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The Autoionization of [TiF$_4$] by Cation Complexation with [15]Crown-5 To Give [TiF$_2$([15]crown-5)][Ti$_4$F$_{18}$] Containing the Tetrahedral [Ti$_4$F$_{18}$]$^{2-}$ Ion[**]

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Crown ethers[1] promote the autoionization of elements and compounds leading to novel anions, driven by the complex-

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Supporting information (full experimental details for the preparation of **1** and full computational details) for this article is available on the WWW under http://www.angewandte.org or from the author (J.P.).

ation energy of the corresponding cation. Examples include the autoionization of alkali metals M on reaction with crown ethers to give complexed M^+ as well as alkalides and electrides,[2] and the autoionization of main-group and transition-metal chlorides to give cationic crown ether complexes and metal chloro anions.[3] We report herein the reaction of TiF_4 and [15]crown-5 to give $[TiF_2([15]crown\text{-}5)][Ti_4F_{18}]\cdot 0.5\,MeCN$ (**1**). This is, as far as we are aware, the first autoionization of a metal fluoride on reaction with a crown ether, and suggests that this is a viable preparative route to other related binary fluoro metal anions. $[Ti_4F_{18}]^{2-}$ (Figure 1) has overall T_d symmetry and is the second example of such a binary $[M_4X_{18}]^{2-}$ cage (M = metal, X = halogen), the first being $[W_4F_{18}]^{2-}$.[4] Its structure is related to the more-elaborate oxo complexes, for example, $[Ti_4F_{12}O_6]^{4-}$,[5] and $[Ti_4O_6(OSMe_2)_{12}]^{4+}$.[6] The related $[Ti_2F_9]^-$ ion was claimed to exist in solution,[7] and the salts $M[Ti_2F_9]$ (M = Cs, NF_4) have been reported,[8] although their X-ray crystal structures were not determined. We predict, on the basis of estimates of the corresponding energetics, that all monocation salts, with the possible exception of those having small cations, favor $[Ti_2F_9]^-$ ions, and salts of dications favor $[Ti_4F_{18}]^{2-}$ ions.

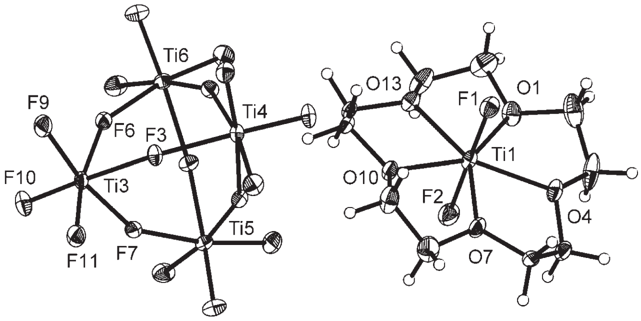

Figure 1. One of the two crystallographically independent dications and dianions in **1** (ellipsoids represent 30% thermal probability). Selected distances [Å] and angles [°]: dication: Ti1−F1 1.769(3), Ti1−F2 1.821(3), Ti1−O1 2.084(3), Ti1−O7 2.089(3), Ti1−O10 2.101(3), Ti1−O13 2.103(3), Ti1−O4 2.113(3); dianion: av $Ti-F_{terminal}$ 1.768 Å, av $Ti-F_{bridging}$ 1.987 Å, av $F_{bridging}$-Ti-$F_{bridging}$ 97.12 °, av $F_{terminal}$-Ti-$F_{terminal}$ 82.84 °.

The structurally characterized binary Ti^{4+} fluorides are $[TiF_4]$,[9] $[TiF_6]^{2-}$,[10] $[TiF_7]^{3-}$,[11] $[Ti_2F_{11}]^{3-}$,[12] $[Ti_2F_{10}]^{2-}$,[13] $\{[Ti_8F_{33}]^-\}_n$,[14] and $\{[Ti_7F_{30}]^{2-}\}_n$.[15] Excess [15]crown-5 and titanium tetrafluoride react in MeCN to form $[TiF_2([15]crown\text{-}5)][Ti_4F_{18}]\cdot 0.5\,MeCN$ (**1**) in 90% yield according to reaction (1), thus effecting the autoionization of $[TiF_4]$ to $[TiF_2]^{2+}$ (stabilized by [15]crown-5) and $[Ti_4F_{18}]^{2-}$. This product is formed in contrast to the neutral adduct isolated from the reaction of $[TiF_4]$ with [18]crown-6, which yielded $[(TiF_4)_2([18]crown\text{-}6)]$.[16] This difference may be because [18]crown-6[17] has a cavity diameter of about 2.9 Å, which is large relative to the ionic diameter of Ti^{4+} (1.4 Å).[18] The diameter of the [15]crown-5 cavity is about 1.95 Å,[17] that is, slightly larger than the ionic diameter of Ti^{4+}, and hence, [15]crown-5 is well suited to promoting the formation of cationic and anionic titanium complexes.

$$5\,TiF_4 + [15]crown\text{-}5 \xrightarrow{MeCN} [TiF_2([15]crown\text{-}5)][Ti_4F_{18}]\cdot 0.5MeCN \quad (1)$$

The ^{19}F NMR spectrum of **1** formed in situ from the reaction of $[TiF_4]$ (4.2 equiv) and [15]crown-5 (1 equiv) in MeCN showed the resonance of the $[TiF_2([15]crown\text{-}5)]^{2+}$ ion at $\delta = 246.8$ ppm.[19] The X-ray crystal-structure determination (Figure 1) showed discrete $[TiF_2([15]crown\text{-}5)]^{2+}$ ions, with structure identical to that found in $[TiF_2([15]crown\text{-}5)][SbF_6]_2$,[19] and $[Ti_4F_{18}]^{2-}$ ions. This $[Ti_4F_{18}]^{2-}$ ion has almost T_d symmetry, with the four titanium atoms situated at the vertices of a tetrahedron, connected by six bridging fluorine atoms and capped by three terminal fluorine atoms each. The $Ti-F_{terminal}$ bond lengths (1.754(3)–1.777(3) Å, av 1.768 Å, 0.98 v.u. (valency units)[20]) and $Ti-F_{bridging}$ bond lengths (1.965(3)–2.010(3) Å, av 1.987 Å, 0.54 v.u.) are similar to those found in oligomeric Ti^{IV} fluoride complexes.[21] The $F_{terminal}$-Ti-$F_{terminal}$ angles (94.94(12)–98.03(13)°, av 97.12°) in **1** are greater than the $F_{bridging}$-Ti-$F_{bridging}$ angles (81.88(10)–83.40(10)°, av 82.84°), as expected from a VSEPR[22] and a ligand–ligand repulsion model.[23]

Consistent with the latter model, the $F_{bridging}\cdots F_{bridging}$ contacts (2.596(4)–2.641(3) Å) are almost equal to the $F_{terminal}\cdots F_{terminal}$ contacts (2.609(5)–2.671(4) Å) in $[Ti_4F_{18}]^{2-}$. We note that the F···F nonbonding distances in other oligomeric Ti−F complexes are very similar (e.g., $[TiF_4]$ ($F_{bridging}\cdots F_{bridging}$ 2.553–2.670 Å, $F_{terminal}\cdots F_{terminal}$ 2.603–2.638 Å),[9] $[Ti_7F_{30}]^{2-}$ ($F_{bridging}\cdots F_{bridging}$ 2.567–2.669 Å, $F_{terminal}\cdots F_{terminal}$ 2.631–2.744 Å),[15] $[TiF_6]^{2-}$(2.636 Å);[10e] the F-Ti-F angles are determined by the almost equal nonbonding F···F distances, in a similar way to various second and third row main group fluorides.[23]

To answer the question as to why $[Ti_4F_{18}]^{2-}$ and not $[Ti_2F_9]^-$ was formed, the optimized structures, vibrational spectra, and ^{19}F NMR shifts of $[Ti_2F_9]^-$ and $[Ti_4F_{18}]^{2-}$ were calculated (see Supporting Information). Unfortunately, the calculated spectroscopic properties were very similar for both anions. The similarity of spectroscopic properties is related to the similarity in the structures of $[Ti_2F_9]^-$ and $[Ti_4F_{18}]^{2-}$ from the perspective of the environments around the titanium and fluorine atoms, and a completely unambiguous distinction between the two is only possible experimentally by X-ray diffraction.

The calculated values of ΔH^{298} and ΔG^{298} for reactions (2)–(5) are given in Table 1. The formation of two $[Ti_2F_9]^-$ ions is favored in the gas phase over dimerization to the $[Ti_4F_{18}]^{2-}$ ion. The situation is less clear for solutions in acetonitrile and dichloromethane, and most likely both anions exist in equilibrium. The energetics in the solid state were estimated by using the equation of Jenkins et al. and applying the "volume-based" thermodynamic (VBT) approach.[24,25] Dimerization to the $[Ti_4F_{18}]^{2-}$ ion and formation of $[TiF_2([15]crown\text{-}5)][Ti_4F_{18}]$ is strongly favored in the solid state over the hypothetical $[TiF_2([15]crown\text{-}5)][Ti_2F_9]_2$ salt of the $[Ti_2F_9]^-$ ion, thus the $[Ti_4F_{18}]^{2-}$ ion is lattice-stabilized in the solid state.[26]

To investigate which conditions promote the formation of a stable salt of $[Ti_2F_9]^-$, the $\Delta H^{298}_{(s)}$ ($\approx \Delta G^{298}_{(s)}$) values of reactions (6) and (7) for salts containing mono- and dications of different sizes were compared (Figure 2).

Table 1: Calculated and estimated thermodynamic enthalpies and free energies [kJ mol^{-1}] of the $[Ti_2F_9]^-$ and $[Ti_4F_{18}]^{2-}$ ions for the gas-phase, solid-state (as salts of $[TiF_2([15]crown\text{-}5)]$),[a,b] and solution dimerization[c] reactions.[d]

	Reaction	$\Delta G(n)^{298}$	$\Delta H(n)^{298}$
(2)	$2[Ti_2F_9]^-{}_{(g)} \rightarrow [Ti_4F_{18}]^{2-}{}_{(g)}$[e]	215	160
(3)	$[TiF_2([15]crown\text{-}5)][Ti_2F_9]_{2(s)} \rightarrow [TiF_2([15]crown\text{-}5)][Ti_4F_{18}]_{(s)}$		−216
(4)	$2[Ti_2F_9]^- \rightarrow [Ti_4F_{18}]^{2-}$ (in MeCN)	−4[c]	
(5)	$2[Ti_2F_9]^- \rightarrow [Ti_4F_{18}]^{2-}$ (in CH_2Cl_2)	19[c]	

[a] $U_{lattice}\{[TiF_2([15]crown\text{-}5)][Ti_2F_9]_{2(s)}\}$ 1289 ± 5 kJ mol^{-1} (see Supporting Information). [b] $U_{lattice}$-$\{[TiF_2([15]crown\text{-}5)][Ti_4F_{18}]_{(s)}\}$ 1665 ± 6 kJ mol^{-1} (see Supporting Information). [c] C-PCM solvation model. [d] Details for the estimation of the energetics in all three phases are included in the Supporting Information. [e] We note that the number of bridging and terminal bonds in $2[Ti_2F_9]^-$ and $[Ti_4F_{18}]^{2-}$ are the same. Thus the reaction is isodesmic and therefore the calculated energy is of good accuracy, ± ca. 10 kJ mol^{-1}. It is not trivial to establish the absolute error in such calculations. However, borderline cases of this kind can be used to obtain upper or lower limits of the gas phase calculated values, e.g. in the dimerization of $2S_2^+$ to S_4^{2+}.[35]

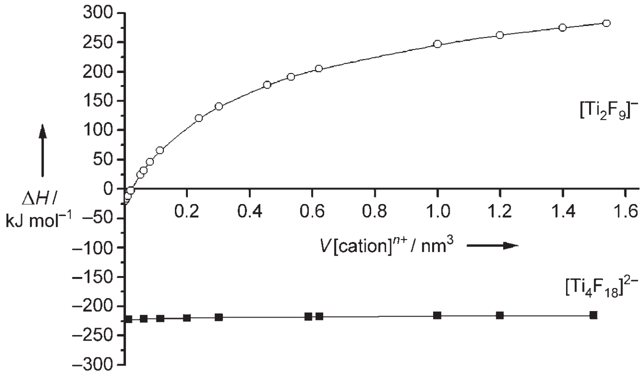

Figure 2. Plot of ΔH ($\approx \Delta G$) versus $V([cation]^{n+})$ for reactions (6) (○, $n = 1$) and (7) (■, $n = 2$). The data used in the calculation of this plot are included with the Supporting Information.

$$2\,[cation]^+[Ti_2F_9]^-{}_{(s)} \rightarrow [cation]_2^+[Ti_4F_{18}]^{2-}{}_{(s)} \qquad (6)$$

$$[cation]^{2+}[Ti_2F_9]_2^-{}_{(s)} \rightarrow [cation]^{2+}[Ti_4F_{18}]^{2-}{}_{(s)} \qquad (7)$$

The VBT approach suggests that the monocations generally favor the formation of [cation]$[Ti_2F_9]$ (since $\Delta H(6)$ ($\approx \Delta G(6)$) is usually >0), whereas dications favor [cation]-$[Ti_4F_{18}]$ (since $\Delta H(7)$ ($\approx \Delta G(7)$) <0, i.e., negative and almost independent of the size of the cation). We predict that the previously reported $[NF_4][Ti_2F_9]$ salt[8] ($\Delta G(6) = 32 \pm (10 + x)$ kJ mol^{-1} [x = uncertainty in the calculated dimerization energy of $2[Ti_2F_9]^-{}_{(g)}$ according to reaction (2)]) probably contains $[Ti_2F_9]^-$ ions; for $Cs[Ti_2F_9]$[8] ($\Delta G(6) = -3 \pm (10 + x)$ kJ mol^{-1}), however, with its slightly smaller Cs^+ ion, it is still an open question as to which anion is present. Notwithstanding borderline cases, this approach has the potential for rationalizing the underlying thermodynamics of related systems and to guide the synthesis of hitherto unknown anions.

Experimental Section

1: A solution of [15]crown-5 (0.54 g, 0.49 mL, 2.5 mmol) in MeCN (20 mL) was added to a solution of $[TiF_4]$ (1.244 g, 10.0 mmol) in MeCN (20 mL). Concentration of the resulting transparent mixture to approximately 20 mL and storage at room temperature for a period of several hours afforded colorless crystals (1.58 g, 90 %). Elemental analysis (%): calcd for $C_{22}H_{43}F_{40}NO_{10}Ti_{10}$: C 15.34, H 2.50, Ti 27.90, F 44.14, N 0.81; found: C 15.47, H 2.40, Ti 27.10, F 43.54, N 0.82. Decomposition occurred above 120 °C without melting; ^{1}H NMR (400 MHz, MeCN, RT): $\delta = 4.61$ ppm (s, *trans*-$[TiF_2([15]crown\text{-}5)]^{2+}$); ^{19}F NMR (376.3 MHz, MeCN, RT): $\delta = 262.8$ (m, $12F_{terminal}$, $[Ti_4F_{18}]^{2-}$), 246.8 (s, 2F, *trans*-$[TiF_2([15]crown\text{-}5)]^{2+}$), −21.6 ppm (m, $6F_{bridging}$, $[Ti_4F_{18}]^{2-}$).

Data were collected on a Bruker AXS P4/SMART 1000 diffractometer ($\lambda(Mo_{K\alpha}) = 0.71073$ Å) by using ω and θ scans. The structure was solved by direct methods and refined against F^2 with non-hydrogen atoms anisotropic and hydrogen atoms in a riding model. The data were reduced (SAINT)[27] and corrected for absorption (SADABS).[28] All calculations were carried out with SHELXTL software,[29] and the structural drawing was prepared by using Diamond.[30] Crystallographic data for **1** ($C_{11}H_{21.50}F_{20}N_{0.50}O_5Ti_5$) at 198 K: $M_r = 860.29$, crystal dimensions $0.30 \times 0.275 \times 0.275$ mm^3, monoclinic, space group $P2_1/c$, $a = 8.3335(9)$, $b = 41.887(5)$, $c = 16.4117(18)$ Å, $\beta = 103.927(2)°$, $V = 5560.4(11)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.055$ Mg m^{-3}, $\mu = 1.531$ mm^{-1}, of 28675 reflections measured ($2.33 < \theta < 25.00°$), 9761 were independent ($R_{int} = 0.0277$), $wR2 = 0.1445$ (all data), $R1 = 0.0482$ (for 7181 reflections with $I > 2\sigma(I)$), 734 parameters, GOF = 1.073. CCDC-272157 contains the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

All theoretical calculations were performed by using the Gaussian 03 program[31] and the MPW91PW91 DFT functional[32] with the NASA AMES cc-pVTZ basis set[33] for titanium and the aug-cc-pVDZ basis set[34] (aug-cc-pVTZ for energy calculations) for fluorine. Solution energetics in acetonitrile and dichloromethane were calculated by using the C-PCM solvation model as implemented in Gaussian 03.[31] Details for all calculations are included in the Supporting Information.

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Keywords: anions · crown compounds · density functional calculations · fluorides · titanium

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