Hydrothermal Synthesis of Nanoporous Metalofluorophosphates. 1. Precursor Solutions of Titanium Fluoride and Fluorophosphate in Water, a ^{19}F and ^{31}P NMR Study

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Aqueous solutions of titanium(IV) fluorides and fluorophosphates were studied by ^{19}F and ^{31}P NMR for variable F/Ti and (F + P)/Ti ratios. The species distribution is described as successive complexation equilibria. For the Ti/F binary system, equilibrium constants were determined for $TiOF(H_2O)_4^+$, $TiF_5(H_2O)^-$, and TiF_6^{2-} and estimated for $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and $TiF_4(H_2O)_2$. Previously reported anionic species are confirmed and for the first time the spectral signatures of $TiOF(H_2O)_4^+$, $TiOF_2(H_2O)_3$, and $TiF_3(OH)(H_2O)_2$ are provided. Fluorophosphates complexes were observed, and several species containing fluorides and phosphates were identified. These species are representatives of the primary building units during hydrothermal synthesis of nanoporous and mesoporous materials.

Introduction

In the field of nanomaterials, rationalization of syntheses is essential for tailoring materials with designed properties.[1−6] This can be achieved only through understanding the crystallogenesis, which is our ultimate goal. Recently, we elucidated the formation mechanism of $AlPO_4$−CJ2, an oxyfluorinated microporous aluminophosphate, using in situ NMR and ex situ techniques.[6−10] The existence of numerous *nano*- and *meso*porous titanium phosphates[11,12] was also reported. Their crystallogenesis is under study using the same approach. NMR data concerning the titanium fluorophosphates complexes are severely lacking. Consequently, the first step of crystallogenesis, which is the aim of this paper, is to elucidate the existing species in water from model solutions containing Ti, P, F, and H_2O. This is required to describe the primary building units (PBU) before investigating the systems which lead to porous solids using templates. Crystallogenesis of the corresponding nanomaterials will appear later.[13]

NMR data concerning titanium fluorides and fluorophosphates in water are quite old.[14−21] In the late 1950s Caglioti et al. first used potentiometric titrations of dilute and acidic titanium perchlorates solutions and reported that the maximum complexation order of titanium by fluorine should not exceed four fluorines per titanium.[22] Several spectroscopic studies, mainly using NMR, showed later on[14,16,17,23] that TiF_6^{2-} ions exist and can be quite stable in water, which made Caglioti results quite doubtful. Buslaev et al. studied the dissolution of TiF_4 into organo-aqueous solutions at low temperature (−30 to −50 °C).[16] TiF_4 was actually

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observed and transforms into $TiF_5(H_2O)^-$, TiF_6^{2-}, and titanium dimers with vertex, edge, and face sharing. About 20 years later, in 1986, Chernyshov et al.[20] confirmed the existence of TiF_6^{2-} and $TiF_5(H_2O)^-$ by ^{19}F NMR and gave first evidences of the existence of $TiF_4(H_2O)_2$ and $TiF_3(OH)(H_2O)_2$ entities. Titanium fluorophosphate, -sulfate, or -selenite mixed complexes were also reported.

Titanium fluorides in organic solvents have also been quite well studied.[18,24−28] Dyer and Ragsdale reported species such as TiF_6^{2-}, $TiF_5(EtOH)^-$, and $TiF_4(EtOH)_2$ in ethanol.[29] TiF_4 adducts have been observed by ^{19}F NMR.[28] More recently, TiF_4 was used as an inorganic precursor to produce organofluorometallic complexes for CVD applications and additional ^{19}F liquid NMR data were reported.[11]

However, despite these data, obtained a few decades ago, few experimental studies have been performed on titanium fluorides or fluorophosphate complexes, neither in water at room temperature or at higher temperatures. The latter case is strongly lined to hydrothermal syntheses, the purpose of our investigations. The Ti/F/P ternary system in water was investigated under such conditions using ^{19}F and ^{31}P NMR to establish evidence of the species and their composition dependency. The results concerning the model systems Ti/F and Ti/F/P in water are reported in this contribution. This work updates the knowledge of titanium fluoride or fluorophosphate systems in water, with confirmation of already known species and identification of some new ones. It provides the essential basic knowledge for further understanding the crystallogenesis of titanium(IV) phosphates nanomaterials.

Materials and Experiments

Sample Preparation. Diluted acidic titanium(IV) fluorides solutions were prepared according to the following procedure. For F/Ti ratios below 4, titanium and fluorine were introduced by dispersing titanium tetraethoxide $Ti(OEt)_4$ (Aldrich, 99%) and titanium tetrafluoride TiF_4 (Aldrich 98%) into nitric acid solutions made from HNO_3 (Prolabo 55% in water) and deionized water. For F/Ti ratios above 4, mixtures of TiF_4 and HF (Prolabo, Normapur, 50% in water) were mixed into the same nitric acid solutions. The final nitric acid concentration is fixed in all cases at 1 mol/L. Titanium fluoride solutions at higher concentration and pH were made directly by dissolving TiF_4 into deionized water. Titanium fluorophosphate solutions were prepared by using the same procedure than above, with the addition of variable amounts of H_3PO_4 (Prolabo, Normapur, 85% in water) into the titanium fluoride solutions.− −

The two-dimensional (2D) experiment used a 5-mm dual probe $^1H/^{19}F$; for F1, TD = 512k and SI = 1k, and for F2, TD = 2k and SI = 2k. D1 was 3 s, P1 = 8 μs, and pL1 = −6 dB. The other parameters were DE = 38 μs, DW = 134 μs, SWH = 3720 Hz, and NS = 16. The references used for all experiments were H_3PO_4 85% (δ = 0 ppm) for ^{31}P spectra and C_6F_6 (δ = −163 ppm/$CFCl_3$ (δ = 0 ppm)) for ^{19}F experiments.

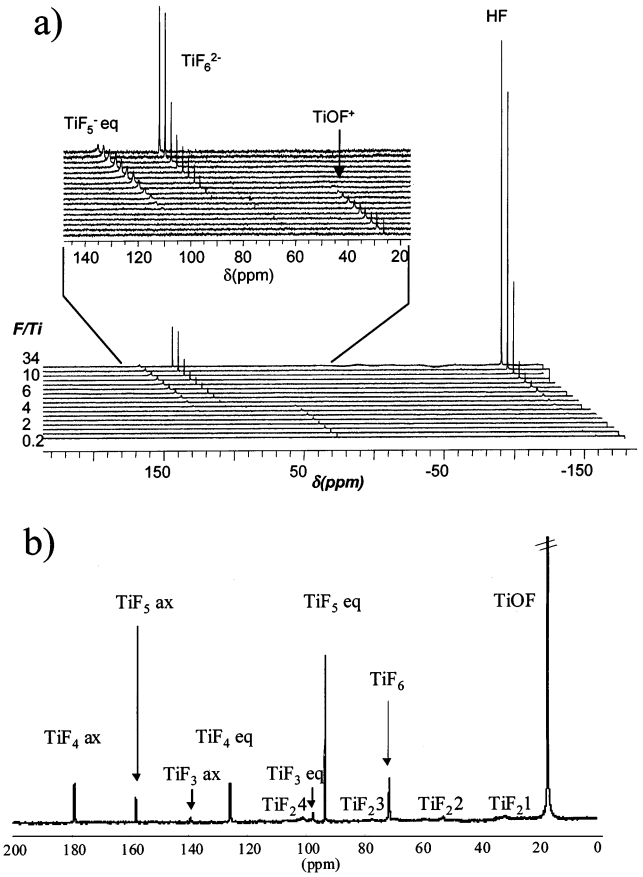

Figure 1. (a) ^{19}F liquid NMR spectra of titanium(IV) fluoride solutions as a function of the F/Ti initial ratio (F/Ti = 0.2/0.5 and then 1−6 (step 0.5) and finally 8/10/18/34). The inset is an expansion of the central part of the spectra. The pH is maintained for each sample at a zero value with 1 M HNO_3 and the titanium concentration kept constant at [Ti] = 0.01 M. For a better understanding, $TiF_5(H_2O)^-$ and $TiOF(H_2O)_4^+$ species are denoted as TiF_5^- and $TiOF^+$ and a systematic offset is applied for NMR shifts. (b) ^{19}F liquid NMR spectrum at −10 °C, F/Ti = 1, [Ti] = 0.1 M.

Results and Discussion

Titanium Fluorides. Let us consider first the water/fluorine/titanium system only. To prevent any precipitation of titanium at low fluorine content, acidic conditions were chosen (pH = 0). Titanium concentrations used were 0.01 M for room temperature and 0.1 M for the −10 °C spectra. By ^{19}F liquid NMR, only four different lines were observed at room temperature, at 163, 99, 76, and 26 ppm, for different F/Ti ratios (Figure 1a), in addition to a HF signal at −160 ppm. The 26 ppm appears for F/Ti ratio up to 4 and no HF is observed within the same range. Above F/Ti = 4, this peak disappears, while TiF_6^{2-} and $TiF_5(H_2O)^-$ show up at +76 and +99 ppm, with a concomitant appearance of an HF signal at −160 ppm. For the spectrum obtained at −10 °C with a F/Ti of 1 (Figure 1b), 12 peaks are observed with a multiplets structure for some of them in addition to a HF signal. They are assigned to the successive complexes TiF_x, with x varying from 1 to 6 (Figure 1b).

At room temperature all lines observed are singlets. TiF_6^{2-} has a singlet line at low as well as room temperature at 76 ppm and a singlet at 71.7 ppm at −10 °C. At low temperature, signals of $TiF_5(H_2O)^-$ were

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reported previously as two multiplets, a doublet at 96 ppm and a quintet at 175 ppm.[20] At room temperature, the strong signals of the four fluorine sites in equatorial position at 99 ppm are observed, as well as the equatorial sites at 163 ppm. At −10 °C, $TiF_5(H_2O)^-$ exhibits two resonances at 93.5 and 158.1 ppm. The former being a doublet and the latter a quintet. The coupling constant is 35 Hz.

On the spectrum at −10 °C, two signals at 125.6 and 179.2 ppm have identical intensity and an unresolved multiplet structure. They are due to $TiF_4(H_2O)_2$ with the axial signals downfield and the equatorial upfield. $TiF_3(OH)(H_2O)_2$ has two peaks at the ratio 1:2, at respectively 139.3 and 97.6 ppm. $TiF_3(OH)(H_2O)_2$ has a *C*2*v* mirror symmetry with all the negative ions F and OH in the equatorial plane and the two water in axial positions. The experimental ratio of 1:2 confirms a TiF_3-$(OH)(H_2O)_2$ conformation. Four other small signals are located at 31.6, 53.2, 72, and 101.2 ppm. Their intensity is weaker than all other signals. They could be assigned to $TiF_2(H_2O)_4$ or $TiOF_2(H_2O)_3$ depending on the existence of the titanyl bond. The first case leads to two isomers, cis and trans (TiF_2 1 and TiF_2 2), and two lines, one for each isomer. The second case leads to three isomers. If the titanyl bond is taken as the axis of reference, then the additional isomer to the two previous ones has one axial fluorine opposite the titanyl bond and the other fluorine in equatorial position (TiF_2 3 and 4). The latter case leads to two doublets. The first two isomers are characterized each by a singlet. The doublets may not be fully resolved, leading to a total of four lines. This is actually the case observed (Figure 1b), so the titanyl bond exists for the difluorinated complex. At room temperature the signal at 26 ppm is assigned to $TiOF(H_2O)_4^+$. At −10 ppm the same species appears at 16.8 ppm. As a general trend, chemical shifts of these species are dependent on temperature, species concentrations, pH, and HF content, though at different rates with different species.

In a second step, integration of all ^{19}F NMR peaks was performed. Simulations of the species distribution were made and compared to the integrated ^{19}F intensities experimentally obtained. Besides protonation of fluorine in water (see (1) and (2)), a successive regime of complexation of titanium by fluorine is assumed (see (3)):

$$(1)\ H^+ + F^- \leftrightarrows HF \quad \beta_{F1} = \frac{[HF]}{[F^-][H^+]}$$

and

$$(2)\ HF + F^- \leftrightarrows HF_2^- \quad \beta_{F_2} = \frac{[HF_2^-]}{[F^-][HF]}$$

$$(3)\ TiF_n^{(4-n)} + F^- \leftrightarrows TiF_{n+1}^{(3-n)} \qquad \beta_{n+1} = \frac{[TiF_{n+1}^{(3-n)}]}{[Ti_n^{(4-n)}][F^-]}\ (n = 0-5)$$

As the pH is fixed at 0 (1 M HNO_3), then $[H^+] = 1$ M. [HF] is thus expressed directly as a function of $[F^-]$ (see (4)). As the total titanium and fluorine concentrations are known, eqs (5) and (6) could be deduced:

$$(4)\ [HF] = \beta_{F1}[F^-]$$

$$(5)\ c_{Ti} = [Ti](t=0) = [Ti](t) + \sum_{n=1-6} [TiF_n^{(4-n)}](t)$$

$$(6)\ c_F = [F_{introduced}](t=0) = (F/Ti)^* c_{Ti} = \rho^* c_{Ti} = [HF_2^-] + [HF] + [F^-] + \sum_{n=1-6} n^*[TiF_n^{(4-n)}](t)$$

Then, using complexation constants according to (3) and conservation equations (5) and (6), concentrations can be expressed as a function of the variable $[F^-]$ (see (7)−(11)):

$$(3) \Rightarrow (7):\ [TiF_n^{4-n}]_{n=0-5} = [TiF_6^{2-}]^* \frac{[F^-]^{n-6}}{\prod_{i=n+1-6} \beta_i}$$

$$(5) \Rightarrow (8):\ [TiF_6^{2-}] = c_{Ti} - \sum_{n=0-5} [TiF_n^{(4-n)}](t)$$

$$(7) + (8) \Rightarrow (9):\ [TiF_6^{2-}] = \frac{c_{Ti}}{1 + \sum_{n=0-5} \frac{[F^-]^{n-6}}{\prod_{i=n+1-6} \beta_i}} \text{ and}$$

$$[TiF_n^{4-n}]_{n=0-5} = [TiF_6^{2-}]^* \frac{[F^-]^{n-6}}{\prod_{i=n+1-6} \beta_i}$$

$$(10)\ F/Ti = \frac{c_F}{c_{Ti}} = \left\{ [F^-] + \beta_{F1}[F^-] + \beta_{F1}\beta_{F2}[F^-]^2 + \frac{c_{Ti}}{1 + \sum_{n=0-5} \frac{[F^-]^{n-6}}{\prod_{i=n+1-6} \beta_i}} * \sum_{n=0-5} n \frac{[F^-]^{n-6}}{\prod_{i=n+1-6} \beta_i} \right\} / c_{Ti}$$

However, for convenience F/(F + Ti) (see (11)) is used instead of F/Ti. The concentrations are eventually normalized (see (11)):

$$(11) \frac{F}{F+Ti} = \frac{F/Ti}{1 + F/Ti} \text{ and } [X]_{(Ti)} = \frac{[X]}{c_{Ti}} \text{ with X = titanium complex}$$

Only three titanium fluorides complexes, $TiOF(H_2O)_4^+$, $TiF_5(H_2O)^-$, and TiF_6^{2-} were observed in the series of spectra at room temperature, but the existence of intermediate complexes such as $TiF_x(H_2O)_{6-x}^{4-x}$ (x = 2, 3, 4) must be included, even if the $TiOF_2(H_2O)_3$ complex amount remains very small. Then, six complexation orders (1−6) and their corresponding complexation constants (β_1, ..., β_6) were used for the simulation with F/(F + Ti) as the variable.

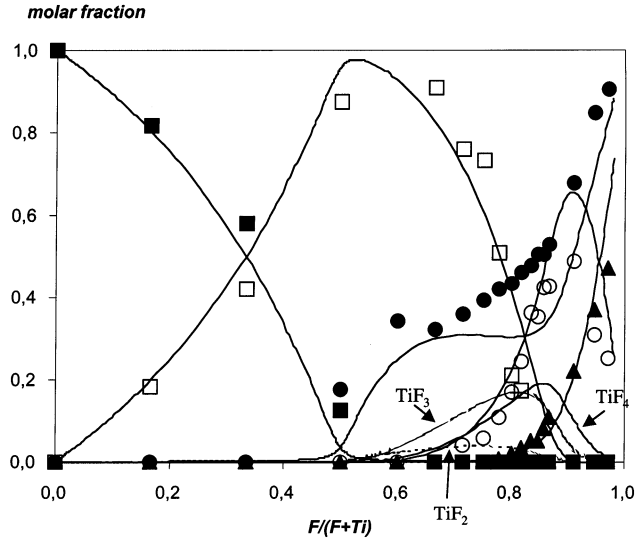

Figure 2. (a) Comparison of theoretical and experimental normalized concentration of the different species involved in the Ti−F−H_2O system at room temperature, pH = 0 and [Ti] = 0.01 mol L^{-1}, as a function of the F/(F + Ti) initial ratio. Theoretical curves are represented as full lines while experimental results are represented as dotted points. For a better understanding, the observed species $TiF_5(H_2O)^-$ and $TiOF(H_2O)_4^+$ species are denoted as TiF_5^- and $TiOF^+$. The theoretical distribution of $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and $TiF_4(H_2O)_2$ complexes are represented using full, semi-dotted, and dotted lines, respectively (see 0.6−0.9 F/(F + Ti) range). ■, TiO^{2+}; □, $TiOF^+$; ○, TiF_5^-; ▲, TiF_6^-; ●, HF.

Table 1. Best Estimates of Successive Formation Constants for the Ti/F/H_2O System Obtained from ^{19}F NMR Spectra at pH = 0 and [Ti] = 0.1 mol L^{-1} [a]

complex	stoichiometry F/Ti	chemical shift (ppm)	Log β_i[b]
$TiOF(H_2O)_4^+$	1	+26	6.0(5)
$TiOF_2(H_2O)_3$	2	not observed at room temp	2.2(2)
$TiF_3(OH)(H_2O)_2$	3	not observed at room temp	3.2(2)
$TiF_4(H_2O)_2$	4	+163	4.0(2)
$TiF_5(H_2O)^-$	5	+99/+163	13.0(7)
TiF_6^{2-}	6	+76	2.25(5)

[a] β_i represents the complexation of titanium by i fluorine atoms ($i = 1-6$). [b] For $i = 5$, log β_5 represents the sum of log β_i ($i = 2-5$) since complexes at 2, 3, and 4 F/Ti are not observed. The theoretical log β_i ($i = 2-5$) values are nevertheless proposed. Chemical shifts were deduced using TiF_6^{2-} as the reference (δ = 76 ppm).

A satisfying fit of the experimental distribution was obtained (Figure 2), with the corresponding constants reported in Table 1. Only the values corresponding to the observed species can be taken into account; the values of the nonobserved complexes, $TiF_x(H_2O)_{6-x}^{4-x}$ ($x = 2, 3, 4$), are therefore only estimated. The theoretical results also agree well with the order of appearance of the different observed complexes with increasing F/(F + Ti) ratios: $TiF(H_2O)_5^{3+}$ then $TiF_5(H_2O)^-$ and TiF_6^{2-}. Besides, as several studies showed previously, Ti^{4+} cation does not exist in water, even in very acidic conditions because of its very small ionic radius; the most likely species is $TiO(H_2O)_5^{2+}$, exhibiting a characteristic Ti═O titanyl bond. Thus, $TiF(H_2O)_5^{3+}$ is commonly assigned to its doubly deprotonated form $TiOF(H_2O)_4^+$, which involves the formation of a titanyl bond. $TiF_2(H_2O)_4^+$ complex must be written actually as

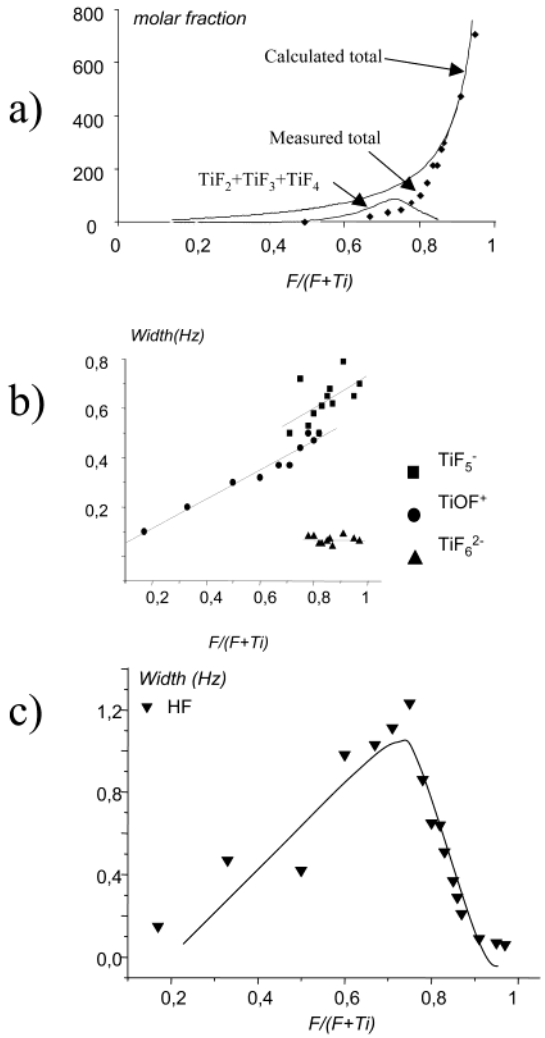

Figure 3. (a) Total integrated theoretical (full line) and experimental (losange) fluorine concentration as a function of the F/(F + Ti) ratio; the calculated sum of the distribution of the theoretical species $TiOF_2(H_2O)_4$, $TiF_3(OH)(H_2O)_2$, and $TiF_4(H_2O)_2$ is also added as a solid line for comparison; (b) full width at half-maximum of ^{19}F NMR peaks of $TiF_5(H_2O)^-$, $TiOF(H_2O)_4^+$ (denoted as TiF_5^- and $TiOF^+$), and TiF_6^{2-} as a function of F/(F + Ti); (c) full width at half-maximum of ^{19}F NMR peaks of HF as a function of F/(F + Ti).

$TiOF_2(H_2O)_3$ if the titanyl bond can be demonstrated. The complexation constant obtained for $TiOF(H_2O)_4^+$, log $\beta_1 = 6.0(5)$, is quite close to the value reported before by Charlot, log $\beta_1 = 6.3$ obtained by potentiometry.[30] The chemical shifts of the species assigned to $TiF_5(H_2O)^-$ and TiF_6^{2-} complexes by the distribution analysis correspond to assignments from previous studies, based on coupling constants patterns.

Besides, a comparative plot of the experimental and calculated total fluorine concentrations vs F/(F + Ti) indicates the existence of a lack of detection in the [0.6−0.8] composition range (Figure 3a). This clearly shows that at room temperature, a fast exchange between $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, $TiF_4(H_2O)_2$, and HF species occurs with a subsequent lack of NMR detected species compared to the total introduced. Plots of the width at half-height of the ^{19}F NMR peaks indicate a

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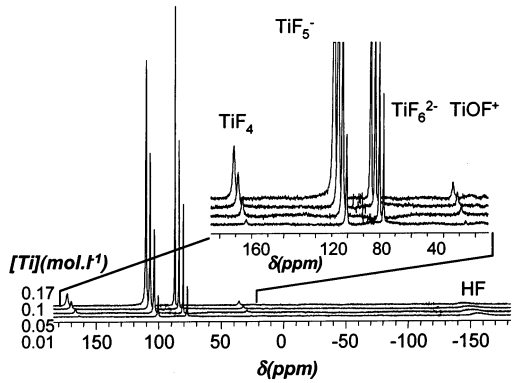

Figure 4. Liquid ^{19}F NMR spectra of titanium(IV) fluoride solutions, made from the dissolution of TiF_4 into water, as a function of the titanium concentration. For a better understanding, $TiF_4(H_2O)_2$, $TiF_5(H_2O)^-$, and $TiOF(H_2O)_4^+$ species are denoted as TiF_4, TiF_5^-, and $TiOF^+$. An enlargement is represented at the top of the figure.

maximum of line width for HF and $TiOF(H_2O)_4^+$ in the corresponding composition range (Figure 3b).

Let us consider the difference curve between the total fluorine introduced and the measured values (Figure 3a):

$$\frac{[F_{tot}] - [F_{NMR}]}{[Ti]} = \frac{[F_{missing}]}{[Ti]}$$

It corresponds to the species that are not be detected by NMR. Inclusion of complexes $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and $TiF_4(H_2O)_2$ in the calculated distribution allows estimation of the missing part of the observed fluorides (Figure 3a). The two less fluorinated species seem to be of less importance than $TiF_4(H_2O)_2$. In the latter case, the maximum of the missing species curve corresponds to the maximum expected for $TiF_4(H_2O)_2$ species, i.e., 0.8. This is in qualitative agreement with the observation of $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$ in the −10 °C spectrum. Furthermore, the maximum of exchange for HF coincides also with 0.8 (Figure 3b). This points out that $TiF_4(H_2O)_2$, in exchange with HF, is the dominant species among the three successive complexes $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and $TiF_4(H_2O)_2$. Only $TiF_3(OH)(H_2O)_2$ seems to influence somehow the final distribution in addition to $TiF_4(H_2O)_2$. As $TiOF_2(H_2O)_3$ complex is in very small concentration, its weight on the complexation constant is small. Actually, the relatively low thermodynamic stability of $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and to a lesser extent $TiF_4(H_2O)_2$ shows that the titanyl bond is only stabilizing the first complex $TiOF(H_2O)_4^+$ and not the following ones. The most probable reason is the balance between electronic repulsion brought by the shortening of distances with titanyl formation and the covalent stabilization energy. With different states of deprotonation, $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and $TiOF(H_2O)_4^+$ are not stabilized.

How does TiF_4 dissolve into water? ^{19}F liquid NMR spectra corresponding to solutions at different concentrations up to the synthesis concentration of 0.17 mol L^{-1} were recorded (Figure 4). At all concentrations, the species observed previously are present as well as an additional signal at +163 ppm. In the previous experiment, under acidic conditions, only one signal for $TiF_5(H_2O)^-$ was observed at 99 and 163 ppm. The line at 163 ppm corresponds to the axial fluorine of $TiF_5(H_2O)^-$. At a concentration of 0.01 mol L^{-1}, the ratio between these two lines at 163 and 99 ppm is 4. $TiF_5(H_2O)^-$ exhibits therefore its two signals at 99 and 163 ppm. They correspond respectively to the four equatorial and the axial fluorine atoms, with some exchange phenomenon that precludes the presence of multiplets structures. The most probable situation to take into account the loss of multiplets structure is the exchange of the axial fluorine with water. If the exchange takes place at a very low rate, enough to average the F−F coupling constants of $TiF_5(H_2O)^-$ (J_{F-F} 35 Hz to less than 10 Hz—the residual width of the F signal—i.e., about 10-ms residence time maximum on the axial fluorine site) but slow enough not to average the chemical shift difference (≈80 ppm, i.e., at this field (35 095 Hz chemical shift difference, i.e., a residence time longer than 23 μs)), then the signals will be approximately at their slow exchange limit positions, but they will lose their coupling constant patterns. This shows up clearly on the −10 °C spectrum where the structure of the multiplets is fully resolved.

$TiF_4(H_2O)_2$ and $TiF_3(OH)(H_2O)_2$ complexes were reported before[16,20] at +129 and +194 ppm and +100 and 147 ppm, [20] respectively. At −10 °C they appear respectively at 125.6 and 179.2 ppm and 97.6 and 139.3 ppm. $TiF_5(H_2O)^-$ is assigned to the 99 ppm (equatorial) and 163 ppm (axial) lines. Increasing amounts of TiF_4 increases both the intensity of $TiF_5(H_2O)^-$ signals, but modifies considerably the equatorial/axial (99/163 ppm) amplitude ratio from 4. Actually, the 163 ppm lines lies close to the average value of $TiF_4(H_2O)_2$ axial and equatorial fluorine sites, 161.5 ppm according to Chernyshov et al.[20], 152.4 ppm from the −10 °C spectrum. As exchange between axial and equatorial fluorine of $TiF_4(H_2O)_2$ involves also HF, the line at 163 ppm contains certainly both the axial fluorine of $TiF_5(H_2O)^-$ and the averaged fluorine signal of $TiF_4(H_2O)_2$ with HF. These results agree with previous studies of the dissolution of TiF_4 in solvents where similar complexes were observed (TiF_6^{2-}, $TiF_5(Solv.)^-$, and $TiF_4(Solv.)_2$).[16,29] The line width of $TiF_4(H_2O)_2$ at +163 ppm increases with titanium content, indicating that it also involves exchange with water and HF. Actually, the HF signal is very broad, in contrast to experiments at lower titanium concentration (0.1 M) (Figure 1), indicating some exchange.

Lowering the temperatures of such solutions decreases the exchange speed and allows recovery of the coupling patterns observed in previous studies. The dissolution of TiF_4 into water follows therefore the reaction

$$TiF_4 \xrightarrow{H_2O} \alpha TiO(H_2O)_5^{2+} + \beta TiOF(H_2O)_4^{+} + \gamma TiOF_2(H_2O)_3 + \delta TiF_3(OH)(H_2O)_2 + \epsilon TiF_4(H_2O)_2 + \eta TiF_5(H_2O)^- + \lambda TiF_6^{2-} + \kappa HF \quad (\alpha + \beta + \gamma + \delta + \epsilon + \eta + \lambda + \kappa = 1)$$

Among these species, $TiO(H_2O)_5^{2+}$, $TiOF_2(H_2O)_3$, and $TiF_3(OH)(H_2O)_2$ are not detected at room temperature, but are at −10 °C. The dissociation reduces at room

temperature to the following apparent reaction:

$$TiF_4 \xrightarrow{H_2O} \alpha TiOF(H_2O)_4^{+} + \beta TiF_4(H_2O)_2 + \gamma TiF_5(H_2O)^{-} + \delta TiF_6^{2-} + \kappa HF$$

Finally, this study confirms the existence of all the successive fluorinated complexes of titanium and shows exchange between the axial and equatorial fluorine of $TiF_4(H_2O)_2$ with HF and also with the fluorine sites present in $TiF_3(OH)(H_2O)_2$ and $TiOF_2(H_2O)_3$ species.

For the first time, the presence of low fluorinated titanium fluorides $TiOF(H_2O)_4^{+}$, $TiOF_2(H_2O)_3$ have been detected; $TiF_3(OH)(H_2O)_2$, $TiF_4(H_2O)_2$ have also been observed. Exchange takes place at room temperature, so detection of $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and $TiF_4(H_2O)_2$ is incomplete.

Titanium complexation by fluorine in water is quite different from what is found with other systems due to the presence of a titanyl bond at low fluorine content, giving rise to species such as $TiOF(H_2O)_4^{+}$ and $TiOF_2(H_2O)_3$. The presence of a titanyl bond markedly affects the stability of the subsequent fluorinated complexes. Only a large excess of fluorine atoms would remove the titanyl bond for fluorine atoms. Thus, an original regime of complexation of titanium by fluorine occurs: a low fluorinated and cationic species exhibiting a titanyl bond ($TiOF(H_2O)_4^{+}$) coexisting with highly fluorinated complexes ($TiF_5(H_2O)^{-}$ and TiF_6^{2-}), the intermediate species, $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and $TiF_4(H_2O)_2$, being in smaller quantities and are, at room temperature, in exchange with HF. The room-temperature ^{19}F spectra make believe that these species hardly exist, a wrong deduction induced by NMR unobservability.

Within other tetravalent systems, the Sn(IV)−F−H_2O system has been well-studied and complexes of composition $SnF_{6-x}(OH)_x^{2-}$ ($x = 0-3$) and $SnF_5(H_2O)^{-}$ have been reported;[19] no low fluorinated tin fluoride complex with a Sn=O bond was observed but as the study was conducted using excess of fluorine (F/Sn = 6), their existence cannot be ruled out in other conditions. With other tetravalent cations (Zr^{4+}, Hf^{4+}), no such behavior has been reported to date. This might be due to their higher ionic radius that favor much less the formation of M=O bonds. As V^{4+} cation exhibits a very strong vanadyl bond in water, a similar fluorinated regime might be expected.

Titanium Fluorophosphates. Hydrothermal syntheses of *nano*- and *meso*porous titanium phosphate are more efficient when fluorine is added to the starting composition. Actually, fluorine is found also in some of the phases formed.[11,12] The species building up the crystalline structures contains therefore fluorides and phosphates as ligands. To clarify if such species are present already in solution or not, aqueous solutions containing titanium fluorine and phosphates were prepared.

First, increasing amounts of phosphoric acid were added to titanium solutions of concentration 0.01 M, in HNO_3 = 1 M, as in the previous section. Hardly any fluorophosphate complexes happen to form when H_3PO_4 is added. ^{19}F spectra are almost identical (Figure 5) and ^{31}P spectra show only the H_3PO_4 signature.

In a second step, composition of such solutions were chosen therefore as close as possible to those of hydrothermal syntheses.[12] Mixtures of TiF_4:$10H_3PO_4$:nH_2O ($360 < n < 5000$) range from [Ti] = 0.01 M to [Ti] = 0.17 M. The F to P ratio was therefore fixed to 4 while titanium concentration is changed. At variance to the study on fluorides, nitric acid is not added to fix the pH to 0. The variable parameter is therefore the ratio P/H_2O, changed from 1/500 to 1/36. Competition between water, phosphate, and fluorine takes place as the water content is modified. pH changes with the titanium concentration from slightly above 0 to approximately 1, when going from 0.01 to 0.17 M.

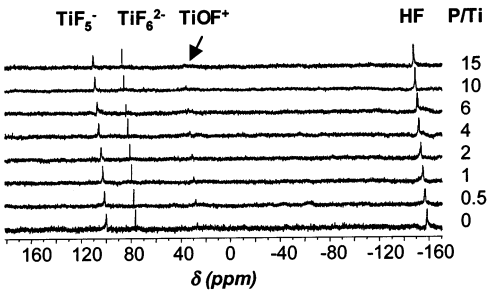

Figure 5. Liquid ^{19}F NMR spectra of titanium(IV) fluorophosphate solutions under very acidic conditions as a function of the initial P/Ti ratio. The samples are made from TiF_4, H_3PO_4, and 1 M HNO_3; the titanium concentration is kept at 0.01 M and the pH at a zero value; for a better understanding, $TiF_5(H_2O)^{-}$ and $TiOF(H_2O)_4^{+}$ species are denoted as TiF_5^{-} and TiOF.

^{19}F NMR spectra exhibit at low concentration of titanium the same species as those observed when no phosphoric acid is added. As the titanium concentration rises, an increasing number of new species appears (Figure 6a). At [Ti] = 0.17 mol/L, at least 25 new peaks are present with their chemical shifts in the range +50 to +180 ppm in addition to HF at −160 ppm. ^{31}P spectra indicate that these species are fluorophosphates (Figure 6b). However, it cannot be ruled out that some of these complexes are not fluorophosphates but titanium fluorides that appear because of slower exchange. The fluorophosphates exhibit ^{31}P lines in addition to phosphoric acid, correlated in intensity to the corresponding increase in intensity of new species in the ^{19}F spectra. Three kinds of ^{31}P lines are observed: free H_3PO_4 (δ = 0 ppm), a first group of titanium fluorophosphates complexes at $\delta = -4$ to -7 ppm and a second group at $\delta = -10$ to -12 ppm. Though the H_3PO_4 line is very intense, no exchange takes place with the additional lines. These chemical shifts correspond respectively to Q1 and Q2 metal−phosphorus connectivity. Q1 and Q2 refer to phosphorus atoms related through oxygen bridges to one and two titanium atoms, respectively. However, unlike ^{19}F spectra, the spread of chemical shifts is much more limited for ^{31}P spectra. It is therefore difficult to assign the chemical shifts to more detailed information on complexes than their connectivity.

However, the appearance of new complexes, rich in diversity of fluorine types, while the concentration increases, indicates a competition of phosphates with water for coordinating titanium. Though the concentration increase of phosphate may induce an increase of exchange between the corresponding species, this is not the case, as the spectra stay resolved both in fluorine and in phosphorus NMR. This reduction of exchange is

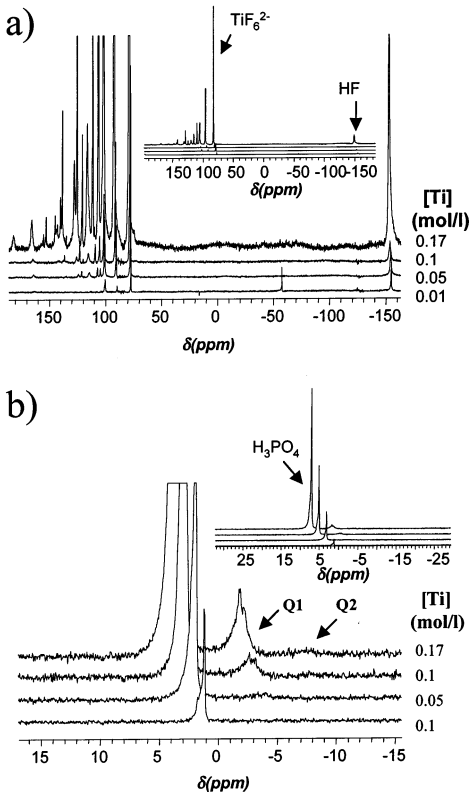

Figure 6. (a) Liquid ^{19}F NMR spectra of titanium(IV) fluorophosphate solutions, made from TiF_4, water, and phosphoric acid, as a function of the titanium concentration. The P/Ti ratio is fixed at 10. For a better understanding, $TiF_5(H_2O)^-$ and $TiOF(H_2O)_4^+$ species are denoted as TiF_5^- and $TiOF^+$ and a systematic offset is applied for NMR shifts. (b) ^{31}P liquid NMR spectra of the corresponding titanium fluorophosphate solutions.

not expected. One would increase the exchange by increasing concentrations, unless the species formed shows higher activation energies for the ligand exchange process. Some of these species are probably oligomers as the presence of Q2 phosphorus sites, observed by ^{31}P NMR, suggests. This reduction of exchange of ligands in the titanium first sphere of coordination is further revealed by a closer examination of the coupling patterns of the ^{19}F spectra. On Figure 7, two peaks have been selected because they exhibit F/F couplings with coupling constants close to 40 Hz. Other signals are broad, either because their coupling pattern is unresolved or because they may be at the onset of exchange.

The observed chemical shifts are reported in Table 2 with their assignments. A 2D COSY $^{19}F-^{19}F$ NMR experiment was conducted in order to elucidate the structure of the complexes. Five species with two-fluorine atoms couplings are observed (Figure 8). The evolution of the ratio Fa/Fb of the two independent fluorine atoms Fa and Fb of the five different coupled fluorine atoms has been followed by changing the P/Ti ratio between 1 and 15; the corresponding ^{19}F and ^{31}P were recorded. The fluorophosphate complexes concentration clearly increases with P/Ti ratio (Figure 9). Integration of ^{19}F spectra show that fluorine complexes are progressively turned into fluorophosphates with increasing amounts of phosphoric acid (Figure 10). Eventually, the ratios of integrated ^{19}F peaks Fa/Fb of the coupled inequivalent fluorine atoms are calculated as a function of P/Ti (Figure 11a). Knowing the nature

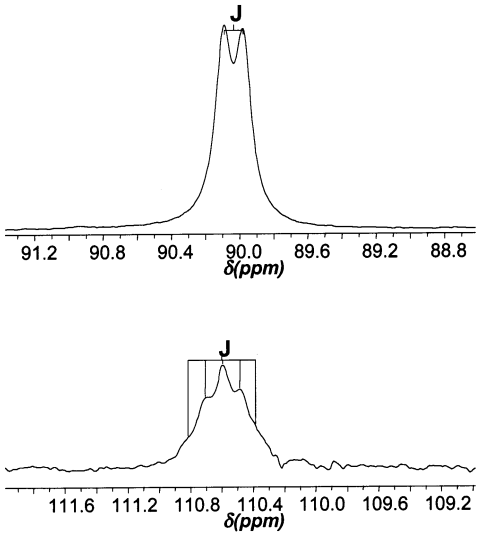

Figure 7. Enlargements of the liquid ^{19}F NMR spectrum of a titanium(IV) fluorophosphate solution corresponding to the axial and equatorial fluorine atoms of the complex $TiF_5(H_2PO_4)^{2-}$ (synthesis conditions: TiF_4:10H_3PO_4 and [Ti] = 0.17 mol L^{-1}).

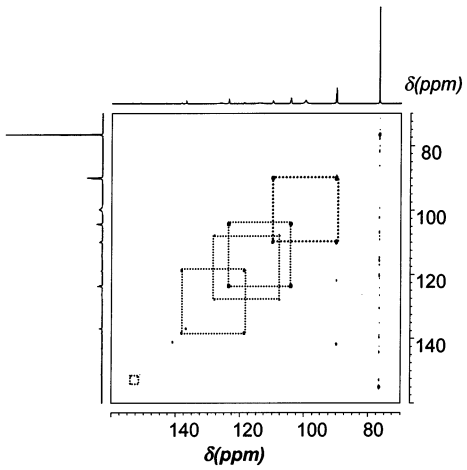

Figure 8. ^{19}F liquid NMR COSY experiment made from a titanium(IV) fluorophosphate solution (synthesis conditions: TiF_4:10H_3PO_4 and [Ti] = 0.17 mol L^{-1}). Squares are represented to point out the F−F coupling results.

of the multiplets, the ratios Fa/Fb, and the coordination of titanium of six for monomeric species, structures were then looked at for these species. Fluorophosphates with two to five fluorine atoms per titanium were found (Figure 11b).

Our results agree very well with Chernyshov et al. assignments (see Table 2). In both cases, titanium fluorophosphates with two to five fluorine atoms per titanium are found. No discrepancies are present between the two sets. Three species, exhibiting ^{19}F couplings, are identical: $TiF_5(H_2PO_4)^-$, $TiF_4(H_2PO_4)_2^{2-}$, and $TiF_3(H_2PO_4)(H_2O)_2$. One of the complexes reported by Chernyshov et al. is observed in our conditions but without any visible coupling: $TiF_4(H_2PO_4)(H_2O)^-$. Two of our complexes were never reported before: one with a $TiF_2(H_2PO_4)_n(H_2O)_{4-n}^{2-n}$ stoichiometry and a probable oligomeric complex $Ti_xFa_yFb_{3y}(H_2PO_4)_z(H_2O)_p$. In the latter case, the Fa/Fb ratio is close to 3 but no monomeric or dimeric structure could be proposed. This is a new species, containing more than a titanium, showing that in the fluorophosphate case, it is possible to observe condensed species and not only monomers.

Table 2. ^{19}F NMR Chemical Shifts and Comparative Proposed Structures of Titanium Fluorides and Fluorophosphates According to This Work and to Chernyshov et al. Results[20] [a]

complexes[b]	chemical shifts (ppm)[c] (this work): [Ti] = 0.17 M and T = 293 K	chemical shifts (ppm)[c] (this work): [Ti] = 0.1 M and T = 263 K	chemical shifts (ppm):[d] (ref 14): [Ti] = 2−5 M and T = 230−303 K
HF	**−160**	**−160**	**−160**
TiF_6^{2-}	**76**	**71.7**	**76**
$TiF_5(H_2O)^-$	***99****(eq)*/***163****(ax)*	**93.6** (eq)/**158.0** (ax)	**96**(eq)/**175**(ax)
$TiF_5(H_2PO_4)^-$	90/111		89/109
$TiF_4(H_2O)_2$	*163 (average ax/eq)*	**125.6** (eq)/**179.2** (ax)	**129**(eq)/**194**(ax)
$TiF_4(H_2PO_4)(H_2O)^-$	114/127/181		**111/125/181**
$TiF_4(H_2PO_4)_2^{2-}$	104/125		**102/122**
$TiF_3(OH)(H_2O)_2$	−	**97.6** (eq)/**139.3** (ax)	**100/147**
$TiF_3(H_2PO_4)(H_2O)_2$	**119/139**		**116/138**
$TiF_3(H_2PO_4)_2(H_2O)^-$	−		−
$TiF_3(H_2PO_4)_3^{2-}$	143		**141**
$TiF_2(H_2O)_3$	−	31.6/53.2/72.0/101.2	−
$TiF_2(H_2PO_4)(H_2O)_2^+$	**107/133**		−
$TiF_2(H_2PO_4)_2(H_2O)$	−		**135/153**
$TiF_2(H_2PO_4)_3^-$			
$TiF_2(H_2PO_4)_4^{2-}$			
$TiOF(H_2O)_4^+$	**26**	16.8	−
$TiOF(H_2PO_4)(H_2O)_3$	-		−
$TiOF(H_2PO_4)_2(H_2O)_2^-$			
$TiOF(H_2PO_4)_3(H_2O)^{2-}$			
$TiOF(H_2PO_4)_4^{3-}$			
$Ti_xFa_yFb_{3y}(H_2PO_4)_zL_p$	**151/154**		−

[a] **Bold** is used in the last two columns for determined, normal for observed, *italic* for exchange, and − for not observed (L = O, OH, H_2O). (δ = 0 ppm: $CFCl_3$). [b] Water in the coordination sphere is represented as H_2O, regardless of its possible deprotonation as OH. Only in the case of the first complex is one water represented as its doubly deprotonated titanyl bond. [c] Assignments of ^{19}F chemical shifts of axial and equatorial fluorine have already been reported before.[20] [d] Chemical shifts of ref 20 were deduced using TiF_6^{2-} as the reference (δ = 76 ppm).

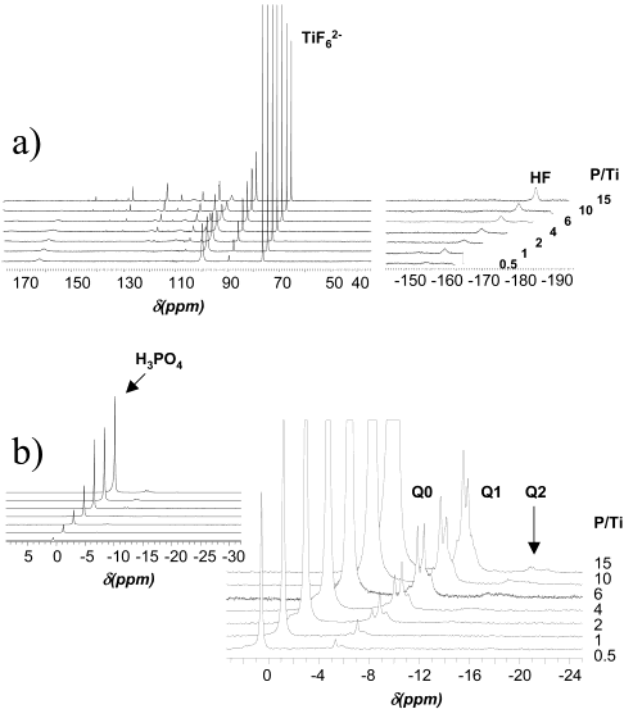

Figure 9. (a) Liquid ^{19}F NMR spectra of titanium(IV) fluorophosphate solutions as a function of the P/Ti introduced ratio. The solutions were made from TiF_4, H_3PO_4, and H_2O at a fixed titanium concentration (0.17 M). For a better understanding, a systematic offset is applied for NMR shifts. (b) ^{31}P liquid NMR spectra of the corresponding titanium(IV) fluorophosphate solutions. In both cases, for a better understanding, a systematic offset is applied for NMR shifts.

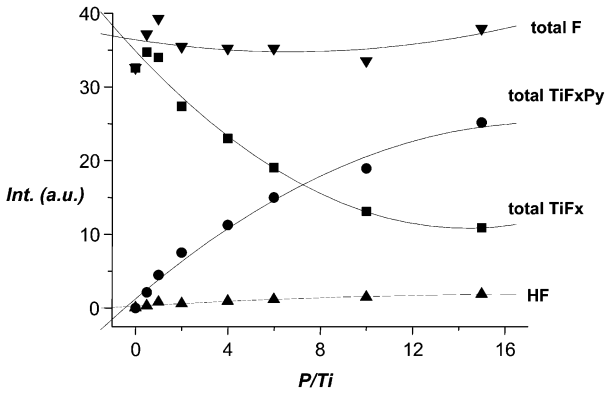

Figure 10. Integrated ^{19}F intensities for different categories of species as a function of the P/Ti initial ratio.

Finally, it seems therefore that apart from slight composition differences, almost all the successive complexes from TiF to TiF_6 are observed with all the combinations of phosphate and water to complete the coordination sphere at six. This competition between water and $H_2PO_4^-$ is to be expected. Henry[31] has shown that their group electronegativity is almost identical, 2.49 for water and 2.48 for $H_2PO_4^-$.

In contrast to the F/H_2O system, species in the F/P/H_2O system, showing off a titanyl bond and one fluorine atom only, have not been evidenced, probably because the F/Ti ratio has not been explored at low values to allow the observation of the phosphated form of the TiOF complex. Furthermore, when dissolving TiF_4 into water, the exchange phenomenon, taking place for the species $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, $TiF_4(H_2O)_2$, and

(31) Henry, M. Molecular tectonics in sol−gel chemistry. In *Handbook of Organic−Inorganic Hybrid Materials and Nanocomposites*; Nalwa, H. S., Ed.; American Scientific Publishers: 2002.

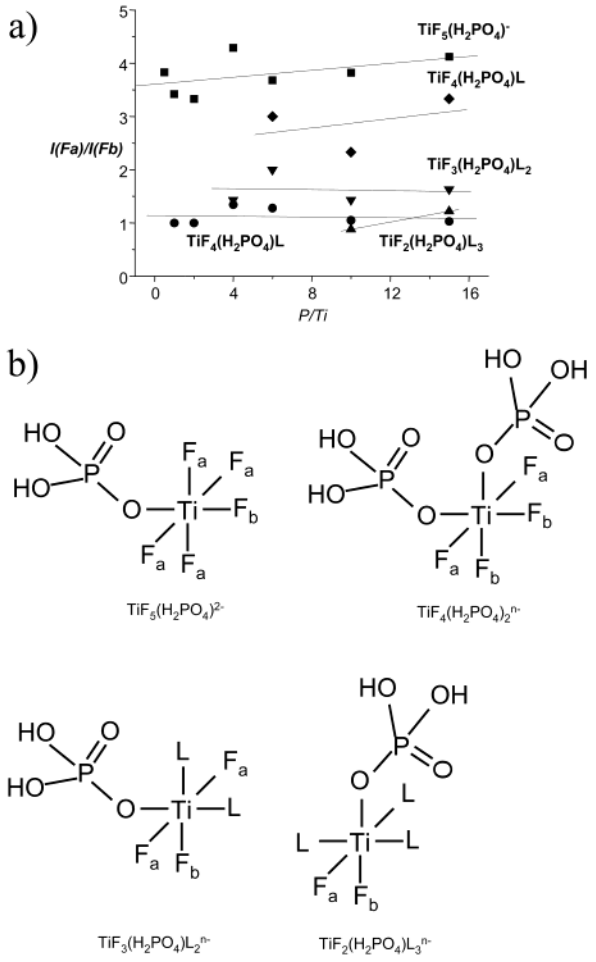

Figure 11. (a) ^{19}F integrated intensity ratios for the two independent fluorides of each titanium fluorophosphates, showing F/F coupling during the COSY experiment, as a function of the P/Ti initial ratio. (b) Representation of the proposed structures of the titanium fluorophosphate complexes with two independent fluorine atoms observed though the COSY experiment.

$TiF_5(H_2O)^-$, is quenched when adding phosphate even at a P/Ti ratio as low as 0.5. This latter result is of utmost importance as it implies most probably a very tight hydrogen bond network within the solvation/complexation sphere of titanium fluorophosphate complexes. This deviates from aluminum fluorophosphate complexes, for which exchange takes place for all compositions.

Conclusion

^{19}F NMR study of the titanium fluorides complexes in water has revealed that fluorine titanium complexes display quite unusual behavior. In acidic and diluted solutions, the successive complexes $TiOF(H_2O)_4^+$, $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, $TiF_4(H_2O)_2$, $TiF_5(H_2O)^-$, and TiF_6^{2-} were studied. $TiOF(H_2O)_4^+$, $TiF_5(H_2O)^-$, and TiF_6^{2-} coexist in slow exchange at room temperature. $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and $TiF_4(H_2O)_2$ are in fast exchange with HF at room temperature, but slow the exchange at −10 °C. In water and within the concentration range considered, no oligomer of titanium is formed. At room temperature, all the fluorinated states of titanium from 0 to 6 do exist. Formation constants have been determined, at room temperature, with estimates only for $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and $TiF_4(H_2O)_2$ complexes in fast exchange. At low temperature a slow exchange leads to observation of the low fluorinated complexes between 2 and 4.

To obtain a closer description of hydrothermal synthesis of *nano*- and *meso*porous titanophosphates using fluorinated conditions, the Ti/F/P has also been investigated. Actually, the NMR spectra are quite complex but once assignments to the species are attained, the system seems to be reasonably simple to describe, with successive fluorine complexes from $TiOF(H_2O)_4$ up to TiF_6^{2-}, where water is progressively replaced by $H_2PO_4^-$. This gives rise to a distribution of possible species, among which only a few are missing, most probably because of too small amounts. An additional oligomeric species, with probably more than two titaniums in it, has also been reported, indicating that fluorophosphates, in contrast to fluorides, are prone to condense, with limited condensation though, a favorable situation for crystal formation. At last, a quite striking aspect of fluorophosphates compared to fluorides is their slow exchange behavior at room temperature for all the species, especially for $TiOF_2(H_2O)_3$, $TiF_3(OH)(H_2O)_2$, and $TiF_4(H_2O)_2$ that were in fast exchange at room temperature for fluorides. Again, this is favorable for condensation of species.

These results were obtained as part of a more systematic undertaking aiming at elucidating the first stages of formation of crystalline solids. They bolster a better understanding of primary building units that may arise in fluorinated conditions, in in situ and ex situ NMR syntheses of *nano*- and *meso*porous titanium phosphates. The next step concerns results from in situ NMR and ex situ studies of the formation mechanism of *nano*- and *meso*porous titanium phosphates and will be reported soon elsewhere.[13]

Acknowledgment. Marc Henry is thanked for many discussions about the environment of titanium by three types of ligands. The CNRS, the French Ministry of Research for their funding of the NMR facilities, and RHODIA are gratefully acknowledged for their financial support.

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