

# Synthesis and Crystal Structure of Trimecaine Hexachlorostannate(IV) Monohydrate

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**Abstract** — Single-crystals of trimecaine (2-diethylamino-N-(2,4,6-trimethylphenyl)acetamide, Tm) hydrochloride monohydrate and its newly synthesized hexachlorostannate(IV) monohydrate have been prepared and characterized by X-ray diffraction analyses.  $TmHCl \cdot H_2O$  crystallizes in the rhombic space group Paac with  $a = 28.999(5)$ ,  $b = 11.190(3)$ ,  $c = 10.573(3)$  Å, and  $Z = 8$ , forming crystal structure, in which  $TmH^+$  ions are united in infinite chains by intermolecular  $NH \dots Cl \dots HN$  bonds, while water molecules connect chains by  $OH \dots Cl \dots HO$  bonds.  $(TmH)_2[SnCl_6] \cdot H_2O$  crystallizes in the rhombic space group  $P2_12_12_1$  with  $a = 10.745(1)$ ,  $b = 14.199(2)$ ,  $c = 26.166(3)$  Å, and  $Z = 4$ , forming structure of molecular crystal with distorted  $SnCl_6^{2-}$  octahedrons asymmetrically associated with water molecule and two  $TmH^+$  ions by two  $Cl \dots HO$ ,  $O \dots HN$ , and bifurcated  $NH \dots 2Cl$  hydrogen bonds.

**Keywords** — Crystal structure, hexachlorostannate(IV), trimecaine, hydrogen bonds.

## I. INTRODUCTION

Coordination compounds play an important role in nature and are vital to many living organisms. Exhibiting different oxidation states, transition metals can interact with a number of organic molecules and this activity led to the recent development of drugs which are based on synthetic transition metal (particularly V(IV), Co(II), Ni(II), Cu(II) and Zn(II)) complexes incorporating nitrogen, oxygen and sulfur donor ligands, and are considered to be potential candidates for pharmacological and therapeutic applications [1].

Tin compounds usually are divided into two main classes: i) inorganic tin (with a valency of +2 or +4) salts which have been used for many centuries in coloured pigments for ceramics, paints, etc.; ii) organotin compounds possessing one or more direct Sn – C bond, which were discovered about 175 years ago, and were only commercialised during the 1950's [2]. The tin halides and many other tin materials act as acceptors and form complexes with neutral donor ligands, tin complexes have received significant attention due to their structural and stereochemical considerations as well as due to their potential biological applications [3]. Tetra- and six-coordinated tin complexes of the types  $SnX_2L_2$  [4] and  $SnX_4L_2$  are known, some tin(IV) complexes have been synthesized and characterized by a variety of physical-chemical techniques and X-ray diffraction measurements [5,6].

2-Diethylamino-N-(2,4,6-trimethylphenyl)acetamide (Tm,  $C_{15}H_{24}N_2O$ , trimecaine) hydrochloride monohydrate ( $TmHCl \cdot H_2O$ ) is white crystalline powder readily soluble in water and ethanol, it is used as a local anesthetic and cardiac antiarrhythmic, also for prophylaxis of sympathetic reaction during tracheal intubations. Like other local anesthetics belonging in the amide group trimecaine decreases the cell membrane permeability, causes depolarization and shortens the action potential, it is an active ingredient in products available under trademarks Trimecaine, Mesdicain, Mesocain, Mesokain and others.

Recently [7] complexes of empirical formula,  $(LH)_2[MX_4] \cdot nH_2O$  (LH = cationic form of the trimecaine or lidocaine (2-diethylamino-N-(2,6-dimethylphenyl)acetamide);

$X = Cl$  or  $NCS$ ;  $M = Co(II)$ ,  $Fe(II)$ ,  $Cu(II)$ ,  $Mn(II)$  or  $Ni(II)$ ;  $n = 0, 1$  or  $2$ ) have been synthesized and characterized. It was established that protonation of the ligand L takes place in the water-ethanol solutions at any ratio of transition metal ions and said organic molecules. As a result, coordination of the metal ion with ligands generates tetrahedral anion  $MX_4^{2-}$ , while the ligands in the form of protonated cation  $LH^+$  remain in an outer coordination field.

It has been shown that under the same conditions of preparation of the specified coordination compounds the tin cation Sn(II) is oxidized to Sn(IV) and forms a six-coordinated complex of another type.

The purpose of this our work was to define the chemical composition and structure of new compound containing the trimecaine molecules.

## II. EXPERIMENTAL

The study included the synthesis of new compound, the determination of its chemical composition, preparation of single crystals of trimecaine and the target product, and finally their research by the X-ray diffraction method.

### A. Synthesis, Crystal Growth, and Elemental Analysis

The synthesis of the target product was carried out as follows: an ethanol solution of trimecaine hydrochloride monohydrate (0.2 mmol of  $TmHCl \cdot H_2O$  in 10 mL) was added to an acidic water solution of tin chloride (0.1 mmol  $SnCl_2$  in 20 mL), the reaction mixture was stirred for 3 hours with the addition of hydrochloric acid (up to 0.25 mmol HCl) without heating, and then left at room temperature for slow evaporation; transparent crystals suitable for the X-ray measurements started to form after *ca.* 4 days, yield 67% based on  $SnCl_2$ ; the sample with dimensions 0.14 mm × 0.10 mm × 0.20 mm was used in the X-ray measurements.

Single-crystals of trimecaine hydrochloride monohydrate have been prepared in the same conditions (0.2 mmol of  $TmHCl \cdot H_2O$  in 10 mL ethanol + 20 mL water), the crystal with dimensions 0.20 mm × 0.20 mm × 0.25 mm was separated for the X-ray measurements.

Elemental analysis has been carried out on the Spectromom 381L plasma and Perkin-Elmer 300 atomic absorption spectrometers, results are given in Table I in comparison with the values calculated for possible structures.

TABLE I. Chemical composition (%) found for the prepared compound and calculated for possible structures.

Compound	Element				
	C	H	N	Cl	Sn
Found	42.18	6.18	6.70	24.92	13.77
(TmH) <sub>2</sub> [SnCl <sub>6</sub> ]	43.40	6.07	6.75	25.62	14.30
<b>(TmH)<sub>2</sub>[SnCl<sub>6</sub>]·H<sub>2</sub>O</b>	<b>42.49</b>	<b>6.18</b>	<b>6.61</b>	<b>25.08</b>	<b>13.98</b>
(TmH) <sub>2</sub> [SnCl <sub>6</sub> ]·2H <sub>2</sub> O	41.60	6.28	6.47	24.56	13.70
(TmH) <sub>2</sub> [SnCl <sub>4</sub> ]	47.46	6.64	7.38	18.68	15.63
(TmH) <sub>2</sub> [SnCl <sub>4</sub> ]·H <sub>2</sub> O	46.36	6.74	7.21	18.24	15.27
(TmH) <sub>2</sub> [SnCl <sub>4</sub> ]·2H <sub>2</sub> O	45.31	6.84	7.05	17.83	14.93

### B. X-Ray Diffraction Measurements

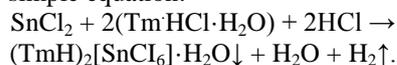
X-ray diffraction measurements have been conducted on the aforementioned single-crystal samples at room temperature. The data were collected on a Nicolet Syntex PI four-circle diffractometer using graphite monochromatized MoK<sub>α</sub> radiation,  $\lambda = 0.71073 \text{ \AA}$ , up to  $\theta = 24^\circ$ . Structural calculation was performed using crystallographic program SHELXS97 [8]. The tin atoms were located from E-map and all other nonhydrogen atoms were found from a subsequent Fourier map; the hydrogen atoms were located from a different Fourier map. Full-matrix least-squares refinement was carried out with anisotropic temperature factors U on heavy atoms and isotropic on the hydrogen atoms until  $R = 0.107$  and  $R = 0.048$ , based on 943 and 2706 reflections for the trimecaine hydrochloride monohydrate TmHCl·H<sub>2</sub>O and its derivative, respectively. Fractional atomic coordinates are given in Tables II and III.

## III. RESULTS AND DISCUSSION

For the determination of chemical composition for prepared compound the data of elemental analysis were used. As far as we know, there is no information in the literature about the crystal structure of the basic trimecaine or its hydrochloride, as well as about complex compounds of any nature with a 2-diethylamino-N-(trimethylphenyl)acetamide ligand or ion.

### A. Chemical Composition

Results of elemental analysis for obtained tin compound are in the best accordance with the calculations carried out for the molecule of trimecaine hexachlorostannate monohydrate, the six-coordinated tin(IV) compound with the empirical formula (TmH)<sub>2</sub>[SnCl<sub>6</sub>]·H<sub>2</sub>O (Table I), the compounds of the type (TmH)<sub>2</sub>[SnCl<sub>4</sub>]·nH<sub>2</sub>O, as well as anhydrous and dihydrate hexachlorostannates can be excluded from consideration, they are not suitable for chemical composition. Thus, chemical transformation during preparation of new compound can be described by simple equation:



### B. Crystal Structure of Trimecaine

Trimecaine hydrochloride monohydrate crystallizes in the rhombic space group Pcca (No. 54) with  $a = 28.599(5) \text{ \AA}$ ,  $b = 11.190(2) \text{ \AA}$ ,  $c = 10.573(2) \text{ \AA}$ , and  $Z = 8$ ; the location of Cl, C, O, and NH atoms of TmHCl·H<sub>2</sub>O is shown in Fig. 1.

TABLE II. Fractional atomic coordinates of nonhydrogen atoms and hydrogen atoms involved in H-bonding in TmHCl·H<sub>2</sub>O.

Atom	X	Y	Z
Cl	0.4326(2)	0.7072(4)	0.1023(5)
O	0.5000	0.5000	0.004(1)
H(1)O	0.469(2)	0.545(1)	0.0470(3)
H(2)O	0.521(2)	0.411(1)	-0.0474(4)
O	0.3557(5)	0.533(1)	0.002(1)
N(1)	0.3679(6)	0.682(1)	-0.114(1)
H-N(1)	0.361(3)	0.702(8)	-0.220(1)
N(2)	0.3423(6)	0.358(1)	-0.169(1)
H-N(2)	0.343(4)	0.306(9)	-0.06(1)
C(1)	0.3873(7)	0.776(1)	-0.062(1)
C(2)	0.3551(7)	0.866(1)	-0.036(1)
C(3)	0.3725(8)	0.960(1)	0.050(1)
C(4)	0.4209(9)	0.963(1)	0.070(2)
C(5)	0.4492(7)	0.870(1)	0.040(2)
C(6)	0.4330(7)	0.778(1)	-0.037(2)
C(7)	0.3063(8)	0.866(1)	-0.068(2)
C(8)	0.4370(8)	1.064(1)	0.171(2)
C(9)	0.4667(7)	0.679(1)	-0.075(2)
C(10)	0.3648(8)	0.567(1)	-0.097(2)
C(11)	0.3379(7)	0.491(1)	-0.201(2)
C(12)	0.3054(7)	0.293(1)	-0.240(2)
C(13)	0.3079(8)	0.343(1)	-0.292(2)
C(14)	0.3937(9)	0.313(2)	-0.186(3)
C(15)	0.428(2)	0.347(5)	-0.202(6)
	0.415(1)	0.251(4)	-0.096(4)

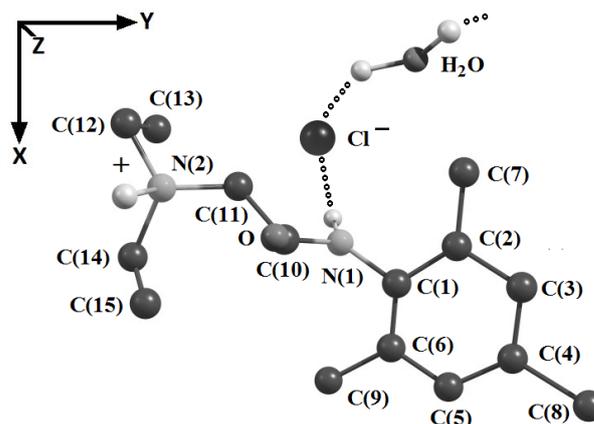


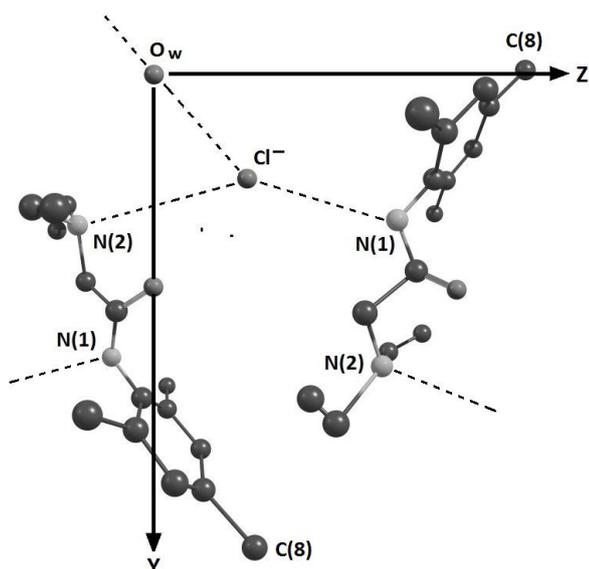
Fig. 1. Location of the TmHCl·H<sub>2</sub>O atoms in crystal structure.

The lengths of the C – C bonds and bond angles in the aromatic ring have approximately normal values, so that the aromatic ring is planar, the nitrogen atom N(1) and carbon atoms of methyl groups C(7), C(8), and C(8) lie in the same plane, which is almost parallel to the XY plane (atom C(1) is located 0.66 Å “below” and atom C(4) is 0.74 Å “above” the plane). However, bond lengths and angles in side chain significantly differ from standard, especially it concerns the nitrogen atom N(2) to which the proton transfer occurs resulting in formation of the TmH<sup>+</sup> ion. The nitrogen atom N(2) loses its symmetry and one of the ethyl groups (C(14) – C(15)) is statically disordered as in the lidocaine crystal [9] with the same 2-diethylamino-group.

Adjacent  $\text{TmH}^+$  ions are united in infinite chains with the help of intermolecular  $\text{N}(1)\text{H}\dots\text{Cl}\dots\text{HN}(2)$  bonds (interatomic distances and angles are shown in Table IIa). Chains are lying almost parallel to the YZ plane, while water molecules are located between chains and connect them by  $\text{OH}\dots\text{Cl}\dots\text{HO}$  bonds, as shown in Fig. 2.

TABLE IIa. Interatomic distances (Å) and angles (°) of atoms involved in H-bonds.

Bond A ... HB	Distance		Angle A - H - B
	A ... B	A ... H	
Cl ... HN(1)	3.22(1)	2.3(1)	150(8)
Cl ... HN(2)	3.16(1)	2.2(1)	136(8)
Cl ... HO <sub>w</sub>	3.206(8)	2.1(1)	158(9)


 Fig. 2. Fragment of the crystal structure of the  $\text{TmHCl}\cdot\text{H}_2\text{O}$  projected onto the plane YZ.

The crystal structure of trimecaine is fully hydrogen bonded, as in lidocaine, but in this case organic cations are linked into “endless chains,” and “adjacent chains related by the screw axes are joined in pairs by chlorine ions, which bind NH and  $\text{H}_2\text{O}$  groups in different chains” [9]. The trimecaine molecule is “longer” than lidocaine only on one methyl group C(8) at aromatic ring, but presence of this group does not allow the aromatic rings to be “stowed” in proper order, and this leads to significant change of a crystal structure.

### C. Crystal Structure of Trimecaine Hexachlorostannate(IV) Monohydrate

Trimecaine hexachlorostannate(IV) monohydrate,  $(\text{TmH})_2[\text{SnCl}_6]\cdot\text{H}_2\text{O}$ , crystallizes in the rhombic space group  $P2_12_12_1$  (No. 19) with  $a = 10.745(1)$  Å,  $b = 14.199(2)$  Å,  $c = 26.166(3)$  Å, and  $Z = 4$ .

The unit cell contains two relatively large  $\text{TmH}^+$  ions, octahedral  $[\text{SnCl}_6]^{2-}$  ion, and one water molecule. Chlorine atoms in the  $[\text{SnCl}_6]^{2-}$  ion are located at different distances from the central tin atom as shown in Figure 3, and the angles between the  $\text{Cl}-\text{Sn}-\text{Cl}$  bonds essentially deviate from 90 and 180 degrees (see Table IIIa).

 TABLE III. Fractional coordinates of nonhydrogen atoms and hydrogen atoms involved in H-bonding in  $(\text{TmH})_2[\text{SnCl}_6]\cdot\text{H}_2\text{O}$ .

Atom	X	Y	Z
Sn	0.2180(1)	0.2177(1)	0.1204(1)
Cl(1)	0.1308(6)	0.0739(4)	0.0813(2)
Cl(2)	0.3395(5)	0.1115(4)	0.1718(2)
Cl(3)	0.3052(6)	0.3484(4)	0.1646(3)
Cl(4)	0.0899(5)	0.3093(5)	0.0658(2)
Cl(5)	0.3830(4)	0.2206(4)	0.0581(2)
Cl(6)	0.0478(4)	0.2158(4)	0.1822(1)
O <sub>w</sub>	0.2630(23)	0.4919(19)	0.0655(10)
H <sub>w</sub> (1)	0.310(2)	0.4654(16)	-0.0932(2)
H <sub>w</sub> (1)	-0.204(2)	0.4462(15)	-0.0532(3)
O	0.1411(14)	0.6510(11)	0.2291(6)
N(1)	0.2306(16)	0.6070(13)	0.1564(5)
H <sub>N(1)</sub>	-0.0130(15)	0.581(2)	0.251(2)
N(2)	-0.0159(17)	0.5379(14)	0.2278(7)
H <sub>N(2)</sub>	0.2230(15)	0.586(3)	0.112(2)
C(1)	0.3258(21)	0.6754(19)	0.1606(9)
C(2)	0.3059(20)	0.7579(23)	0.1308(8)
C(3)	0.3928(22)	0.8307(17)	0.1358(8)
C(4)	0.4973(22)	0.8231(18)	0.1650(8)
C(5)	0.5140(21)	0.7370(23)	0.1912(8)
C(6)	0.4321(19)	0.6651(18)	0.1880(8)
C(7)	0.1893(21)	0.7741(21)	0.0983(9)
C(8)	0.5879(21)	0.9008(15)	0.1722(10)
C(9)	0.4468(21)	0.5741(15)	0.2167(8)
C(10)	0.1487(18)	0.5968(17)	0.1926(8)
C(11)	0.0524(19)	0.5205(15)	0.1892(9)
C(12)	-0.1611(20)	0.5775(21)	0.2057(10)
C(13)	-0.1437(27)	0.6641(21)	0.1790(9)
C(14)	-0.0762(33)	0.4574(23)	0.2607(12)
C(15)	0.0261(39)	0.4342(23)	0.2958(14)
O	0.8274(11)	0.4362(8)	0.1115(4)
N(1)	0.7601(13)	0.4648(11)	0.0318(5)
H <sub>N(1)</sub>	0.7320(15)	0.439(2)	-0.0020(15)
N(2)	0.7655(16)	0.2543(9)	0.1116(5)
H <sub>N(2)</sub>	0.8330(15)	0.280(2)	0.129(2)
C(1)	0.7839(21)	0.5675(12)	0.0322(6)
C(2)	0.6935(16)	0.6233(15)	0.0537(6)
C(3)	0.7221(24)	0.7210(17)	0.0549(6)
C(4)	0.8307(26)	0.7554(15)	0.0384(8)
C(5)	0.9137(18)	0.6943(14)	0.0173(8)
C(6)	0.8944(21)	0.6022(15)	0.0143(7)
C(7)	0.5745(20)	0.5836(17)	0.0721(8)
C(8)	0.8519(28)	0.8617(13)	0.0455(8)
C(9)	0.9916(18)	0.5358(15)	-0.0097(9)
C(10)	0.7854(18)	0.4097(11)	0.0723(7)
C(11)	0.7491(19)	0.3079(11)	0.0635(7)
C(12)	0.6497(20)	0.2743(19)	0.1442(9)
C(13)	0.6538(25)	0.2828(25)	0.1923(10)
C(14)	0.7910(29)	0.1561(18)	0.1027(14)
C(15)	0.7105(30)	0.1073(18)	0.0715(12)

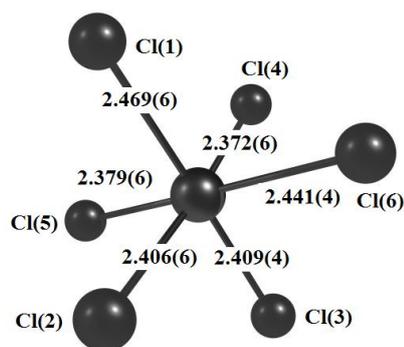

 Fig. 3. Length (Å) of Sn-Cl bonds in  $(\text{TmH})_2[\text{SnCl}_6]\cdot\text{H}_2\text{O}$

TABLE IIIa. Bond angles ( $^{\circ}$ ) in the  $[\text{SnCl}_6]^{2-}$  ion.

Bonds	Angle	Bonds	Angle
Cl(1)–Sn–Cl(2)	85.4(1)	Cl(1)–Sn–Cl(2)	90.8(1)
Cl(4)–Sn–Cl(6)	88.3(1)	Cl(4)–Sn–Cl(6)	91.5(1)
Cl(3)–Sn–Cl(6)	89.0(1)	Cl(3)–Sn–Cl(6)	91.7(1)
Cl(1)–Sn–Cl(4)	89.1(1)	Cl(1)–Sn–Cl(4)	95.4(1)
Cl(2)–Sn–Cl(5)	89.4(1)	Cl(2)–Sn–Cl(5)	174.4(2)
Cl(1)–Sn–Cl(6)	89.91(1)	Cl(1)–Sn–Cl(6)	175.0(2)
Cl(1)–Sn–Cl(6)	90.2(1)	Cl(1)–Sn–Cl(6)	178.8(2)
Cl(1)–Sn–Cl(6)	90.6(1)		

Distortions of the  $\text{SnCl}_6^{2-}$  octahedrons in methylammonium  $(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$  [10] and bis(triethylammonium)  $((\text{CH}_3\text{CH}_2)_3\text{NH})_2\text{SnCl}_6$  [11] hexachlorostannates(IV) were found to be insignificant, in 4-chloropyridinium hexachloro-stannate(IV)  $(\text{C}_5\text{H}_4\text{ClNH})_2\text{SnCl}_6$  [12] octahedron “is distorted with three crystallographically inequivalent Sn–Cl bonds (2.414(4), 2.419(2), and 2.463(3) Å).” According to Fig. 3, there are at least four “crystallographically inequivalent” Sn–Cl bonds in the  $(\text{TmH})_2[\text{SnCl}_6]\cdot\text{H}_2\text{O}$ : 1<sup>st</sup> and 2<sup>nd</sup> with atoms Cl(1) and Cl(6), the most distant from the atom of tin, 3<sup>rd</sup> with atoms Cl(2) and Cl(3), which can be considered to be equally remote from the central atom, and 4<sup>th</sup> with atoms Cl(4) and Cl(5), closest to the tin atom (Sn–C bond lengths 2.469(6), 2.441(4), and averaged values 2.408(9), and 2.376(9) Å).

The greatest deviations from a right angle in the  $\text{SnCl}_6^{2-}$  octahedron are observed for angles Cl(1)–Sn–Cl(2) ( $-4.6^{\circ}$ ) and Cl(3)–Sn–Cl(4) ( $+5.4^{\circ}$ ), and from a corner in 180 degrees for an angle Cl(2)–Sn–Cl(4) ( $-5.6^{\circ}$ ). Thus the sum of angles Cl(1)–Sn–Cl(2), Cl(2)–Sn–Cl(3), Cl(3)–Sn–Cl(4) and Cl(1)–Sn–Cl(4) is equal to  $360.0(2)^{\circ}$ , so that atoms of chlorine Cl(1), Cl(2), Cl(3), and Cl(4), and also a tin atom lie in one plane, but two other planes of octahedron are slightly distorted (the sum of angles Cl(1)–Sn–Cl(6) + Cl(3)–Sn–Cl(6) + Cl(3)–Sn–Cl(5) + Cl(1)–Sn–Cl(5) =  $361.2(2)^{\circ}$ ; Cl(2)–Sn–Cl(6) + Cl(4)–Sn–Cl(6) + Cl(4)–Sn–Cl(5) + Cl(2)–Sn–Cl(5) =  $362.1(2)^{\circ}$ ).

In contrast to the structure of trimecaine hydrochloride, in hexachlorostannate(IV) is no disordering of ethyl groups at the atom N(2), but both organic cations  $\text{TmH}^+$  are distorted and differ from each other not only in location (bond lengths and angular parameters are given in Tables IIIb and IIIc). So, one ion  $\text{TmH}^+$  has a planar aromatic ring, as in a trimecaine crystal structure, while the ring of the second ion is essentially deformed.

 TABLE IIIb. Bond lengths (Å) in the  $\text{TmH}^+$  ions.

Bond	$\text{TmHCl}\cdot\text{H}_2\text{O}$	$(\text{TmH})_2[\text{SnCl}_6]\cdot\text{H}_2\text{O}$	
C–C in aromatic ring	1.40(3)	1.38(3)	1.37(3)
C(2)–C(7)	1.45(2)	1.53(3)	1.48(3)
C(4)–C(8)	1.61(2)	1.48(3)	1.54(3)
C(6)–C(9)	1.53(2)	1.50(3)	1.54(3)
N(1)–C(1)	1.48(2)	1.42(3)	1.48(2)
N(1)–C(10)	1.37(2)	1.30(2)	1.34(2)
C(10)=O	1.17(2)	1.23(3)	1.18(2)
C(10)–C(11)	1.60(2)	1.50(3)	1.51(2)
N(2)–C(11)	1.53(2)	1.48(3)	1.48(2)
N(2)–C(12)	1.49(2)	1.48(3)	1.53(3)
N(2)–C(14)	1.58(3)	1.47(4)	1.44(3)
C(12)–C(13)	1.57(2)	1.43(4)	1.26(3)
C(14)–C(15)	1.33(5)	1.43(5)	1.38(4)

 TABLE IIIc. Angular parameters ( $^{\circ}$ ) of the  $\text{TmH}^+$  ions.

Bonds	$\text{TmHCl}\cdot\text{H}_2\text{O}$	$(\text{TmH})_2[\text{SnCl}_6]\cdot\text{H}_2\text{O}$	
C–C–C in aromatic ring	127(1)	117.3(20)	114.8(17)
	113(1)	122.8(22)	122.6(21)
	116(1)	116.5(22)	118.1(20)
	122(1)	122.8(21)	1.54(3)
	119(2)	119.9(24)	1.48(2)
	116(1)	120.4(23)	1.34(2)
$\text{H}_3\text{C}-\text{C}-\text{C}$ of aromatic ring	126(1)	116.5(21)	121.7(19)
	118(1)	123.4(20)	123.5(19)
	113(1)	123.4(24)	116.7(22)
	120(1)	119.0(25)	125.3(23)
	118(1)	123.5(22)	121.4(19)
124(1)	119.9(21)	120.5(18)	
C(2)–C(1)–N(1)	112(1)	114.5(20)	116.7(17)
C(2)–C(1)–N(1)	119(1)	125.1(23)	120.1(17)
C(1)–N(1)–C(10)	118(1)	120.6(18)	122.2(13)
N(2)–C(10)=O	128(1)	122.7(21)	125.1(15)
C(11)–C(10)=O	125(1)	116.9(19)	122.3(15)
C(10)–C(11)–N(2)	108(1)	109.3(18)	109.3(14)
C(11)–N(2)–C(12)	107(1)	113.1(18)	106.3(15)
C(11)–N(2)–C(14)	110(1)	115.4(20)	112.4(17)
C(12)–N(2)–C(14)	117(1)	109.8(21)	115.0(19)
C(13)–C(12)–N(2)	109(1)	114.2(21)	122.8(21)
C(15)–C(14)–N(2)	121(3) and 141(3)	112.0(28)	117.7(25)

It is obvious that the hydrogen bonding is the source of abovementioned distortion of organic cations and octahedron  $\text{SnCl}_6^{2-}$ , but unlike trimecaine and lidocaine hydrochlorides, in which crystal structure is fully hydrogen-bonded and all potential donor and acceptor groups are utilized to establish H-bonds, in trimecaine hexachlorostannate(IV) monohydrate not all chlorine atoms are involved in this process. However, it is not surprising, in  $(\text{Et}_3\text{NH})_2\text{SnCl}_6$  each  $\text{SnCl}_6^{2-}$  anion has two  $\text{Et}_3\text{NH}^+$  cations centrosymmetrically associated with it through bifurcated hydrogen bonds to four of the Cl atoms, leaving two of the six chlorines unengaged [11].

In the  $(\text{TmH})_2[\text{SnCl}_6]\cdot\text{H}_2\text{O}$  structure atoms of chlorine Cl(3) and Cl(4), closest to the central atom of tin Sn, are also located near the water molecule, and the oxygen atom of water  $\text{O}_w$  lies at a distance of 4.67(5) Å from the central atom. The oxygen atom  $\text{O}_w$  is also located near acetamide N(1)H-group of one  $\text{TmH}^+$  ion. The protonated diethylamino-N-group of another  $\text{TmH}^+$  ion not involved in H-bonding with a water molecule is located near the next  $\text{SnCl}_6^{2-}$  ion and it can form a bifurcated N–H...2Cl bond. Hydrogen bonding with participation of four chlorine atoms is illustrated in Fig. 4, relevant distances and angles are given in Table IIIc.

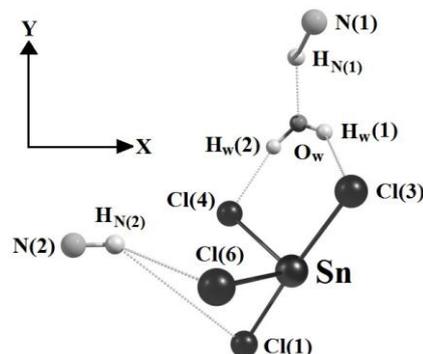
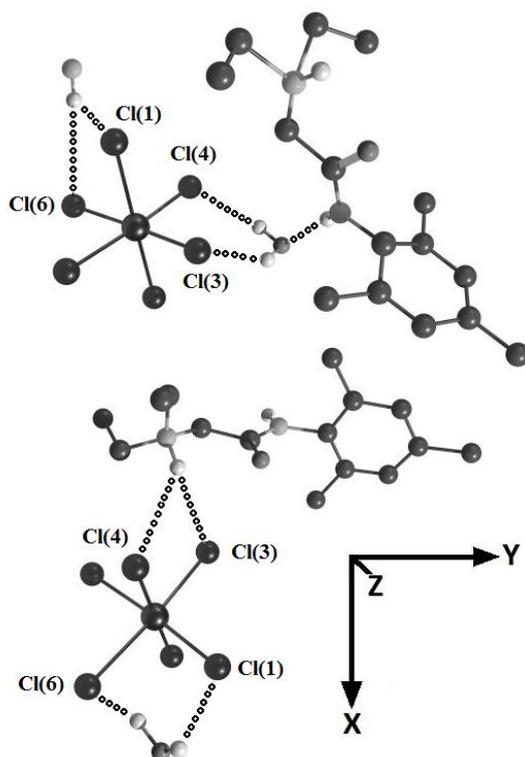

 Fig. 4. Hydrogen bonds in  $(\text{TmH})_2[\text{SnCl}_6]\cdot\text{H}_2\text{O}$ .

TABLE IIIId. Interatomic distances (Å) and angles (°) of atoms involved in hydrogen bonding of  $(\text{TmH})_2[\text{SnCl}_6] \cdot \text{H}_2\text{O}$  structure.

Bond A ... HB	Distance		Angle A – H – B
	A ... B	A ... H	
Cl(3) ... H <sub>w</sub> (1)O <sub>w</sub>	3.19(2)	2.32(2)	150(5)
Cl(4) ... H <sub>w</sub> (2)O <sub>w</sub>	3.33(2)	2.50(2)	145(3)
O <sub>w</sub> ... H <sub>N(1)</sub> N(1)	2.90(2)	1.87(1)	143(3)
Cl(1) ... H <sub>N(2)</sub> N(2)	3.80(3)	3.03(3)	143(3)
Cl(6) ... H <sub>N(2)</sub> N(2)	3.64(3)	2.85(3)	145(4)

Nitrogen atom N(2) is located at a distance of 4.95(8) Å from the atom of tin of the neighboring anion  $\text{SnCl}_6^{2-}$ , not forming hydrogen bond through a water molecule with the same cation  $\text{TmH}^+$ . Between the atoms of nitrogen N(2) and tin are lying the atoms of chlorine Cl(1) and Cl(6), the most removed from the central tin atom of the  $\text{SnCl}_6^{2-}$  anion. For  $(\text{C}_5\text{H}_4\text{ClNH})_2\text{SnCl}_6$  [12], Cl...H–N hydrogen bonding was found “between the long Sn–Cl bonds of  $\text{SnCl}_6^{2-}$  and the cations.” The distance between atoms Cl(1) and H<sub>N(2)</sub>, 3.03 Å, is quite large, and the hydrogen bond will be relatively weak.

The H<sub>N(2)</sub>...Cl(6) distance in the bifurcated hydrogen bond, 2.85 Å, is somewhat longer than H...Cl distance in the cubic  $(\text{NH}_4)_2\text{SnCl}_6$ , 2.79 Å [11]. Unlike in the latter crystal, but like in  $(\text{Et}_3\text{NH})_2\text{SnCl}_6$ , the N–H vector in  $(\text{TmH})_2[\text{SnCl}_6] \cdot \text{H}_2\text{O}$  points in the direction of the Sn atom. This bifurcated N–H...2Cl bond is not symmetric, but the H atom is only about 0.12 Å away from the respective N(2) – Cl(1) – Cl(6) plane.


 Fig. 5. Schematic representation of hydrogen bonds in the spatial structure of  $(\text{TmH})_2[\text{SnCl}_6] \cdot \text{H}_2\text{O}$ .

Hydrogen bonding in  $(\text{TmH})_2[\text{SnCl}_6] \cdot \text{H}_2\text{O}$  do not lead to formation of chains as it occurs in trimecaine and lidocaine hydrochlorides. In trimecaine hexachlorostannate(IV) a three-dimensional molecular crystal structure is formed in which each  $\text{SnCl}_6^{2-}$  anion is asymmetrically associated with two  $\text{TmH}^+$  cations: chlorine atoms Cl(3) and Cl(4) form Cl...HO hydrogen bonds with a molecule of water forming O...HN hydrogen bond with the nitrogen atom N(1) resulting in distortion of the aromatic ring, while the nitrogen atom N(2) of another  $\text{TmH}^+$  cation remaining planar aromatic ring form bifurcated hydrogen bonds NH...2Cl with chlorine atoms Cl(1) and Cl(6). The hydrogen-bonding network of trimecaine hexachloro-stannate(IV) monohydrate is illustrated in Fig. 5. The resulting trimecaine dimer is not joined to its neighbors by any forces stronger than van der Waals.

In summary, we first synthesized trimecaine hexachlorostannate(IV) monohydrate and described its structure. Study of physical-chemical properties of the  $(\text{TmH})_2[\text{SnCl}_6] \cdot \text{H}_2\text{O}$  and feasibility of its application are in progress.

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