TU Clausthal

Synthesis and Crystal Structure of $[EMIm]_2TiCl_6$ and $[EMIm][TiCl_5 \cdot MeCN]$

Introduction

Homoleptic chlorotitanates 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 are known, the hexachlorotitanate $[TiCl_6]^{2-}$, the decachlorotitanate $[Ti_2Cl_{10}]^{2-}$, the pentachlorotitanate $[TiCl_5]^-$, the enneachlorotitanate $[Ti_2Cl_9]^-$, the pentachlorotitanateacetonitrile $[TiCl_5 \cdot MeCN]^-$ and the bisacetonitriletetrachloro-titanate $[TiCl_4 \cdot 2\ MeCN]$ [1, 2]. All these complexes were prepared by using inorganic chlorides such as CsCl, quarternary ammonium or phosphonium salts and a few ionic liquids [3].

Experimental

Both compounds were prepared by addition of titanium tetrachloride to [EMIm]Cl in acetonitrile. After a reaction time of a few minutes a color change from colorless to yellow was observed. The mixtures were concentrated under reduced pressure and yellow crystals precipitated.

Structure description

$[EMIm]_2[TiCl_6]$ (**I**) crystallizes in the orthorhombic space group *Pbca* (no. 61) with the unit cell parameters a = 11.081(1) Å, b = 14.723(1) Å, c = 12.890(1) Å and V = 2103.3(4) Å^3 with Z = 4. [EMIm][TiCl5 · MeCN] (**II**) crystallizes in the monoclinic space group *P21/c* (no. 14) with the unit cell parameters a = 11.211(1) Å, b = 10.405(1) Å, c = 14.090(1) Å, β = 97.48(1)° and V = 1629.9(3) Å^3 with Z = 4. Compound (**I**) is formed by two [EMIm] cations and one $[TiCl_6]$ anion. The structure consists of parallel layers of hexachlorotitanate units and IL-molecules (Fig.1). The bond arrangement around Ti is approximately octahedral O_h with Ti—Cl bond lengths between 2.334(1) and 2.355(1) Å. The Cl—Ti—Cl angles are on the one hand 180.00(5)° and on the other between 89.48(3)° and 90.20(2)°. Compound (**II**) involves one [EMIm] cation, one $[TiCl_5]$ anion and one acetonitrile molecule. The structure is build up by parallel layers of alternating blocks of one IL and one pentachloroacetonitriletitanate (Fig.2). Due to the acetonitrile the octahedral symmetry around Ti is distorted with bond lengths between 2.252(1) and 2.347(1) Å. The Cl—Ti—Cl angles are between 88.07(3)° and 95.56(3)°.

Tab. 1 Crystallographic data for $[EMIm]_2[TiCl_6]$ and $[EMIm][TiCl_5 \cdot MeCN]$

	I	II
Empirical formula	$C_{12}H_{22}N_4TiCl_6$	$C_8H_{14}N_3TiCl_5$
Formula weight/g mol^{-1}	482.94	377.37
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	*P2$_1$/c*
a / Å	11.081(1)	11.211(1)
b / Å	14.723(1)	10.405(1)
c / Å	12.890(1)	14.090(2)
β /°	-	97.48(1)
Volume / Å^3	2103.3(4)	1629.9(3)
Z	4	4
D_{calc} /g cm^{-3}	1.525	1.538
F(000)	984	760
$\Theta_{min,\ max}$ /°	2.77, 25.68	1.83, 29.90
Index ranges	-13 ≤ h ≤ 13	-15 ≤ h ≤ 15
	-17 ≤ k ≤ 17	-14 ≤ k ≤ 14
	-15 ≤ l ≤ 15	-19 ≤ l ≤ 19
Unique reflections	1995	4676
Data / restrains /parameters	1995/0/150	4676/0/210
Goodness-of-fit on F^2	1.153	1.073
R indeces [I>2σI]	R1 = 0.0382	R1 = 0.0433
	wR2 = 0.0647	wR2 = 0.0769
R indeces (all data)	R1 = 0.0534	R1 = 0.0673
	wR2 = 0.0684	wR2 = 0.0769
Largest diff. peak and hole/e Å^3	0.262 and -0.204	0.333 and -0.424

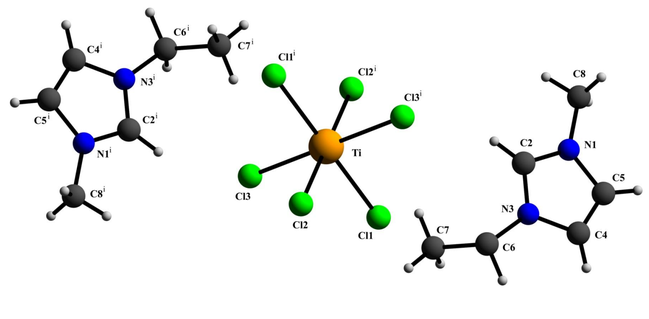

Fig. 1 Coordination Polyeder in $[EMIm]_2[TiCl_6]$

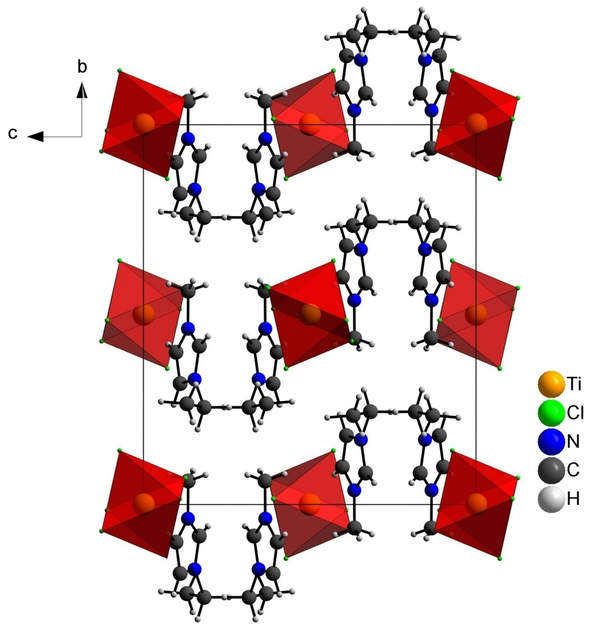

Fig. 2 Perspective view of the unit cell of (I) along *a*-axis

Tab. 2 Selected bond length [Å] and angles [°] for compound (I)

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)		

Symmetry code: i) –x, -y, -z

Tab. 3 Final atomic coordinates and U_{eq} for (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)

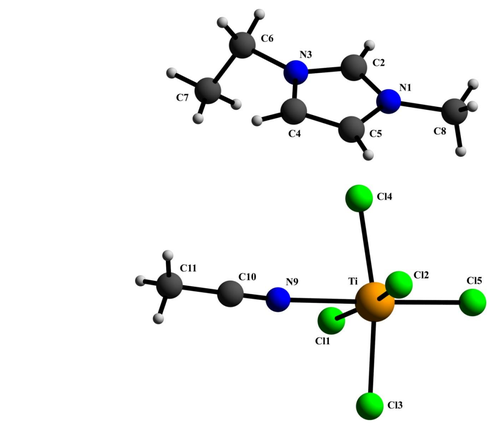

Fig. 3 Coordination Polyeder in $[EMIm][TiCl_5MeCN]$

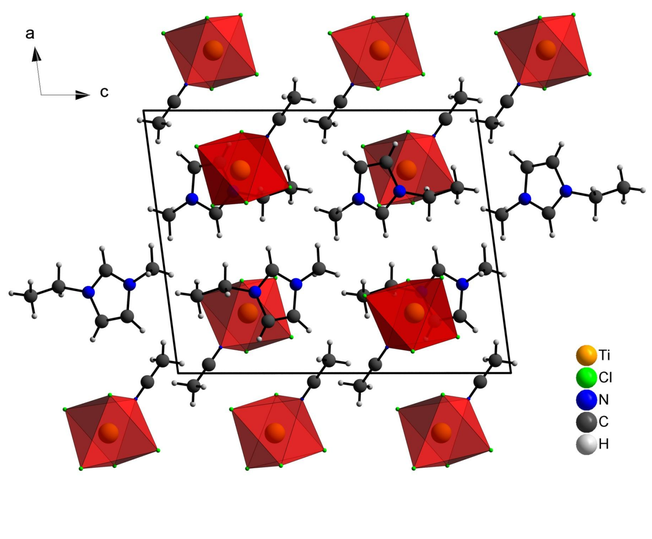

Fig. 4 Perspective view of the unit cell of (II) along *b*-axis

Tab. 4 Selected bond length [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)		

Tab. 5 Final atomic coordinates and U_{eq} for (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)

References

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