeCN, -35 ºC), δ_F (ppm) = 233.0 (m, nF, 7%), 220.7 (m, 2nF, 14%), 210.7 (*cis* - TiF_4(H_2O)$_2$, 24%), 148.3 (*cis* - TiF_4(H_2O)$_2$, 24%), -11.7 (m, 2nF, 14%), -19.70 (m, 2nF, 14%).

*Reaction leading to the crystalline **2**:* Complex **1** (0.46 g, 0.9 mmol) was loaded in the 50 mL Schlenk flask and 5 mL of MeCN added *via* syringe. By means of micro syringe H_2O 35 · 10^{-3} mL (1.94 mmol) was added. The mixture was filtered and concentrated to *ca.* 2 mL. and left undisturbed at -24 ºC for 7 days. Finally colourless crystals (0.06 g) deposited. EI-Mass spectra, NMR and IR spectra for **2** obtained by both methods were the same.

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