

Synthesis, Spectroscopic Properties, and Crystal Structure of the Oxonium Acid $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$

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The oxonium acid $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**) was obtained by the reaction of TiCl_4 with Et_2O in *n*-pentane and subsequent partial hydrolysis. Suitable single crystals of **1** were obtained by sublimation at 5 °C ($[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$, $P2_12_12_1$ (no. 19), $Z = 4$, $a = 1101.08(8)$, $b = 1328.4(2)$, $c = 1525.0(2)$ pm, $T = 193(2)$ K, 4489 independent reflections, 197 parameters, $R1 = 0.049$). The cation is made up from two independent Et_2O molecules and one disordered proton on two split positions. Both ether molecules exhibit a W form, and their molecular planes include an angle of $74.1(7)^\circ$. Thus a distorted tetrahedron is formed by the four methyl carbon atoms of the two ether molecules. The distance $\text{O}\cdots\text{O}$ amounts to 237.7(1) pm. The proton of the cation was characterized both by ^1H NMR (CDCl_3 , $T = 23$ °C: $\delta = 11.7$ ppm, $w_{1/2} = 100$ Hz) and IR spectroscopy (3120 cm^{-1} , ν vbr). The $[\text{Ti}_2\text{Cl}_9]^-$ ion consists of two face sharing octahedra. ^{47}Ti and ^{49}Ti NMR spectra were recorded in solution (CH_2Cl_2 , $T = 23$ °C: $\delta^{49}\text{Ti} = 137$ ppm, $w_{1/2} = 175$ Hz; $\delta^{47}\text{Ti} = -124$ ppm, $w_{1/2} = 250$ Hz). The absence of a signal for TiCl_4 at $\delta^{49}\text{Ti} = 0$ ppm indicates the stability of the dinuclear anion in solution.

Key words: Oxonium Ion, ^1H NMR, $^{47,49}\text{Ti}$ NMR, Hydrogen Bonding

Introduction

Recently, we have investigated the reactivity of weak silazane bases with strong Lewis acids like titanium tetrachloride [1]. Additionally, we are also searching for a possibility to reduce the acidity of TiCl_4 by introducing weak Lewis bases like diethyl ether.

By serendipity we now discovered $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**), a quite simple representative of an oxonium acid. Most of the hitherto known crystalline examples of this class of oxonium acids exhibit rather complex anions and are difficult to synthesize [2–8]. Another simple example is $([\text{H}(\text{OEt}_2)_2]^+)_2[\text{Zn}_2\text{Cl}_6]^{2-}$ [9]. Such oxonium acids containing solvated protons gained relevance for several applications. Examples are the generation of metallocene cations as used in Ziegler-Natta catalysis or of Pd(II) complexes for copolymerization reactions [2, 4, 5, 10, 11]. Weakly basic and non-interacting anions are important for the solvation of protons, which may be utilized for acid promoted or acid catalyzed reactions [6, 12].

Results and Discussion

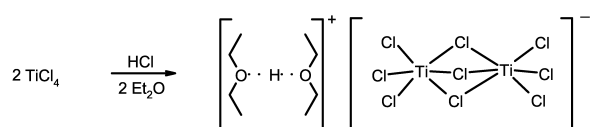
A yellow precipitate formed after addition of TiCl_4 to a solution of Et_2O and *n*-pentane. By evaporating the reaction mixture (≥ 1 hPa), the solvents were frozen at the bottom of a liquid nitrogen cooled trap and a yellow solid was isolated from the down pipe of the trap. From this solid deep yellow single crystals of $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**) suitable for X-ray diffraction were obtained by sublimation at 5 °C. Details of the data acquisition and structure solution are summarized in Table 1.

Apparently, the formation of **1** is initiated by a partial hydrolysis of TiCl_4 . The resulting HCl leads to the formation of the complex anion $[\text{Ti}_2\text{Cl}_9]^-$ and protonation of Et_2O molecules (Scheme 1). A comparable reactivity was observed for a mixture of hexamethyldisilazane and TiCl_4 . After condensation and by elimination of HCl the uncommon salt $[(\text{Me}_3\text{Si})_2\text{NH}_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**2**) was formed by a proton transfer to the weak base hexamethyldisilazane [13].

Formula, weight	$\text{C}_8 \text{H}_{21} \text{Cl}_9 \text{O}_2 \text{Ti}_2$, 564.10
Crystal size / mm^3	$0.20 \times 0.20 \times 0.10$
Crystal color and habit	yellow prism
Crystal system, space group, Z	orthorhombic, $P2_12_12_1$ (No. 19), 4
Unit cell dimensions / pm	$a = 1101.08(8)$, $b = 1328.4(2)$, $c = 1525.0(2)$
Volume / 10^6 pm^3	2230.6(3)
Temperature	193(2) K
Density (calculated)	1.680 g/cm^3
$F(000)$	1128
Absorption coefficient μ	1.792 mm^{-1}
Radiation and wavelength	Mo- K_α ($\lambda = 71.073 \text{ pm}$)
Diffractometer used	Siemens SMART area-detector
Range for data collection	$4.06^\circ \leq 2\theta \leq 58.38^\circ$; $-13 \leq h \leq 13$; $-17 \leq k \leq 17$; $-16 \leq l \leq 18$
Reflections collected	13024
Independent reflections	4489 ($R_{\text{int}} = 0.0550$, $R_{\text{sig}} = 0.0642$); $3200 (F_o > 4\sigma(F_o))$
Absorption correction	SADABS
Max., min. transmission	0.8411, 0.7158
Structure solution	direct methods, SHELXS [23]
Refinement method	full-matrix least-squares on F_o^2 , SHELXL [23]
Flack parameter [24]	0.04(6)
Parameters	197, no restraints
Goodness of Fit on F_o^2	1.02
Largest difference / $10^{-6} \text{ e pm}^{-3}$	max. 0.781 / min. -0.460
Final R1	0.0490 ($F_o > 4\sigma(F_o)$), 0.0833 (all)
Final $wR2$	0.1147 ($F_o > 4\sigma(F_o)$), 0.1277 (all)

Table 1. Data acquisition* and structure solution of $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**).

* Further details may be requested at Cambridge Crystallographic Data Centre, 12 Union road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: fileserv@ccdc.cam.ac.uk), quoting the deposition number CCDC 206996.



Scheme 1.

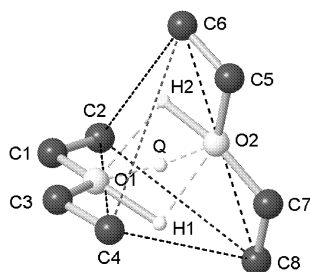


Fig. 1. Cation of $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**) in the solid. Both diethyl ether molecules are in the W form, the methyl carbon atoms forming a distorted tetrahedron. The hydrogen atom is disordered (H1, H2 and Q). Selected distances in pm, angles and torsion angles in $^\circ$: O1...O2 237.7(1), O1-C1 149(2), O1-C3 153(2); C1-C2 151(2), C5-C6 138(2); O1-H1 150.4, O2-H2 143.6, O1-H2 205.6, O2-H1 188.2; O1-H1-O2 88.4, O1-H2-O2 83.8; O1-Q 126.3, O2-Q 115.7; O1-Q-O2 158.3; C2-C1...C3-C4 7.43(1), C6-C5...C7-C8 0.70(1).

In the solid the complex salt **1** is made up from $[\text{Ti}_2\text{Cl}_9]^-$ ions and the oxonium ion $[\text{H}(\text{OEt}_2)_2]^+$ (Fig. 1). The refined atomic parameters are given in

Table 2. Atomic parameters of $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**), $U_{\text{eq}} \equiv 1/3 \sum U_{ii} / 10^4 \text{ pm}^2$.

Atom	x	y	z	U_{eq}
Ti1	1.04447(9)	0.10275(8)	1.02432(7)	0.0365(3)
Ti2	0.9751(2)	0.16533(8)	0.81422(7)	0.0358(3)
Cl1	0.9112(2)	0.0160(2)	1.1035(2)	0.0608(5)
Cl2	1.2063(2)	0.0095(2)	1.0509(2)	0.0631(5)
Cl3	1.0797(2)	0.2249(2)	1.1195(2)	0.0540(5)
Cl4	1.1555(2)	0.1947(2)	0.9085(2)	0.0402(4)
Cl5	0.8802(2)	0.2026(2)	0.9567(2)	0.0438(4)
Cl6	0.9944(2)	0.0007(2)	0.8935(2)	0.0394(3)
Cl7	0.7992(2)	0.1194(2)	0.7564(2)	0.0543(5)
Cl8	1.0943(2)	0.1059(2)	0.7090(2)	0.0532(4)
Cl9	0.9716(2)	0.3242(2)	0.7762(2)	0.0723(6)
O1	0.3956(6)	-0.1180(5)	0.8938(5)	0.089(2)
O2	0.6095(5)	-0.1005(4)	0.9081(3)	0.069(2)
C1	0.343(2)	-0.2143(9)	0.926(2)	0.174(9)
C2	0.422(2)	-0.2558(8)	0.9982(9)	0.189(9)
C3	0.3289(9)	-0.0636(9)	0.8192(7)	0.091(3)
C4	0.391(2)	0.026(2)	0.8086(9)	0.126(5)
C5	0.6806(8)	-0.1307(8)	0.8256(7)	0.087(3)
C6	0.6437(9)	-0.2261(8)	0.8017(7)	0.102(4)
C7	0.6467(8)	-0.0020(7)	0.9495(7)	0.087(3)
C8	0.5838(7)	0.0173(6)	1.0299(5)	0.071(2)
H1	0.4659	-0.0239	0.9145	0.02(3) ^a
H2	0.5546	-0.1984	0.9034	0.02(3) ^a
Q	0.5059	-0.1125	0.9158	0.05 ^b

^a U_{iso} and site occupancy factor (s.o.f.) about 0.5; ^b electron density about 0.3; refinement as H atom results in a s. o. f. of 0.2.

Table 2. The anion consists of two face sharing TiCl_6 octahedra. The distances Ti-Cl to the terminal Cl are

Table 3. Distances / pm and angles / ° in $[\text{Ti}_2\text{Cl}_9]^-$ and $[\text{Ti}_2\text{Cl}_9]^{3-}$ anions.

Cation	Ti-Cl	Ti- μ -Cl	Cl-Ti-Cl	Ti \cdots Ti	Lit.
$[\text{H}(\text{OEt}_2)_2]^+$ (1)	218.9(2)–222.2(2)	246.2(2)–250.8(2)	77.64(6)–99.31(9)	164.02(8)–166.85(8)	339.7(2) this work
$[(\text{Me}_3\text{Si})_2\text{NH}_2]^+$ (2)	217.9(1)–222.6(2)	246.2(6)–255.6(1)	76.82(3)–100.49(4)	163.68(4)–165.96(4)	344.4(1) [13]
$[(\text{Me}_4\text{C}_4\text{S})\text{H}]^+$	220(2)–223(2)	246(2)–251(2)	76.84(5)–99.18(6)	164.70(8)–167.25(7)	341(7) [20]
$[(\eta^6\text{-C}_6\text{Me}_6)\text{TiCl}_3]^+$	218.6(6)–222.0(5)	245.4(5)–251.1(5)	77.5(2)–99.7(2)	163.8(2)–168.1(2)	339.4(4) [25]
$[(\text{C}_6\text{H}_5)_4\text{P}]^{++}$	235(2)–238(2)	249(5)–252(5)	81.7(1)–96.5(2)	169.9(2)–172.3(2)	322(5) [26]
$[(\text{C}_2\text{H}_5)_4\text{N}]^{++}$	236.1(6)–236.5(6)	248.2(9)–251.1(9)	82.8(2)–95.3(2)	171.1(2)–173.0(1)	322(3) [27]

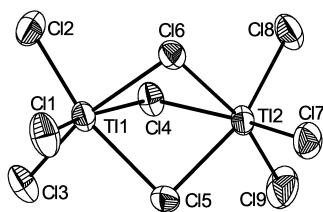
* $[\text{Ti}_2\text{Cl}_9]^{3-}$.

Fig. 2. Anion of $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**) in the solid. Selected distances in pm and angles in °: Ti1–Cl1 222.2(2), Ti1–Cl2 220.8(2), Ti1–Cl3 221.1(2); Ti2–Cl7 221.4(2), Ti2–Cl8 221.8(2), Ti2–Cl9 218.9(2); Ti1–Cl4 247.1(2), Ti1–Cl5 246.9(2), Ti1–Cl6 247.5(2); Ti2–Cl4 248.3(2), Ti2–Cl5 246.2(2), Ti2–Cl6 250.8(2); Ti1 \cdots Ti2 339.7(2); Cl1–Ti1–Cl4 166.23(8), Cl2–Ti1–Cl5 165.83(8); Cl4–Ti2–Cl7 166.85(8), Cl5–Ti2–Cl8 164.02(8).

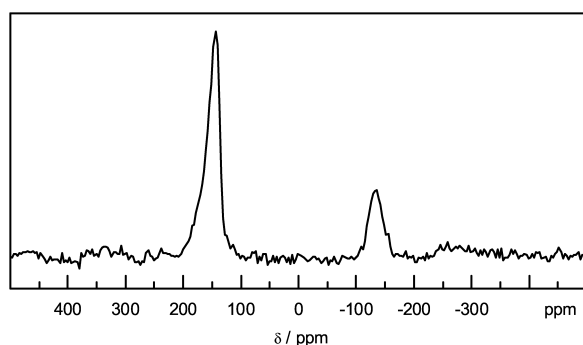


Fig. 3. 22.560 MHz $^{47,49}\text{Ti}$ NMR spectrum of $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**) in CH_2Cl_2 at 23 °C. $w_{1/2}(^{49}\text{Ti}) = 175$ Hz, $w_{1/2}(^{47}\text{Ti}) = 250$ Hz, $\delta^{49}\text{Ti} - \delta^{47}\text{Ti} = 261$ ppm, 52000 scans.

shorter as compared to those of the bridging ones (Fig. 2). The geometrical parameters of the anion are comparable to those of **2** and other salts comprising $[\text{Ti}_2\text{Cl}_9]^-$ ions (Table 3). As $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**) is soluble in Et_2O and rather soluble in CH_2Cl_2 and CDCl_3 , the anion could be characterized by $^{47,49}\text{Ti}$ NMR. No signal of TiCl_4 ($\delta^{49}\text{Ti} = 0$ ppm) was observed, thus excluding the dissociation of the anion in solution. At room temperature chemical shifts of

$\delta^{49}\text{Ti} = 137$ ppm ($w_{1/2} = 175$ Hz) and $\delta^{47}\text{Ti} = -124$ ppm ($w_{1/2} = 250$ Hz) in CH_2Cl_2 solution were observed (Fig. 3). The ^{35}Cl NMR spectrum of **1** in Et_2O exhibits only one very broad signal ($w_{1/2} = 2$ kHz) at $\delta^{35}\text{Cl} = 730$ ppm. The resolution of an IR spectrum (PE pellets) of **1** at low wave numbers was quite poor, however the anion unequivocally was detected in the Raman spectrum. The vibrational frequencies are in-between those for TiCl_4 and $[\text{TiCl}_6]^{2-}$ [14]. The vibrations $\nu(\text{TiCl})$ exhibit the highest wave numbers and are observed at 422 cm^{-1} in **1** (TiCl_4 500 cm^{-1} , $[\text{TiCl}_6]^{2-}$ 320 cm^{-1}). The observed frequencies are in good agreement with the values reported for $[\text{Ti}_2\text{Cl}_9]^-$ in the literature [15] and calculated for D_{3h} point-group symmetry [16].

In the solid the cation is built up from two molecules of Et_2O coordinating one proton (Fig. 1). Both Et_2O molecules exhibit a W form with a maximum (rms) deviation of the least-squares planes of 3.3(7) (rms: 2.6) and 8.1(6) (rms: 4.3) pm, respectively. These planes include an angle of $74.1(7)^\circ$. The stable polymorph of solid Et_2O crystallizes with two independent molecules in trans-trans configuration (W form), whereas the maximum and rms deviation from planarity are 3.7 and 2.7 pm for one, and 0.9 and 0.8 pm for the other molecule [17]. The conformation of the Et_2O molecules can be characterized by both the torsion angle between the $\text{Me-CH}_2\cdots\text{CH}_2\text{-Me}$ carbon atoms and the maximum deviation of the methyl groups from the C–O–C plane. Apparently, the methyl groups exhibit severe thermal displacement or disorder. Therefore, the torsion angles represent a mean value for the deviation from the C–O–C plane. Geometric calculations were performed using PLATON [18], the parameters are summarized in Table 4. The angles C–O–C in these $[\text{H}(\text{OEt}_2)_2]^+$ salts range between 114 and 121° and thus they are enlarged as compared to unprotonated Et_2O (112° in the solid state and $113.5(4)^\circ$ at 27°C) [17, 19].

Anion	O...O / pm	$\tau_a; \tau_b / ^\circ$	$d_a; d_b / \text{pm}$	Lit.
$[\text{Ti}_2\text{Cl}_9]^-$ (1)	237.7(1)	7.0; 0.7	11.3; 13.2	this work
$[(\text{C}_3\text{H}_3\text{N}_2)\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$	240(2)	38.8; 1.1	133.6; 28.8	[2]
$[\text{C}_6\text{F}_4-1,2-\{\text{B}(\text{C}_6\text{F}_5)_2\}_2(\mu\text{-OCH}_3)]^-$	239.4(7)	16.6 ^a ; 0.0	16.4 ^a ; 12.1	[3]
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	244.6(9)	88.3; 20.1	126.7; 59.4	[4]
$[\text{CHB}_{11}\text{H}_5\text{Cl}_6]^-$	240 ^b	120.5 ^a ; 118.2/156.4 ^b	128.1 ^a ; 129.5/128.1 ^b	[6]
$[(\mu\text{-Cl-ZnCl}_2)_2]^{2-}$	239(2)	102.9; 92.0	136.8; 134.4	[9]
HF calculation	262.5	4.2; 2.7	10.9; 20.5	this work
DFT calculation	238.6	58.5; 41.8	47.6; 66.2	[6]

^a Calculated referring to the center of split positions; ^b calculated from the supplementary data; the results indicate the presence of different conformations of the Et_2O molecules, τ_a and d_b were determined for both conformations. The distance O...O ranges between 224(2) to 255(2) pm.

Anion	$\delta(\text{s, 1H, H}^+)$	$\delta(\text{q, 8H, O-CH}_2)$; $^3J_{\text{HH}}$	$\delta(\text{t, 12H, CH}_3)$; $^3J_{\text{HH}}$	Lit.
$[\text{Ti}_2\text{Cl}_9]^-$ (1) ^a	11.7 br	3.83; 7.0	1.32; 7.0	this work
$[(\text{C}_3\text{H}_3\text{N}_2)\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ ^b	16.3 br	4.08; 7.0	1.44; 7.0	[2]
$[\text{C}_6\text{F}_4-1,2-\{\text{B}(\text{C}_6\text{F}_5)_2\}_2(\mu\text{-OCH}_3)]^-$ ^b	16.4 br	4.08; 6.8	1.43	[3]
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b	15.5 br	7.55; 7.2	1.42; 7.2	[4]
$[(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)_4\text{B}]^-$ ^b	11.1 br	3.85	1.32	[5]
$[\text{CHB}_{11}\text{H}_5\text{Cl}_6]^-$ ^c	13.8 br	3.32	0.78	[6]
$[\text{CHB}_{11}\text{Me}_5\text{Br}_6]^-$ ^c	11.7 br	3.22	0.75	[6]
$[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ ^b	16.6 br	4.06	1.43	[10]

^a CDCl_3 ; ^b CD_2Cl_2 ; ^c C_6D_6 .

The methyl carbon atoms form a distorted tetrahedron with oxygen centering two opposite edges with a distance of 237.7(1) pm. The distances C-O are 149(2)–153(2) pm and the distances C-C 138(2)–151(2) pm without any corrections for libration. During the structure determination two equivalent split positions for the proton were identified within the tetrahedron despite the low scattering factor of H for X-rays. These split positions are located between the oxygen and two methyl carbon atoms nearly on the corresponding tetrahedron face. A significantly lower electron density (Q) is found at the expected position, nearby both, the center of the O...O trajectory and of the tetrahedron. The conformation of the non-hydrogen atoms of $[\text{H}(\text{OEt}_2)_2]^+$ in **1** agrees well with the situation in $[\text{H}(\text{OEt}_2)_2]^+[\text{C}_6\text{F}_4-1,2-\{\text{B}(\text{C}_6\text{F}_5)_2\}_2(\mu\text{-OCH}_3)]^-$ [3].

In solution this proton could be observed by NMR as a broad signal ($w_{1/2} = 100$ Hz) at $\delta^1\text{H} = 11.7$ ppm. Similar spectroscopic data are reported for the other compounds containing the $[\text{H}(\text{OEt}_2)_2]^+$ ion, as summarized in Table 5.

In contrast to the spectroscopic data reported for the cation in combination with $[\text{CHB}_{11}\text{H}_5\text{Cl}_6]^-$ or $[\text{FeCl}_4]^-$ [6, 12], the IR spectrum of **1** (in KBr) reveals a broad absorption with a maximum $\nu(\text{OH}) = 3120$ cm^{-1} . The broad absorption $\delta(\text{OHO})$

Table 4. Geometric parameters O...O, τ and d of compounds with $[\text{H}(\text{OEt}_2)_2]^+$ ion. τ is the torsion angle $\text{Me-CH}_2\cdots\text{CH}_2\text{-Me}$ and d the max. deviation of the Me carbon atoms from the $(\text{H}_2)\text{C-O-C}(\text{H}_2)$ plane, values are given for the two Et_2O molecules a and b.

Table 5. ^1H NMR spectroscopic data (δ / ppm; $^3J_{\text{HH}}$ / Hz) of compounds comprising $[\text{H}(\text{OEt}_2)_2]^+$ in solution.

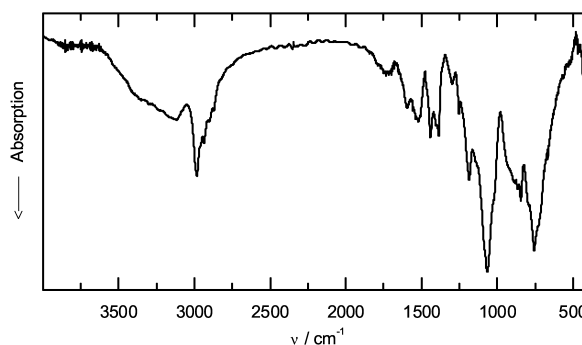


Fig. 4. IR spectrum of $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**) in KBr.

at 1520 cm^{-1} shows a second resolved peak at 1594 cm^{-1} . A band at 935 cm^{-1} is assigned to $\nu_{\text{as}}(\text{OHO})$ and exhibits a fine structure. The $\nu_{\text{as}}(\text{COC})$ vibration of unprotonated Et_2O (1120 cm^{-1}) is significantly shifted to 1066 cm^{-1} in **1** indicating rather strong hydrogen bonds in the cation (Fig. 4).

The shortest distances between C and Cl atoms in **1** range between 365 and 379 pm, thus there is no evidence for significant interactions between $[\text{H}(\text{OEt}_2)_2]^+$ cations and $[\text{Ti}_2\text{Cl}_9]^-$ anions.

Excluding the position of the proton, the structure of the cations in **1** and in $[\text{H}(\text{OEt}_2)_2]^+[\text{C}_6\text{F}_4-1,2-\text{B}(\text{C}_6\text{F}_5)_2\}_2(\mu\text{-OCH}_3)]^-$ [3] are in good agreement with the optimized geometry of $[\text{H}(\text{OEt}_2)_2]^+$ obtained by

DFT methods [6]. Those calculations on $[\text{H}(\text{OEt}_2)_2]^+$ indicate that the proton is centered between the two oxygen atoms in a flat potential. Shifting the proton along the O...O trajectory leads only to a minor increase in total energy [6]. In most of the crystalline compounds summarized in Table 4 a significant deviation of the non-hydrogen atoms from the cation's ideal geometry is observed. This might be ascribed to cation-anion interactions in these compounds. Surprisingly, this ideal conformation of the cation is retained in $[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**). Thus $[\text{Ti}_2\text{Cl}_9]^-$ may be classified as a quite weakly coordinating anion. Therefore its hypothetical corresponding acid "HTi₂Cl₉" should exhibit strong protonating properties *e.g.* forming $[\text{Cl}_3\text{Ti}(\mu\text{-Cl})_3\text{-TiCl}_3]^-$ [13, 20] or related anions $[\text{Cl}_3\text{Ti}(\mu\text{-Cl})_3\text{-TiCl}_2\text{OR}]^-$ [8] and $[\text{Cl}_3\text{Ti}(\mu\text{-Cl})_3\text{-TiCl}(\text{NSiMe}_3)_2\text{SiClNEt}_2]^-$ [21].

Experimental Section

All manipulations were carried out in a dry argon atmosphere, the solvents were refluxed with LiAlH₄ and stored over molecular sieve under argon. TiCl₄ was used as purchased (99.9%, Aldrich). ¹H, ⁷Li, ¹³C, ³⁵Cl and ^{47,49}Ti NMR spectra were recorded with a 5 mm probe (EX400, Jeol) and a 10 mm probe (eclipse 400, Jeol), respectively. All NMR experiments were carried out at room temperature (23(3) °C). Neither the solvents nor the solution of **1** exhibited any ⁷Li NMR signals. IR spectra were recorded on a Bruker IFS 66v/S spectrometer in a KBr matrix. Raman spectra were recorded on a Perkin-Elmer 2000 instrument in a sealed tube.

$[\text{H}(\text{OEt}_2)_2]^+[\text{Ti}_2\text{Cl}_9]^-$ (**1**)

TiCl₄ (1 ml, 9 mmol) was added to a solution of Et₂O (p.A., Fluka, 7 ml, 67 mmol) and *n*-pentane (p.A., Fluka, 150 ml) at -78 °C. A yellow precipitate formed. Unreacted Et₂O and the solvent were evaporated after warming to room temperature (≥ 1 hPa). The solvents were condensed out on the bottom of a liquid nitrogen cooled trap and a yellow solid

precipitated within the trap. The product **1** was isolated from the down pipe in good yield (80%). **1** melts at room temperature and decomposes in air within a few minutes. In an inert atmosphere **1** is stable below -30 °C. Storing **1** at 5 °C for 1 week led to the formation of crystals of a size up to 1 mm with an orthorhombic habit due to sublimation. Suitable single crystals could be isolated at -30 °C and were mounted in perfluoropolyether oil. All non-hydrogen atoms were located by direct methods and difference Fourier syntheses, and their positions were refined anisotropically by full matrix least squares applied on F_o^2 . The methyl and methylene H atoms were added at calculated positions and refined using a riding model. Between the oxygen atoms the two highest electron density maxima were observed at positions nearby two different tetrahedron faces (each about 0.98 10⁻⁶ e pm⁻³). At the expected position, nearby the center of the O...O trajectory, only a significantly lower electron density was found (0.30 10⁻⁶ e pm⁻³). HF calculations (RHF/6-31G(d)) and the reported DFT calculations [6] were carried out using Gaussian98 [22]. Both calculations indicate a proton position nearby the O...O trajectory.

IR (KBr): $\nu = 3120$ v br, 2985, 2939, 2903, 2873, 1700 br, 1594, 1520, 1442, 1386, 1186, 1066, 930 sh, 884, 866, 845, 756 br, 415 cm⁻¹. – Raman (sealed tube): $\nu = 2982, 2938, 2872, 1446, 1087, 422$ vs, 399, 390 sh, 362, 339, 311, 237, 211, 192, 173 w, 143 cm⁻¹. – ¹H NMR (399.78 MHz, CDCl₃): $\delta = 1.32$ (t, ³J_{HH} = 7.0 Hz, J_{CH} = 127.0 Hz, 12 H, CH₃), 3.83 (q, ³J_{HH} = 7.0 Hz, J_{CH} = 143.7 Hz, 8 H, CH₂), 11.7 (w_{1/2} = 100 Hz, < 1 H, H⁺). – ¹³C{¹H} NMR (100.54 MHz, CDCl₃): $\delta = 15.61$ (J_{CC} = 39.2 Hz, CH₃), 66.32 (J_{CC} = 39.2 Hz, CH₂). – ³⁵Cl NMR (39.19 MHz, Et₂O): $\delta = 730$ (w_{1/2} = 2 kHz). – ^{47,49}Ti NMR (22.56 MHz, CH₂Cl₂): $\delta = 137$ (w_{1/2} = 175 Hz), -124 (w_{1/2} = 250 Hz).

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