TU Clausthal

Hexachloridometallate(IV) Complexes of Zr, Hf and Sn with Ionic Liquids: Syntheses, Crystal Structures and Spectroscopic Characterizations

Introduction

Group IV metal tetrahalides usually act as Lewis acids by forming octahedral $[MeCl_6]^{2-}$ units with chlorine donors. When comparing the titanium-, zirconium-, hafnium-, germanium- and tinbased complexes the known compounds show the same structural features. Also the associated cations coming from inorganic chlorine donors like cesium and rubidium chloride as well as organic chlorides like tetra butyl ammonium or tetraphenyl phosphonium chloride make hardly any difference with respect to the structures of the formed hexachloridometallates [1]. Therefore, it is worth investigating how ionic liquids as chlorine donors affect the crystal structure. It is known that on the one hand ionic liquids fulfill their expected coordination chemistry and on the other hand show new and unexpected results [2].

Experimental

$[EMIm]_2[MeCl_6]$ was prepared by addition of metal tetrachloride to [EMIm]Cl in acetonitrile. After one hour reaction time the mixture was concentrated under reduced pressure and colourless crystals of the title compounds were obtained.

Structure description

The three title compounds (**I** - **III**) crystallize in the orthorhombic space group *Pbca* with the unit cell parameters *a* = 9.664(2) – 9.538(1) Å, *b* = 14.485(3) – 14.386(1) Å, *c* = 15.444(3) – 15.504(2) Å, *V* = 2162.0(8) – 2127.2(4) Å^3 with *Z* = 4. The structures are isotypic. All crystal structures consist of isolated cations and anions. The cation and anion ratio in all compounds is two to one (Fig. 2). The unit cell is build up by parallel layers of one hexachloridometallate unit and two IL molecules (Fig 1). The anionic unit is situated in an approximately octahedral O_h symmetry. The Me—Cl bond lengths range from 2.428 to 2.436 Å. The Cl2—Me—Cl1 angles are 89.9°, the Cl2—Me—Cl3 angles 89.8° and the Cl1—Me—Cl3 one 90.3°.

Spectroscopic characterization

FT-IR and FT-Raman measurements were accomplished to confirm the octahedral symmetry of the anionic units, which result according to the vibrational analysis for $[MeCl_6]^{2-}$ units with O_h symmetry in

Γ_{vib} ($[MeCl_6]^{2-}$ / O_h) = A_{1g} (RE) + E_g (RE) + 2 F_{1u} (IR) + F_{2g} (RE) + F_{2u} (i.a.) [3],

with RE = Raman, IR = Infrared and i.a. = inactive and with A_{1g} + E_g + F_{1u} as stretching vibrations and F_{1u} + F_{2g} as bendings vibrations.

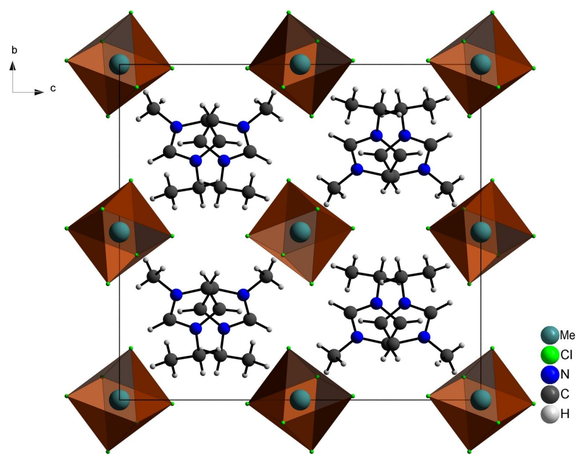

Fig. 1 Perspective view of the unit cell along *a*-axis

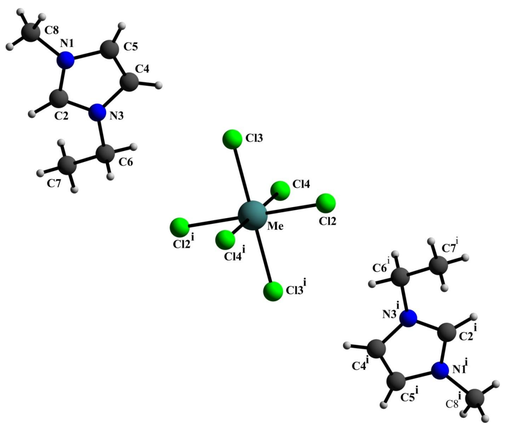

Fig. 2 Coordination polyhedron of $[MeCl_6]^{2-}$

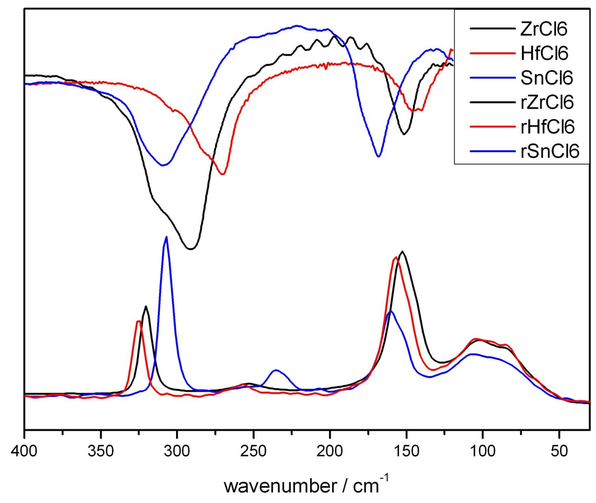

Fig. 3 FT-Raman/IR spectra of compounds I - III

Tab. 3 Raman frequencies (cm^{-1})

	I	II	III	$[ZrCl_6]^{2-}$		$[HfCl_6]^{2-}$		$[SnCl_6]^{2-}$
				[4]	[5]	[5]	[6]	[7]
ν_1	320s	325s	307s	326s	327	333	329	310
ν_3	290vs	266vs	309vs		290	288		303
ν_2	253vw	257vw	235w	249w	237vw	237vw		234
ν_5	152s	157s	161m	161s	153	157	156	165
ν_4	152s	144s	168s		150	145		162

Tab. 1 Crystallographic data for $[EMIm]_4[MeCl_6]$

Empirical formula	$C_{12}H_{22}N_4ZrCl_6$	$C_{12}H_{22}N_4HfCl_6$	$C_{12}H_{22}N_4SnCl_6$
Formula weight / g mol^{-1}	526.26	613.53	507.65
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pbca*	*Pbca*	*Pbca*
a / Å	9.664(2)	9.593(1)	9.538(1)
b / Å	14.485(3)	14.420(1)	14.386(1)
c / Å	15.444(3)	15.418(1)	15.504(2)
Volume / Å^3	2162.0(8)	2132.7(3)	2127.2(4)
Z	4	4	4
D_{calc} / g cm^{-3}	1.617	1.911	1.729
F(000)	1056	1184	1096
$\Theta_{min, max}$ / °	2.81, 25.35	2.64, 25.03	2.63, 25.03
Index ranges	-7 ≤ h ≤ 11 -17 ≤ k ≤ 16 -15 ≤ l ≤ 18	-11 ≤ h ≤ 11 -17 ≤ k ≤ 17 -18 ≤ l ≤ 17	-11 ≤ h ≤ 11 -16 ≤ k ≤ 17 -18 ≤ l ≤ 18
Unique reflections	1911	1885	1884
Data / restrains / parameters	1911/0/151	1885/0/140	1884/0/151
Goodness-of-fit on F^2	1.040	1.249	1.190
R indices [$I > 2\sigma(I)$]	*R*1 = 0.0495 *wR*2 = 0.0688	*R*1 = 0.0403 *wR*2 = 0.1127	*R*1 = 0.0243 *wR*2 = 0.0516
R indices (all data)	*R*1 = 0.0949 *wR*2 = 0.0769	*R*1 = 0.0423 *wR*2 = 0.1149	*R*1 = 0.0297 *wR*2 = 0.0533
Larg diff. peak and hole / e Å^3	0.391 and -0.334	2.362 and -3.481	0.541 and -0.322

Tab. 2 Selected bond lengths [Å] and angles [°] for $[EMIm]_2[MeCl_6]$

Me—Cl1	2.4284(7)	Me—Cl1^i	2.4284(7)
Me—Cl2	2.4330(7)	Me—Cl2^i	2.4330(7)
Me—Cl3	2.4358(7)	Me—Cl3^i	2.4358(7)
Cl2—Me—Cl2^i	180.0	Cl2—Me—Cl3	89.81(2)
Cl2^i—Me—Cl3	90.19(2)	Cl2—Me—Cl3^i	90.19(2)
Cl2^i—Me—Cl3^i	89.81(2)	Cl3—Me—Cl3^i	180.0
Cl2—Me—Cl1^i	90.08(3)	Cl2^i—Me—Cl1^i	89.92(3)
Cl3—Me—Cl1^i	89.75(2)	Cl3^i—Me—Cl1^i	90.25 (2)
Cl2—Me—Cl1	89.92(3)	Cl2^i—Me—Cl1	90.08(3)
Cl3—Me—Cl1	90.25(2)	Cl3^i—Me—Cl1	89.75(2)
Cl1^i—Me—Cl1	180.0		

Symmetry codes: i) –x, -y, 1-z ; ii) -1-x, -y, -z

Tab. 4 Fractional atomic coordinates and thermal parameters of $[EMIm]_2[MeCl_6]$

	x	*y*	*z*	U_{eq}
Me	0	0	0.5000	0.0242(1)
Cl1	0.2195(1)	0.0685(1)	0.5480(1)	0.4440(2)
Cl2	-0.0909(1)	0.1543(1)	0.4682(1)	0.0442(2)
Cl3	-0.0931(1)	0.0115(1)	0.6459(1)	0.0355(2)
N1	-0.3455(2)	0.3131(1)	0.1572(2)	0.0340(5)
N3	-0.2031(2)	0.2125(2)	0.2109(2)	0.0359(5)
C2	-0.2671(3)	0.2397(2)	0.1391(2)	0.0343(6)
C4	-0.2438(3)	0.2707(2)	0.2763(2)	0.0430(7)
C5	-0.3315(3)	0.3334(2)	0.2429(2)	0.0437(7)
C6	-0.1056(4)	0.1332(2)	0.2205(2)	0.0486(8)
C7	-0.0165(4)	0.1195(3)	0.1426(3)	0.0565(9)
C8	-0.4238(4)	0.3680(3)	0.0940(3)	0.0496(8)

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J.-C. Leye, M. Gjikaj and A. Adam

Institute of Inorganic and Analytical Chemistry
Clausthal University of Technology
Paul-Ernst-Straße 4 • D-38678 Clausthal-Zellerfeld