DOI: 10.1002/ejic.200900507

Syntheses, Crystal Structures, Thermal Properties and Spectroscopic Characterization of Complex Chloridotitanates(IV) with Ionic Liquids

Johann-Christian Leye,[a] Mimoza Gjikaj,[a] and Arnold Adam*[a]

Dedicated to Professor Dr. Gerd Meyer on the occasion of his 60th birthday

Keywords: Titanium / Ionic liquids / Solid-state structures / Structure elucidation

By the reaction of [EMIm]Cl with $TiCl_4$ in two different solvents the three new chloridotitanate complexes $[EMIm]_2[TiCl_6]$ (**I**), $[EMIm][TiCl_5MeCN]$ (**II**) and $[EMIm]_4[TiCl_6][Ti_2Cl_{10}]$ (**III**) were obtained. The crystal structures and the unit cell parameters were determined. The Raman spectra were measured to investigate the distorted octahedral symmetry of the corresponding anionic unit. Differential scanning calorimetry and thermal gravimetric measurements were accomplished to characterize the thermal stability. In addition, NMR and IR spectroscopy and elemental analysis were made to complete the characterization.

Introduction

Homoleptic chloridotitanates(IV) and their adducts with acetonitrile are a class of fundamentally important coordination compounds. In general, they are accessible by addition of halide ions to titanium tetrachloride. Four different homoleptic anionic complexes and two adducts with acetonitrile are known, the enneachloridotitanate $[Ti_2Cl_9]^-$, the decachloridodititanate $[Ti_2Cl_{10}]^{2-}$, the pentachloridotitanate $[TiCl_5]^-$, the hexachloridotitanate $[TiCl_6]^{2-}$,[1] the acetonitrile pentachloridotitanate $[TiCl_5{\cdot}MeCN]^-$ and the acetonitrile tetrachloridotitanate $[TiCl_4{\cdot}2MeCN]$.[2] Additionally, a complex of undecachloridodititanate $[Ti_2Cl_{11}]^{3-}$ is proposed, which exists as a mixture of $[Ti_2Cl_{10}]^{2-}$ and $[TiCl_6]^{2-}$.[3] All of these complexes were prepared by using inorganic salts like CsCl, quaternary ammonium or phosphonium salts and only a few by ionic liquids.[4] Ionic liquids (ILs) have received much attention due to their widespread applications in extraction chemistry,[5] as "green" solvents in organic synthesis,[6] as precursor materials for catalysts[7] and as electrolytes in electrochemistry.[8] Commonly used ILs are dialkylimidazolium and *N*-alkylpyridinium salts, because of their easy synthetic route. As a result of the growing interest in metal-ion-containing ILs for example as catalysts, the increase in information about crystal structure and chemical behaviour is essential. Thomson and Scheffler already prepared a number of mixtures with different metal halides and [EMIm]Cl as the IL.[9] Furthermore, the workgroup of Chongmin et al. determined a series of $[BMIm]_2[MCl_4]$ metal-ion-containing ILs.[10] Also, the crystal structures of $[EMIm]_2[CoCl_4]$,[11] $[BMIm]_2[AuCl_6]$,[12] $[EMIm]\,[VOCl_4]$,[13] $[EMIm]_2[PtCl_6]$,[14] $[EMIm][PF_6]$,[15] $[EMIm][NbF_6]$, $[EMIm][TaF_6]$[16] and $[EMIm]_2[IrCl_4]$[14] have been reported. Though, both metal-ion-containing ILs and chloridotitanates are of interest. In this work, we present the syntheses of three new complexes $[EMIm]_2[TiCl_6]$ (**I**), $[EMIm]\,[TiCl_5{\cdot}MeCN]$ (**II**) and $[EMIm]_4[TiCl_6][Ti_2Cl_{10}]$ (**III**), which were characterized by X-ray, Raman and NMR spectroscopy and thermal (DSC, TG) and elemental analysis.

Results and Discussion

Syntheses

The addition of two equivalents of [EMIm]Cl as a chloride donor to $TiCl_4$ in acetonitrile at room temperature results in a colour change in the reaction mixture from colourless to yellow. The crystalline product of this reaction is the hexachloridotitanate(IV) complex $[EMIm]_2[TiCl_6]$ (**I**) [Equation (1)].

$$\mathrm{TiCl_4 + 2\,[EMIm]Cl \xrightarrow{MeCN} [EMIm]_2[TiCl_6]} \tag{1}$$

(EMIm = 1-methyl-3-ethylimidazolium)

When changing the stoichiometry to one equivalent of the chlorine donor, [EMIm]Cl, the acetonitrile pentachloridotitanate(IV) complex **II** was obtained [Equa-

---

[a] Institute of Inorganic and Analytical Chemistry, Clausthal University of Technology,
Paul-Ernst-Str. 4, 38678 Clausthal-Zellerfeld, Germany
Fax: +49-5323-72-2229
E-mail: arnold.adam@tu-clausthal.de

tion (2)]. By changing the stoichiometry to one equivalent of chlorine donor to two $TiCl_4$, the already known $TiCl_4{\cdot}2MeCN$ was found.

$$TiCl_4 + [EMIm]Cl \xrightarrow{MeCN} [EMIm][TiCl_5MeCN] \qquad (2)$$

In the next step, the solvent was switched from acetonitrile to the donor-free dichloromethane. When using the same stoichiometric relation as depicted in Equation 2, the mixed decachloridodititanate(IV) hexachloridotitanate(IV) complex was obtained [Equation (3)].

$$3\,TiCl_4 + 4\,[EMIm]Cl \xrightarrow{CH_2Cl_2} [EMIm]_4[TiCl_6][Ti_2Cl_{10}] \qquad (3)$$

All products were received in a pure state, which was confirmed by comparison of the X-ray data of the corresponding powder and single crystal.

Crystal Structures

Title compounds **II** and **III** belong to the monoclinic crystal system with the same crystallographic space group *P*2$_1$/*c*. Compound **I** crystallizes in the orthorhombic space group *Pbca*. All crystal structures consist of isolated cations and anions. Compound **I** involves two cations and one anion (Figure 1), compound **II** one cation, one anion and one solvent molecule (Figure 2) and compound **III** four cations and two anions (Figure 3).

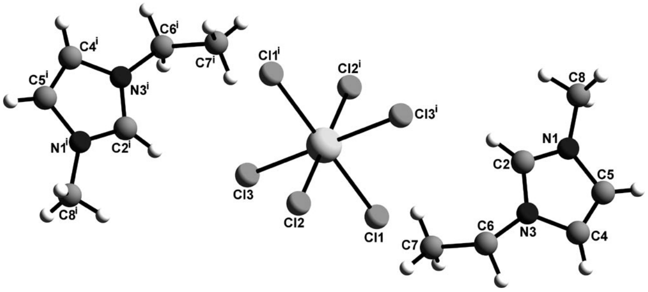

Figure 1. Coordination polyhedron in $[EMIm]_2[TiCl_6]$.

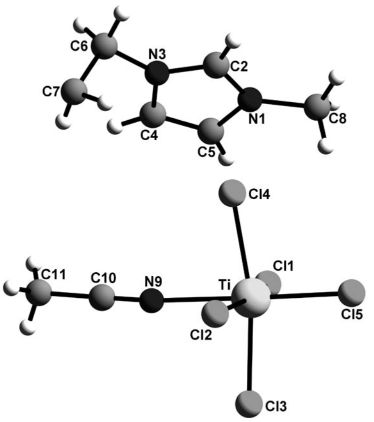

Figure 2. Coordination polyhedron in $[EMIm][TiCl_5{\cdot}MeCN]$.

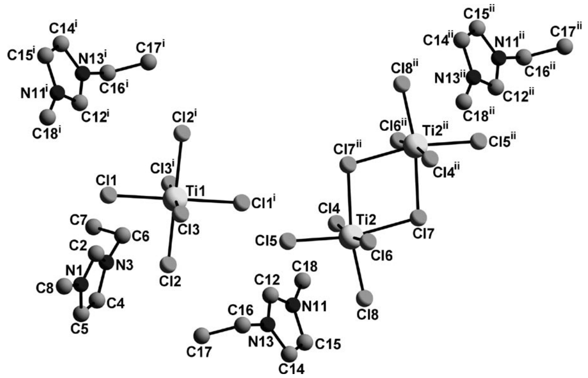

Figure 3. Coordination polyhedron in $[EMIm]_4[TiCl_6][Ti_2Cl_{10}]$.

Details of the X-ray structure analyses and crystallographic data for compound **I**, **II** and **III** are presented in Table 9. Fractional atomic coordinates and equivalent thermal parameters of the three different structures are shown in Tables 1, 2 and 3, and selected bond lengths and angles are gathered in Tables 4, 5 and 6.

Table 1. Fractional atomic coordinates and thermal parameters of **I**.

	x	*y*	*z*	U_{eq}
Ti	0	0	0	0.0278(1)
Cl1	–0.1227(1)	0.0700(1)	–0.1259(1)	0.0380(2)
Cl2	0.0428(1)	0.1421(1)	0.0714(1)	0.0380(2)
Cl3	0.1675(1)	0.0152(1)	–0.1095(1)	0.0384(2)
N1	–0.5413(1)	0.0374(2)	0.1338(2)	0.0345(5)
N3	–0.4639(2)	0.1708(2)	0.1537(2)	0.0333(5)
C2	–0.4455(3)	0.0829(2)	0.1678(2)	0.0348(6)
C4	–0.5762(3)	0.1815(2)	0.1103(3)	0.0462(8)
C5	–0.6241(3)	0.0990(2)	0.0978(3)	0.0487(8)
C6	–0.3792(3)	0.2443(2)	0.1825(3)	0.0451(7)
C7	–0.2591(3)	0.2346(3)	0.1305(5)	0.0722(14)
C8	–0.5547(4)	–0.0618(2)	0.1345(3)	0.0451(7)

Table 2. Fractional atomic coordinates and thermal parameters of **II**.

	x	*y*	*z*	U_{eq}
Ti	0.2282(1)	0.4875(1)	0.2333(1)	0.0290(1)
Cl1	0.2936(1)	0.4161(1)	0.0908(1)	0.0358(2)
Cl2	0.1370(1)	0.5777(1)	0.3546(1)	0.0415(2)
Cl3	0.0826(1)	0.3295(1)	0.2135(1)	0.0399(2)
Cl4	0.3518(1)	0.6646(1)	0.2279(1)	0.0422(2)
Cl5	0.3628(1)	0.3709(1)	0.3300(1)	0.0451(2)
N1	0.3377(2)	0.8964(2)	0.3893(1)	0.0363(4)
N3	0.3084(2)	1.0143(2)	0.2627(1)	0.0354(4)
N9	0.0979(2)	0.6059(2)	0.1376(1)	0.0396(5)
C2	0.3912(2)	0.9557(2)	0.3233(1)	0.0350(5)
C4	0.1977(3)	0.9907(3)	0.2911(2)	0.0473(6)
C5	0.2167(3)	0.9167(3)	0.3695(2)	0.0482(7)
C6	0.3300(3)	1.0841(3)	0.1754(2)	0.0472(6)
C7	0.2948(8)	1.0079(5)	0.0877(3)	0.0903(17)
C8	0.3974(3)	0.8132(3)	0.4647(2)	0.0499(7)
C10	0.0331(2)	0.6758(2)	0.0956(1)	0.0360(5)
C11	–0.0483(3)	0.7662(3)	0.0417(2)	0.0499(7)

The angles and bond lengths of the relevant cationic unit $[EMIm]^+$ were investigated intensely by X-ray analysis.[17] Therefore, just the anionic unit is described in detail. Com-

Table 3. Fractional atomic coordinates and thermal parameters of **III**.

	x	*y*	*z*	U_{eq}
Ti1	0	0	0.5	0.0301(2)
Ti2	–0.3923(1)	0.0945(1)	0.0442(1)	0.0366(2)
Cl1	0.0511(2)	0.0365(1)	0.6620(1)	0.0707(4)
Cl2	0.1573(1)	0.0935(1)	0.4708(1)	0.0500(3)
Cl3	–0.1537(1)	0.0935(1)	0.4719(1)	0.0620(3)
Cl4	–0.2312(1)	0.0003(1)	0.0933(1)	0.0512(3)
Cl5	–0.3549(1)	0.1541(1)	0.1920(1)	0.0512(3)
Cl6	–0.5727(1)	0.1750(1)	–0.0044(1)	0.0544(3)
Cl7	–0.4595(1)	0.0087(1)	–0.1023(1)	0.0368(2)
Cl8	–0.2688(1)	0.1724(1)	–0.0310(1)	0.0675(5)
N1	0.4521(3)	0.0937(2)	0.6701(2)	0.0448(8)
N3	0.5238(3)	–0.0218(2)	0.6282(2)	0.0376(7)

pound **I** consists of parallel layers of one hexachloridotitanate unit and two IL molecules (Figure 4). The anionic unit is situated in an approximately octahedral O_h symmetry. The Ti–Cl bond lengths range from 2.335 to 2.355 Å. The Cl2–Ti–Cl1 angle is 89.8°, the Cl2–Ti–Cl3 angle 89.5° and the Cl1–Ti–Cl3 angle 90.0° (Table 4). These values compare well with those of reported hexachloridotitanate(IV) complex.[18] Compound **II** consists of parallel layers of alternating blocks comprising one IL and one acetonitrile pentachloridotitanate (Figure 5).

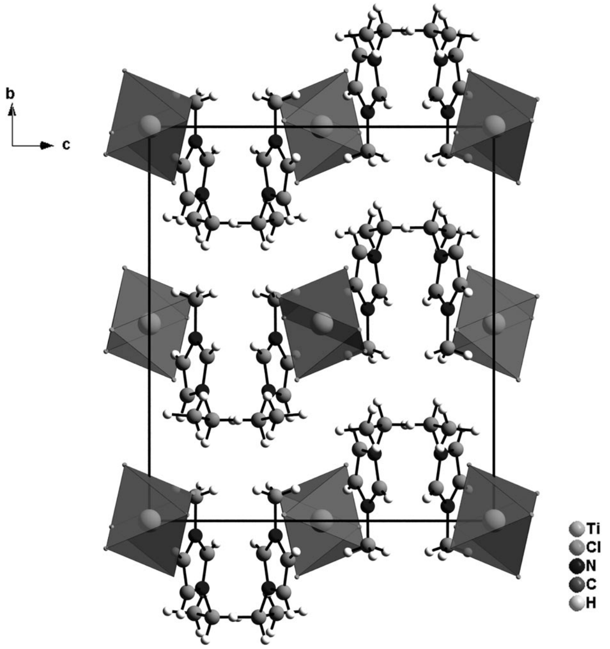

Figure 4. Perspective view of the unit cell of **I** along the *a* axis.

Table 4. Selected bond lengths [Å] and angles [°] for compound **I**.[a]

Ti–Cl1	2.3545(7)	Ti–Cl1^i	2.3545(7)
Ti–Cl2	2.3345(7)	Ti–Cl2^i	2.3345(7)
Ti–Cl3	2.3432(7)	Ti–Cl3^i	2.3432(7)
Cl2–Ti–Cl2^i	180.00(5)	Cl2–Ti–Cl3	89.48(3)
Cl2^i–Ti–Cl3	90.52(3)	Cl2–Ti–Cl3^i	90.52(3)
Cl2^i–Ti–Cl3^i	89.48(3)	Cl3–Ti–Cl3^i	180.00(2)
Cl2–Ti–Cl1^i	90.20(2)	Cl2^i–Ti–Cl1^i	89.80(2)
Cl3–Ti–Cl1^i	89.98(3)	Cl3^i–Ti–Cl1^i	90.02(3)
Cl2–Ti–Cl1	89.80(2)	Cl2^i–Ti–Cl1	90.20(2)
Cl3–Ti–Cl1	90.02(3)	Cl3^i–Ti–Cl1	89.98(3)
Cl1^i–Ti–Cl1	180.00(4)		

[a] Symmetry code i: –*x*, –*y*, –*z*.

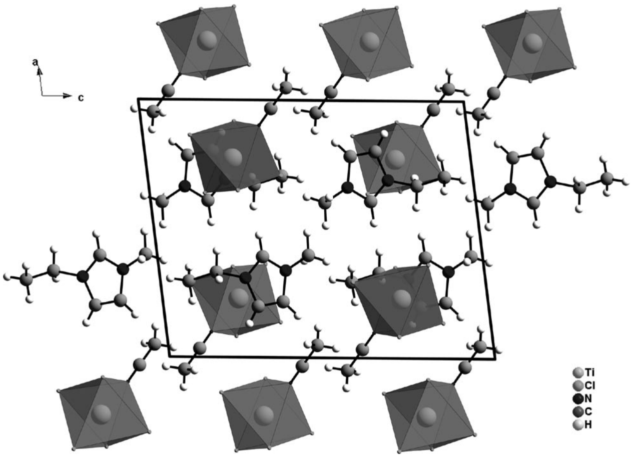

Figure 5. Perspective view of the unit cell of **II** along the *b* axis.

As a result of the acetonitrile ligand, the octahedral symmetry is distorted. The average Ti–Cl_{eq} bond lengths are between 2.303 and 2.347 Å. The Ti–Cl bond length for Cl5 (2.252 Å) is slightly shorter than the Ti–N bond length (2.226 Å). The orientation of the other chlorine towards the acetonitrile molecule is the reason for this distance. Consequentially, the Cl5–Ti–Cl*n* angles are greater than 90°: Cl5–Ti–Cl1 95.0, Cl5–Ti–Cl2 95.6, Cl5–Ti–Cl3 95.6 and Cl5–Ti–Cl4 95.3°. The angles within the chlorine plane are nearly 90° (88.1–91.5°) (Table 5). These values compare well with those of the reported acetonitrile pentachloridotitanate(IV).[19]

Table 5. Selected bond lengths [Å] and angles [°] for compound **II**.

Ti–N9	2.2261(2)	Ti–Cl5	2.2521(8)
Ti–Cl2	2.3031(7)	Ti–Cl3	2.3079(7)
Ti–Cl4	2.3133(7)	Ti–Cl1	2.3468(7)
N9–Ti–Cl5	178.85(6)	N9–Ti–Cl2	84.52(6)
Cl5–Ti–Cl2	95.59(3)	N9–Ti–Cl3	85.58(6)
Cl5–Ti–Cl3	95.56(3)	Cl2–Ti–Cl3	90.25(3)
N9–Ti–Cl4	83.57(6)	Cl5–Ti–Cl4	95.29(3)
Cl2–Ti–Cl4	91.47(3)	Cl3–Ti–Cl4	168.79(3)
N9–Ti–Cl1	84.90(6)	Cl5–Ti–Cl1	95.01(3)
Cl2–Ti–Cl1	169.38(3)	Cl3–Ti–Cl1	88.07(3)
Cl4–Ti–Cl1	88.21(3)		

Compound **III** consists of two different chloridotitanate(IV) anions, $[TiCl_6]^{2-}$ and $[Ti_2Cl_{10}]^{2-}$, and $[EMIm]^+$ as the cationic species. The $[Ti_2Cl_{10}]^{2-}$ units are located on the cell edges and in the middle of the unit cell. The $[TiCl_6]^{2-}$ ions are situated in the middle of the edges and the cation is arranged in between (Figure 6). The anionic $[TiCl_6]^{2-}$ unit has an approximately octahedral O_h symmetry in agreement with compound **I**. As a result of the point symmetry, there are three different Ti–Cl bond lengths: 2.329 (Cl1), 2.343 (Cl2) and 2.328 Å (Cl3). The Cl1–Ti–Cl2 angle is 88.4°, the

Cl1–Ti–Cl3 angle 90.1° and the Cl2–Ti–Cl3 angle 89.2°. The $[Ti_2Cl_{10}]^{2-}$ unit features an edge-sharing dichlorido-bridged bioctahedral geometry. The Ti–Cl bond lengths for Cl4, Cl5, Cl6 and Cl8 range from 2.227 to 2.298 Å, and the bond lengths of the bridging Cl7 and Cl7^{ii} are 2.486 and 2.535 Å, respectively. As a result of this bridging geometry, the octahedral symmetry is distorted. Especially, the Cl–Ti–Cl angles involving the bridging chlorine are slightly deformed. The Cl5–Ti2–Cl7^{ii} angle is 169.8°, the Cl5–Ti2–Cl7 angle is 168.3° and the Cl4–Ti2–Cl6 angle is 172.4° (Table 6). These values compare well with those reported for hexachloridotitanate(IV)[18] and decachloridodititanate(IV).[1]

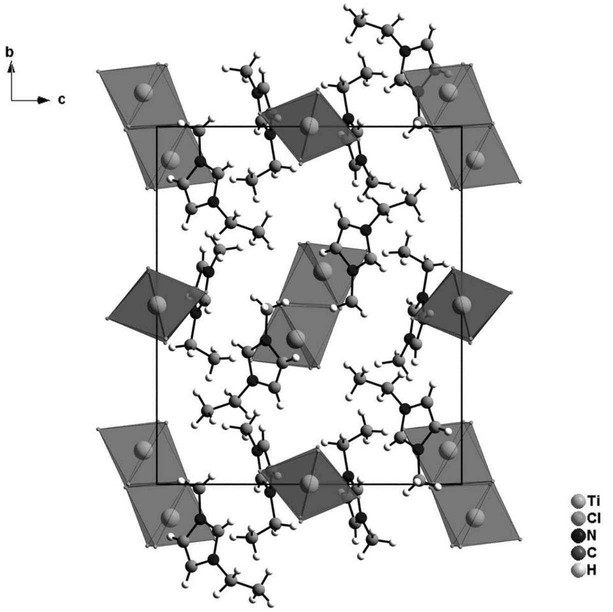

Figure 6. Perspective view of the unit cell of **III** along the *a* axis.

Table 6. Selected bond lengths [Å] and angles [°] for compound **III**.[a]

Ti–Cl1	2.3289(10)	Ti–Cl1^{i}	2.3290(10)
Ti–Cl2	2.3425(9)	Ti–Cl2^{i}	2.3425(9)
Ti–Cl3	2.3277(10)	Ti–Cl3^{i}	2.3276(10)
Ti2–Cl8	2.2274(12)	Ti2–Cl5	2.2705(12)
Ti2–Cl4	2.2914(12)	Ti2–Cl6	2.2983(12)
Ti2–Cl7	2.4867(10)	Ti2–Cl7^{ii}	2.5355(10)
Cl7–Ti2^{ii}	2.5356(10)		
Cl3^{i}–Ti–Cl3	180.00(4)	Cl3^{i}–Ti–Cl1	89.87(5)
Cl3–Ti–Cl1	90.13(5)	Cl3^{i}–Ti–Cl1^{i}	90.13(5)
Cl3–Ti–Cl1^{i}	89.87(5)	Cl1–Ti–Cl1^{i}	180.00(8)
Cl3^{i}–Ti–Cl2^{i}	89.18(4)	Cl3–Ti–Cl2^{i}	90.82(4)
Cl1–Ti–Cl2^{i}	91.60(4)	Cl1^{i}–Ti–Cl2^{i}	88.40(4)
Cl3^{i}–Ti–Cl2	90.82(4)	Cl3–Ti–Cl2	89.18(4)
Cl1–Ti–Cl2	88.40(4)	Cl1^{i}–Ti–Cl2	91.60(4)
Cl2^{i}–Ti–Cl2	180.0	Cl8–Ti2–Cl2	100.62(5)
Cl8–Ti2–Cl4	93.47(5)	Cl5–Ti2–Cl4	91.18(5)
Cl8–Ti2–Cl6	93.26(5)	Cl5–Ti2–Cl6	91.04(5)
Cl4–Ti2–Cl6	172.40(5)	Cl8–Ti2–Cl7	91.07(4)
Cl5–Ti2–Cl7	168.29(5)	Cl4–Ti2–Cl7	87.19(4)
Cl6–Ti2–Cl7	89.17(4)	Cl8–Ti2–Cl7^{ii}	169.82(5)
Cl5–Ti2–Cl7^{ii}	89.55(4)	Cl4–Ti2–Cl7^{ii}	85.57(4)
Cl6–Ti2–Cl7^{ii}	87.17(4)	Cl7–Ti2–Cl7^{ii}	78.76(3)
Ti2–Cl7–Ti2^{ii}	101.24(3)		

[a] Symmetry code i: $-x, -y, 1-z$; symmetry code ii: $-1-x, -y, -z$.

Spectroscopic Characterization

The title compounds are composed of the respective cationic and anionic units, and compound **II** additionally contains one acetonitrile molecule. The relevant cationic unit $[EMIm]^+$ was investigated intensely by vibrational spectroscopy.[20] Therefore, just the Raman frequencies of the corresponding anionic units are shown in detail in Figure 7 and summarized with their assignments in Table 7. For the octahedral anion $[TiCl_6]^{2-}$, three Raman active vibrations are expected because of its O_h symmetry, the total stretching vibration (A_{1g}) at 320 cm^{-1}, the symmetric stretching vibration (E_g) at 271 cm^{-1} and the deformation vibration (T_{2g}) at 173 cm^{-1}. Two of these expected vibrations could be observed in agreement with earlier reports, the A_{1g} and the T_{2g} one. The E_g vibration was not found because of its extreme weakness. The intensities of bands of an ideal octahedral complex decrease in the order $I_{A1g} > I_{T2g} > I_{Eg}$.

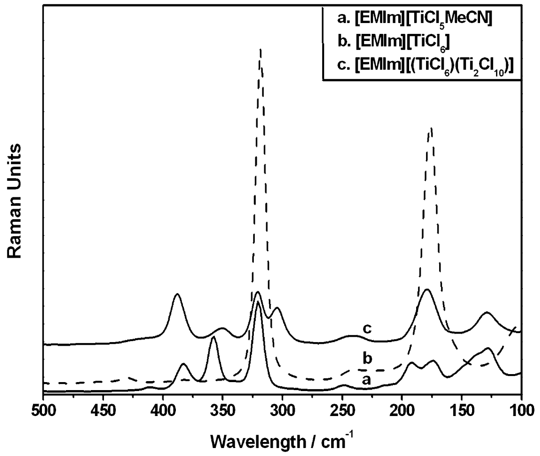

Figure 7. Raman spectra (λ_{exc} = 1064 nm) of compounds **I**, **II** and **III**.

The spectrum of compound **II** shows two vibrations associated to the O_h symmetry, which are split as a result of the minor symmetry of the distorted octahedron. The A_{1g} vibration splits up into three bands at 320, 358 and 383 cm^{-1}. The T_{2g} vibration is subdivided into two bands at 174 and 192 cm^{-1}. The spectrum of compound **III** presents a combination of two pure spectra when compared to the literature. On the one hand the two vibrations at 320 and 176 cm^{-1} can be identified as the A_{1g} and T_{2g} vibration belonging to the $[TiCl_6]$ octahedron. On the other hand the vibrations at 387, 350, 305 and 242 cm^{-1} can be attributed to the edge-sharing dichlorido-bridged bioctahedron $[Ti_2Cl_{10}]$. Furthermore, the dimer–monomer conversion [see Equation (4) in the next subchapter] could be observed by temperature-dependent Raman measurements (Figure 8).

Table 7. Raman frequencies.[a]

I	II	III		$[TiCl_6]$[b]	$[TiCl_5]$[c]	$[Ti_2Cl_{10}]$[d]
		r.t.	373 K			
		387				389 (s), 381 (vs)
	383					
	358	350	350		351 (s)	355 (m), 351 (m)
320	320	320	320	320 (vs)	317 (vw)	
		305				308 (s), 309 (s)
				271 (vw)		
	248					
		242	242		252 (ms)	233 (m), 244 (m)
	192					
176	174	176	176	173 (s)	180 (s)	
	128					

[a] Band intensities are denoted as: very strong (vs), strong (s), medium (m), weak (w) and very weak (vw). [b] From ref.[24] [c] From ref.[21] [d] From ref.[25]

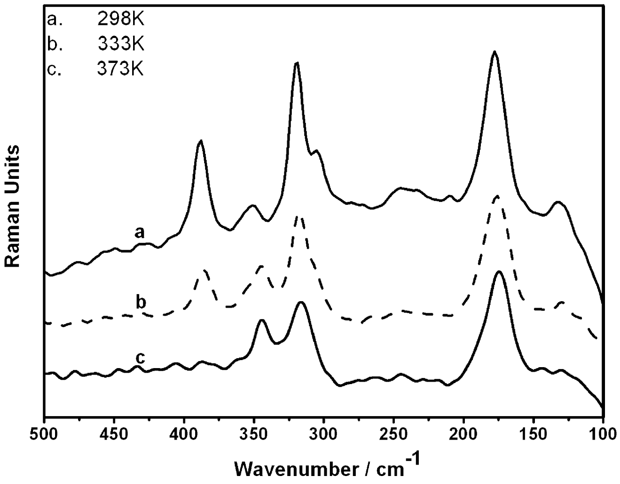

Figure 8. FT-Raman spectra of compound **III** at different temperatures.

When comparing the Raman spectra at room temperature and at 373 K, the disappearance of the specific vibrations of the $[Ti_2Cl_{10}]$ complex anion at 387, 305 and 242 cm^{-1} is noticed, whereas the medium intensity of the vibration at 350 cm^{-1}, which is characteristic for "$TiCl_5$", becomes stronger.

Thermal Properties

Melting points and decomposition temperatures of the three chloridotitanate(IV) complexes were measured (Table 8). The melting points were determined using differential scanning calorimetry (DSC) methods.

In addition, the reversible dimer–monomer conversion for compound **III** could be detected by Raman spectroscopy and DSC [Equation (4); Figures 8 and 9].

$$Ti_2Cl_{10}{}^{2-} \underset{333\ K}{\overset{363\ K}{\rightleftharpoons}} 2\ \text{"}TiCl_5{}^{-}\text{"} \qquad (4)$$

This conversion is similar to the one published by Brockner.[21] In the present case it is accompanied by a reversible colour change from yellow to red.

Table 8. Melting points and decomposition temperatures.

Compounds	M.p. [K]	$T_{decomp.}$ [K]	Ref.
$[EMIm]_2[TiCl_6]$	435	558	this work
$[EMIm][TiCl_5\ MeCN]$		348, 582	this work
$[EMIm]_4[TiCl_6][Ti_2Cl_{10}]$		567	this work
[EMIm]Cl	357	564	[22]
[EMIm]Br	354		[22]
[EMIm]I	354	576	[22]
$[EMIm][PF_6]$	333	648	[22]
$[EMIm][NbF_6]$	272		[23]
$[EMIm][TaF_6]$	275		[23]

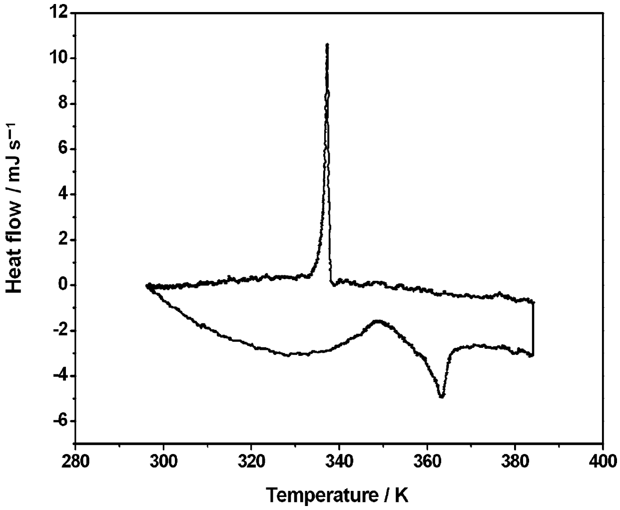

Figure 9. Differential scanning calorimetry results for compound **III**.

$[EMIm]_2[TiCl_6]$ melts at 435 K. The melting point of [EMIm] $[TiCl_5MeCN]$ could not be determined because it decomposes at 348 K, resulting from the loss of acetonitrile. $[EMIm]_4[TiCl_6][Ti_2Cl_{10}]$ possessed no melting point.

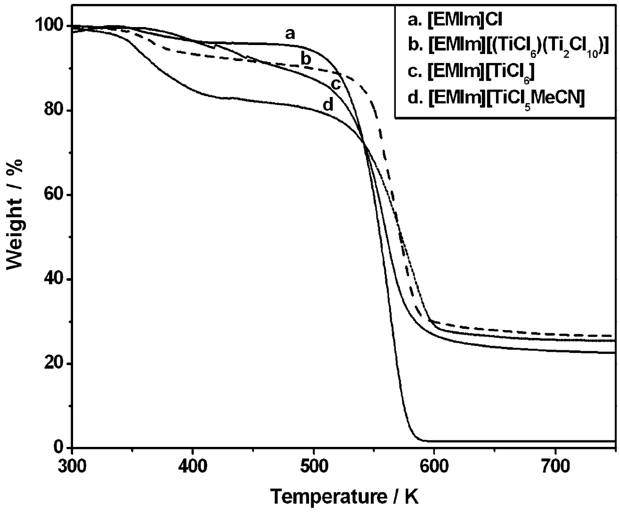

Figure 10. TGA measurements for **I**, **II**, **III** and [EMIm]Cl.

The thermal stability for all compounds was studied by thermal gravimetric analysis (TGA), which is shown in Figure 10.

Compound **I** possessed a slight weight loss at 350–500 K, which may be attributed to desorption of acetonitrile, and it decomposed at 558 K. Compound **II** decomposed in two steps. The first step occurring at 348 K can be ascribed to the loss of acetonitrile. Compound **III** decomposes at 567 K. In comparison to the pure IL (564 K), all these compounds decomposed in the same range, which means that the decomposition is dependent on the IL. In contrast to the pure IL, all three compounds show incomplete decomposition up to a temperature of 800 K, which may be attributed to stable titanium compounds.

Conclusions

This work shows that the coordination chemistry of chloridotitanate(IV) complexes with ionic liquids is based on the known titanium coordination chemistry with halogens. So, the hexachloridotitanate(IV) complex $[EMIm]_2[TiCl_6]$ (**I**) and $[EMIm][TiCl_5MeCN]$ (**II**) can be predicted as reaction products with 1-ethyl-3-methylimidazolium chloride. However, a new compound with two different anionic species, $[Ti_2Cl_{10}]$ and $[TiCl_6]$, could surprisingly be obtained. Furthermore, the monomer–dimer conversion of $[Ti_2Cl_{10}] \leftrightarrow 2[TiCl_5]$ could be investigated for $[EMIm]_4[TiCl_6][Ti_2Cl_{10}]$ (**III**) by DSC and Raman measurements in detail. Future experimental work is expected to provide indication of additional chloridotitanate(IV) species with ionic liquids.

Experimental Section

General: Manipulations were performed under a dry nitrogen or argon atmosphere by using Schlenk line and glove box techniques. Acetonitrile was purified by distillation from phosphor pentoxide and dichloromethane by distillation from calcium hydride. All other reagents were obtained from commercial sources and used without further purification. NMR spectroscopic data were recorded with a Digital FT NMR (Bruker Digital FT-NMR “Avance DPX 200”, Bruker Optik GmbH). Infrared and Raman spectra were recorded with an FTIR/Raman spectrometer (Bruker IFS 66v with Raman-Modul FRA 106, Bruker Optik GmbH) by using vessels and CsI pellets. Elemental analyses of C, N and H were determined by using a Heraeus CHNS Elemental Analyzer. X-ray powder diffractions (XRPD) patterns of the samples were recorded with a STOE STADI P diffractometer. Thermal analyses were recorded by using a TA Instruments 951 Thermogravimetric Analyzer and a Linseis HDSC L62H1550.

$[C_6N_2H_{11}]_2[TiCl_6]$ (I): To a solution of 1-ethyl-3-methylimidazolium chloride (2 mmol, 0. 29 g) dissolved in acetonitrile (10 mL) was dropwise added titanium tetrachloride (1 mmol, 0.19 g, 0.11 mL). The slightly yellow mixture was concentrated under reduced pressure and yellow crystals were obtained. ^{1}H NMR (300 MHz, [D$_6$]-DMSO, 25 °C): δ = 9.54 (s, 1 H, C2), 7.89 (s, 1 H, C4), 7.78 (s, 1 H, C5), 4.20 (q, 2 H, 6C), 3.85 (s, 3 H, 8C), 1.38 (t, 3 H, 7C) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO, 25 °C): δ = 136.5 (C2), 123.6 (C4), 122.0 (C5), 44.1 (C6), 35.7 (C8), 15.3 (C7) ppm. $[C_6N_2H_{11}]_2[TiCl_6]$ (482.91): calcd. C 29.85, H 4.59, N 11.60; found C 29.84, H 4.52, N 11.61. IR (CsI): ṽ = 3112, 2979, 1621, 1571, 1453, 1344, 1166, 1123, 826, 761, 640, 619, 326, 184 cm^{-1}.

$[C_6N_2H_{11}][TiCl_5CH_3CN]$ (II): To a solution of 1-ethyl-3-methylimidazolium chloride (1 mmol, 0.15 g) dissolved in acetonitrile (10 mL) was dropwise added an equimolar amount of titanium tetrachloride (1 mmol, 0.19 g, 0.11 mL). After concentration under

Table 9. Crystal data and refinement parameters for compound **I**, **II** and **III**.

	I	II	III
Empirical formula	$C_{12}H_{22}N_4TiCl_6$	$C_8H_{14}N_3TiCl_5$	$C_{24}H_{44}N_8Ti_3Cl_{16}$
Formula weight [g mol^{-1}]	482.94	377.37	1155.57
Crystal colour	yellow	yellow	dark yellow
Temperature [K]	293	293	293
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic
Space group, Z	*Pbca* (no. 61), 4	$P2_1/c$ (no. 14), 4	$P2_1/c$ (no. 14), 2
a [Å]	11.081(1)	11.211(1)	10.517(1)
b [Å]	14.723(1)	10.405(1)	16.275(1)
c [Å]	12.890(1)	14.090(2)	14.156(1)
β [°]	–	97.48(1)	101.16(1)
Volume [Å^3]	2103.3(4)	1629.9(3)	2377.3(3)
Z	4	4	2
$D_{calcd.}$ [g cm^{-3}]	1.525	1.538	1.614
F(000)	984	760	1164
$\Theta_{min,}$ Θ_{max} [°]	2.77, 25.68	1.83, 29.90	1.93, 25.03
Index ranges	$-13 \le h \le 13$	$-15 \le h \le 15$	$-12 \le h \le 11$
	$-17 \le k \le 17$	$-14 \le k \le 14$	$-19 \le k \le 19$
	$-15 \le l \le 15$	$-19 \le l \le 19$	$-16 \le l \le 16$
Unique reflections	1995	4676	4198
Data, restrains, parameters	1995, 0, 150	4676, 0, 210	4198, 0, 320
GooF on F^2	1.153	1.073	1.056
R indexes	R_1 = 0.0382	R_1 = 0.0433	R_1 = 0.0438
[$I > 2\sigma I$]	wR_2 = 0.0647	wR_2 = 0.0769	wR_2 = 0.0978
R indexes	R_1 = 0.0534	R_1 = 0.0673	R_1 = 0.0511
(all data)	wR_2 = 0.0684	wR_2 = 0.0769	wR_2 = 0.1016
Largest diff. peak, hole [e Å^3]	0.262, –0.204	0.333, –0.424	1.390, –1.009

reduced pressure yellow crystals were obtained. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 9.47 (s, 1 H, C2), 7.86 (s, 1 H, C4), 7.76 (s, 1 H, C5), 4.21 (q, 2 H, 6C), 3.85 (s, 3 H, 8C), 2.07 (s, 3 H, CH_3CN), 1.39 (t, 3 H, 7C) ppm. ^{13}C NMR (50 MHz, [D$_6$]-DMSO, 25 °C): δ = 136.9 (C2), 124.0 (C4), 122.4 (C5), 118.6 (CN), 44.5 (C6), 36.1 (C8), 15.6 (C7), 1.7 (CH_3CN) ppm. $[C_6N_2H_{11}]$-$[TiCl_5(CH_3CN)]$ (377.35): calcd. C 25.46, H 3.74, N 11.14; found C 24.63, H 4.16, N 10.58.

$[C_6N_2H_{11}]_4[TiCl_6][Ti_2Cl_{10}]$ (III): To a solution of 1-ethyl-3-methylimidazolium chloride (1 mmol, 0.15 g) dissolved in dichloromethane (10 mL) was dropwise added titanium tetrachloride (1 mmol, 0.19 g, 0.11 mL). The yellow mixture was concentrated under reduced pressure and yellow crystals were obtained. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 9.60 (s, 1 H, C2), 7.98 (s, 1 H, C4), 7.89 (s, 1 H, C5), 4.30 (q, 2 H, 6C), 3.96 (s, 3 H, 8C), 1.50 (t, 3 H, 7C) ppm. ^{13}C NMR (50 MHz, [D$_6$]DMSO, 25 °C): δ = 136.5 (C2), 123.5 (C4), 121.9 (C5), 44.0 (C6), 35.8 (C8), 15.2 (C7) ppm. $[C_6N_2H_{11}]_4[TiCl_6][Ti_2Cl_{10}]$ (1155.57): calcd. C 21.17, H 3.53, N 8.03; found C 20.70, H 3.18, N 8.05. IR (CsI): $\tilde{\nu}$ = 3149, 3110, 2986, 1572, 1465, 1431, 1388, 1339, 1292, 1167, 1091, 847, 762, 703, 649, 622, 598, 329, 189 cm^{-1}.

X-ray Diffraction Analysis: Data were collected by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) with a STOE IPDS II diffractometer. The crystal structures were solved by direct methods using SHELXS-97,[26] whereas in all cases heavy atom positions were obtained. Subsequent difference Fourier analyses and least-squares refinements with SHELXL-97[26] allowed localization of remaining atom positions. All H-atoms attached to carbon could be localized by different Fourier maps. The drawing of the structures were realized with the help of Diamond[27] and POV-Ray.[28] Crystal data and refinement parameters for the three compounds are shown in Table 9. CCDC-714259 (for **I**), -714260 (for **II**) and -714261 (for **III**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors thank Karin Bode for recording the IR/Raman spectra, Dirk Vollbrecht for arranging the DSC measurements, Adelgunde Strohschein for preparing the TG measurements, Petra Lassen for measuring the C, H, N values, Jan Chr. Namyslo for determining the NMR spectra, Claus Ehrhardt for the XRD powder measurements and Prof. Brockner for discussing the temperature-dependent Raman spectra.

---

[1] T. J. Kistenmacher, G. D. Stucky, *Inorg. Chem.* **1971**, *10*, 122–132.

[2] a) A. Feltz, *Z. Anorg. Allg. Chem.* **1965**, *323*, 147; b) A. Feltz, *Z. Anorg. Allg. Chem.* **1963**, *323*, 35; c) Y. Kawano, Y. Hase, O. Sala, *J. Mol. Struct.* **1976**, 45–55.

[3] E. Robé, J.-C. Daran, S. Vincendeau, R. Poli, *Eur. J. Inorg. Chem.* **2004**, 4108–4114.

[4] a) G. Laus, G. Bentivoglio, K. Wurst, H. Schottenberger, G. Nauer, *Z. Kristallogr. - New Cryst. Struct.* **2005**, *220*, 577–578; b) P. Bonnet, E. Lacroix, J.-P. Schirmann, *US 2004/0033892 A1* **2004**.

[5] a) R. Sheldon, *Chem. Commun.* **2001**, 2399; b) J. D. Holbrey, K. R. Seddon, *Clean Prod. Proc.* **1999**, *1*, 223.

[6] a) K. R. Seddon, *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351; b) T. Welton, *Chem. Rev.* **1999**, *99*, 2071; c) P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley, Weinheim, **2003**; d) P. Wasserscheid, R. van Hal, A. Bosmann, *Green Chem.* **2002**, *4*, 400; e) R. P. Swatloski, J. D. Holbrey, R. D. Rogers, *Green Chem.* **2003**, *5*, 361.

[7] a) J. E. L. Dullius, P. A. Z. Suarez, S. Einloft, R. F. de Souza, J. Dupont, *Organometallics* **1998**, *17*, 815; b) D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *J. Am. Chem. Soc.* **2004**, *126*, 15876; c) C. Baudequin, J. Baudoux, J. Levillain, D. Cahard, A.-C. Gaumont, J.-C. Plaquevent, *Tetrahedron: Asymmetry* **2003**, *14*, 3081–3084.

[8] a) T. Nishida, Y. Tashiro, M. Yamamoto, *J. Fluorine Chem.* **2003**, *120*, 135–141; b) D. R. MacFarlane, J. Huang, M. Forsyth, *Nature* **1999**, *402*, 792; c) B. Garcia, S. Lavallée, G. Perron, C. Michot, M. Armand, *Electrochim. Acta* **2004**, *49*, 4583; d) R. F. de Souza, J. C. Padilha, R. S. Goncalves, J. Dupont, *Electrochem. Commun.* **2003**, *5*, 728–731; e) P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar, M. Gratzel, *J. Am. Chem. Soc.* **2003**, *125*, 1166–1167.

[9] T. B. Scheffler, M. S. Thomson, *Sevens International Conference on Molton Salts* **2001**, Montreal, Canada, p. 281.

[10] C. Zhong, T. Sasaki, A. Jimbo-Kobayashi, E. Fujiwara, A. Kobayashi, M. Tada, Y. Iwasawa, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2365–2374.

[11] P. B. Hitchcock, K. R. Seddon, T. Welton, *J. Chem. Soc., Dalton Trans.* **1993**, 2639.

[12] M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, A. Steiner, N. Winterton, *Inorg. Chem.* **1999**, *38*, 5637.

[13] P. B. Hitchcock, R. J. Lewis, T. Welton, *Polyhedron* **1993**, *12*, 2039.

[14] M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, C. Femoni, A. Steiner, N. Winterton, *Inorg. Chem.* **2001**, *40*, 795.

[15] J. Fuller, R. T. Carlin, H. C. De Long, D. Haworth, *J. Chem. Soc., Chem. Commun.* **1994**, 299.

[16] K. Matsumoto, R. Hagiwara, R. Yoshida, Y. Ito, Z. Mazej, P. Benkič, B. Žemva, O. Tamada, H. Yoshino, S. Matsubara, *Dalton Trans.* **2004**, 144–149.

[17] C. J. Dymek Jr, D. A. Grossie, A. V. Fratini, W. W. Adams, *J. Mol. Struct.* **1989**, *213*, 25–34.

[18] E. Hey, U. Müller, *Z. Naturforsch., Teil B* **1981**, *36*, 135.

[19] S. Rabe, U. Müller, *Z. Anorg. Allg. Chem.* **2001**, *627*, 201–205.

[20] a) K. Dong, S. Zhang, D. Wang, X. Yao, *J. Phys. Chem. A* **2006**, *110*, 9775–9782; b) B. v. Ahsen, B. Bley, S. Proemmel, R. Wartchow, H. Willner, F. Aubke, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1225–1234; c) B. Swanson, D. F. Shriver, *Inorg. Chem.* **1970**, *9*, 1406–1416; d) B. Swanson, D. F. Shriver, *Inorg. Chem.* **1971**, *10*, 1354–1365.

[21] A. F. Demiray, W. Brockner, *Spectrochim. Acta* **1978**, *35A*, 659–662.

[22] H. L. Ngo, K. LeCompte, L. Hargens, A. B. McEwen, *Thermochim. Acta* **2000**, *357–358*, 97–102.

[23] K. Matsumoto, R. Hagiwara, Y. Ito, *J. Fluorine Chem.* **2002**, *115*, 133.

[24] R. J. H. Clark, L. Maresca, R. J. Puddephatt, *Inorg. Chem.* **1968**, *7*, 1603.

[25] C. S. Creaser, J. A. Creighton, *J. Chem. Soc., Dalton Trans.* **1975**, 1402–1405.

[26] G. M. Sheldrick, *SHELX-97 and SHELXL-97*, University of Göttingen, Germany, **1997**.

[27] *DIAMOND – Visual Crystal Structure Information System*, Crystal Impact, Bonn, Germany, **2004**.

[28] *POV-Ray*™, version 3, Copyright by the POV-Ray-Team, **1997**.

Received: June 7, 2009