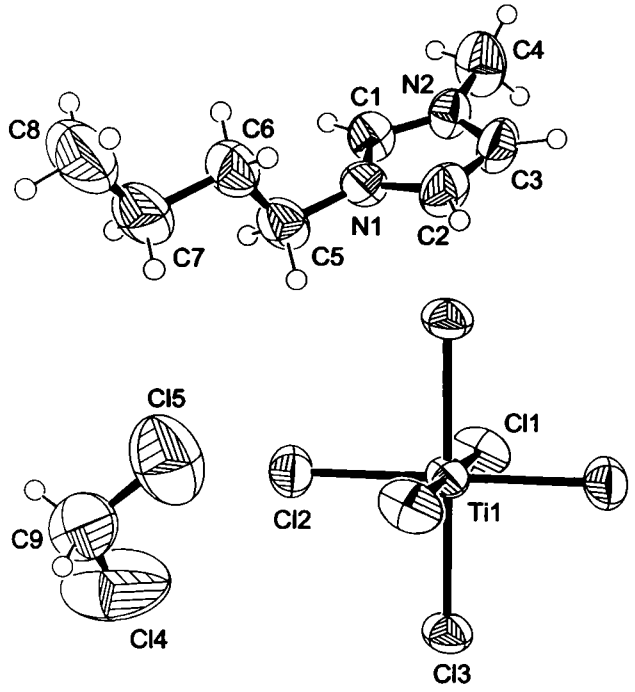
Crystal structure of bis(1-butyl-3-methylimidazolium) hexachlorotitanate(IV) bis(dichloromethane) solvate, $(C_8H_{15}N_2)_2[TiCl_6] \cdot 2CH_2Cl_2$

G. Laus[I], G. Bentivoglio[I], K. Wurst[I], H. Schottenberger*[,I] and G. Nauer[II]

[I] University of Innsbruck, Faculty of Chemistry and Pharmacy, Innrain 52a, 6020 Innsbruck, Austria
[II] University of Vienna, Institute of Physical Chemistry, Waehringerstrasse 42, 1090 Vienna, Austria

Received September 15, 2005, accepted and available on-line December 3, 2005; CCDC no. 1267/1648



Abstract

$C_{18}H_{34}Cl_{10}N_4Ti$, monoclinic, $P12_1/n1$ (no. 14), $a = 12.8243(4)$ Å, $b = 9.2932(2)$ Å, $c = 14.3634(5)$ Å, $\beta = 100.572(2)°$, $V = 1682.8$ Å^3, $Z = 2$, $R_{gt}(F) = 0.041$, $wR_{ref}(F^2) = 0.112$, $T = 233$ K.

Source of material

In analogy to the preparation of $(Ph_4As)_2TiCl_4(N_3)_2$ [1], bis(1-butyl-3-methylimidazolium) diazidotetrachlorotitanate(IV) was prepared from the non-explosive ionic liquid 1-butyl-3-methylimidazolium (BMI) azide and $TiCl_4$ [2]. Upon attempted crystallization of this promising precursor composite for electrodeposition of metallic Ti from ionic liquids, surprisingly the title compound was obtained as slightly yellow plate-shaped crystals. Obviously, the azide ligands had reacted with the solvent dichloromethane to form potentially hazardous diazidomethane, thereby yielding the title hexachlorotitanate.

Discussion

The title compound crystallizes with half a formula unit in the asymmetric part of the unit cell around the centrosymmetric hexachlorotitanate anion. The butyl chain is twisted out of the imidazolium plane by 88.6°, and the torsion angle around the C5—C6 bond is 177.6°. Thus, the antiperiplanar conformation of the butyl chain in this BMI cation is in line with other BMI and 1-butyl-2,3-dimethylimidazolium (BMMI) cations in salts such as (BMI)Cl [3], (BMMI)Cl [4], (BMMI)BF_4 [5], and (BMMI)$FeCl_4$ [6]. In contrast, a synclinal conformation around the C5—C6 bond was observed in the crystal structures of (BMMI)HSO_4 [6], (BMMI)PF_6 [5], (BMMI)SbF_6 [5], and in one form of (BMMI)Cl [4] and (BMI)Cl [3], respectively. Polymorphism of imidazolium salts of this kind, where both conformations of the butyl chain (antiperiplanar or synclinal) were observed, was previously reported [3,4].

Table 1. Data collection and handling.

Crystal:	light yellow plate, size 0.05 × 0.20 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.63 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	46°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8402, 2328
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1991
$N(param)_{refined}$:	153
Programs:	SHELXS-97 [7], SHELXL-97 [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.4781	−0.2149	0.3270	0.069
H(2)	4e	0.2955	−0.0055	0.1177	0.081
H(3)	4e	0.4114	0.1695	0.2142	0.081
H(4A)	4e	0.5214	0.1255	0.4078	0.129
H(4B)	4e	0.6068	0.1060	0.3418	0.129
H(4C)	4e	0.5874	−0.0191	0.4116	0.129
H(5A)	4e	0.2437	−0.2752	0.1531	0.083
H(5B)	4e	0.3195	−0.3570	0.2357	0.083
H(6A)	4e	0.4443	−0.3831	0.1373	0.095
H(6B)	4e	0.3648	−0.3065	0.0544	0.095
H(7A)	4e	0.3117	−0.5671	0.1404	0.115
H(7B)	4e	0.2421	−0.4945	0.0502	0.115
H(8A)	4e	0.3316	−0.6854	0.0061	0.246
H(8B)	4e	0.4409	−0.6167	0.0553	0.246
H(8C)	4e	0.3726	−0.5421	−0.0349	0.246
H(9A)	4e	−0.2171	−0.1097	0.1212	0.141
H(9B)	4e	−0.2180	0.0263	0.1875	0.141

* Correspondence author (e-mail: herwig.schottenberger@uibk.ac.at)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	2*a*	0	0	0	0.0412(5)	0.0350(5)	0.0391(5)	–0.0024(3)	–0.0059(3)	0.0005(3)
Cl(1)	4*e*	0.02792(8)	–0.0619(1)	0.16011(6)	0.0790(7)	0.0563(6)	0.0400(5)	–0.0123(4)	–0.0073(4)	0.0058(4)
Cl(2)	4*e*	–0.12318(7)	0.17449(9)	0.02590(7)	0.0504(5)	0.0494(5)	0.0701(6)	0.0081(4)	–0.0057(4)	–0.0114(4)
Cl(3)	4*e*	0.13563(6)	0.17061(8)	0.03376(6)	0.0480(5)	0.0434(5)	0.0554(5)	–0.0105(3)	–0.0050(4)	0.0000(3)
Cl(4)	4*e*	–0.2587(3)	–0.1724(2)	0.2593(2)	0.316(3)	0.149(2)	0.204(2)	0.056(2)	0.154(2)	0.064(2)
Cl(5)	4*e*	–0.3814(2)	–0.0177(3)	0.1053(2)	0.113(1)	0.212(2)	0.158(2)	0.003(1)	0.048(1)	–0.023(2)
N(1)	4*e*	0.3692(2)	–0.1571(3)	0.2134(2)	0.048(2)	0.056(2)	0.053(2)	–0.000(1)	–0.000(1)	0.008(1)
N(2)	4*e*	0.4720(2)	–0.0044(3)	0.2963(2)	0.063(2)	0.047(2)	0.054(2)	0.005(1)	0.004(1)	–0.004(1)
C(1)	4*e*	0.4465(3)	–0.1405(4)	0.2873(2)	0.062(2)	0.058(2)	0.048(2)	–0.000(2)	–0.002(2)	0.011(2)
C(2)	4*e*	0.3462(3)	–0.0254(4)	0.1723(3)	0.064(2)	0.063(3)	0.069(2)	0.016(2)	–0.004(2)	0.014(2)
C(3)	4*e*	0.4098(3)	0.0697(4)	0.2247(3)	0.073(3)	0.047(2)	0.077(3)	0.016(2)	0.003(2)	0.007(2)
C(4)	4*e*	0.5539(4)	0.0572(5)	0.3707(3)	0.104(3)	0.069(3)	0.074(3)	–0.005(3)	–0.014(2)	–0.016(2)
C(5)	4*e*	0.3181(3)	–0.2935(4)	0.1810(3)	0.059(2)	0.066(3)	0.074(3)	–0.012(2)	–0.011(2)	0.010(2)
C(6)	4*e*	0.3692(3)	–0.3671(5)	0.1108(3)	0.071(3)	0.069(3)	0.091(3)	–0.014(2)	–0.002(2)	–0.011(2)
C(7)	4*e*	0.3150(4)	–0.5120(6)	0.0829(4)	0.086(3)	0.089(4)	0.107(4)	–0.030(3)	0.004(3)	–0.026(3)
C(8)	4*e*	0.3695(6)	–0.5959(8)	0.0224(6)	0.156(6)	0.130(6)	0.229(9)	–0.071(5)	0.096(6)	–0.086(6)
C(9)	4*e*	–0.2562(5)	–0.0621(7)	0.1651(5)	0.129(5)	0.115(4)	0.123(5)	–0.001(4)	0.060(4)	0.001(4)

References

1. Dyck, W. M.; Dehnicke, K.; Weller, F.; Müller, U.: Tetraphenylarsonium tetrachlorodiazidotitanate(IV); preparation, IR spectrum and crystal structure of $(AsPh_4)_2[TiCl_4(N_3)_2]$. Z. Anorg. Allg. Chem. **470** (1980) 89-94.
2. Bentivoglio, G.: Neue ionische Flüssigkeiten für materialwissenschaftliche Anwendungen. Diploma Thesis, University of Innsbruck 2005.
3. Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Johnston, S.; Seddon, K. R.; Rogers, R. D.: Crystal polymorphism in 1-butyl-3-methylimidazolium halides: supporting ionic liquid formation by inhibition of crystallization. Chem. Commun. (2003) 1636-1637.
4. Andre, M.; Loidl, J.; Laus, G.; Schottenberger, H.; Bentivoglio, G.; Wurst, K.; Ongania, K.-H.: Ionic liquids as advantageous solvents for headspace gas chromatography of compounds with low vapor pressure. Anal. Chem. **77** (2005) 702-705, Supporting Information.
5. Kölle, P.; Dronskowski, R.: Synthesis, crystal structures and electrical conductivities of the ionic liquid compounds butyldimethylimidazolium tetrafluoroborate, hexafluorophosphate and hexafluoroantimonate. Eur. J. Inorg. Chem. (2004) 2313-2320.
6. Kölle, P.; Dronskowski, R.: Hydrogen bonding in the crystal structures of the ionic liquid compounds butyldimethylimidazolium hydrogen sulfate, chloride, and chloroferrate(II,III). Inorg. Chem. **43** (2004) 2803-2809.
7. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
8. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.