

Dedicated to the memory of
Professor Candin Liteanu on his 100th anniversary

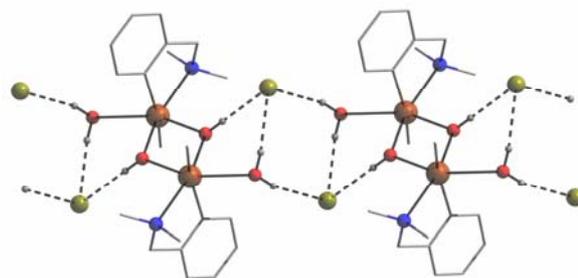
[2-(Me₂NCH₂)C₆H₄]SnMeCl₂ AND ITS HYDROLYSIS PRODUCT, [{2-(Me₂NCH₂)C₆H₄} SnMe(OH)(OH₂)]₂²⁺ · 2Br⁻ - SOLUTION AND SOLID STATE CHARACTERIZATION

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The diorganotin(IV) dichloride [2-(Me₂NCH₂)C₆H₄]SnMeCl₂ (**1**) was prepared by treating MeSnCl₃ with [2-(Me₂NCH₂)C₆H₄]Li. After the workup of the reaction mixture between **1** and [2-((CH₂O)₂CH)C₆H₄]MgBr, in air, the hydrolysis product [{2-(Me₂NCH₂)C₆H₄} SnMe(OH)(OH₂)]₂²⁺ · 2Br⁻ (**2**) was isolated. The solution behavior of compound **1** was investigated by multinuclear (¹H, ¹³C and ¹¹⁹Sn) NMR spectroscopy, while the low solubility of compound **2** only allowed recording the ¹H NMR spectrum in D₂O. Single-crystal X-ray diffraction analyses revealed a pentacoordinated tin atom in **1** and a hexacoordinated metal centre in **2**. Supramolecular architectures are formed in solid state based on X...H (X = Cl, Br) interactions.



INTRODUCTION

Several diorganotin(IV) dichlorides containing at least one 2-(Me₂NCH₂)C₆H₄ pendant arm ligand or related organic groups have been reported in the recent years.¹ Single-crystal X-ray diffraction studies revealed a hexacoordinated metal center for symmetric compounds with two 2-(R₂NCH₂)C₆H₄ (R = Me,² Et³) fragments bonded to tin, while for the mixed derivatives with either *n*-Bu¹ or Ph^{4,5} groups as the second organic ligand bonded to tin a pentacoordinated metal centre is present. For the related [2-(Me₂NCH₂)C₆H₄]SnMeCl₂ a trigonal bipyramidal geometry around the tin atom was proposed based on ¹H NMR studies.⁶

On the other hand, structural studies were made on a series of hydrolysis products isolated after the interaction of protic acids on diorganotin(IV) derivatives with 2-(Me₂NCH₂)C₆H₄ moieties. Various structural features were identified by single-crystal X-ray diffraction studies, *i.e.*

- *binuclear species* with (i) a bridging oxygen atom, [{2-(Me₂NCH₂)C₆H₄}₂Sn(OH)]₂O⁷ and [{2-(Me₂NCH₂)C₆H₄}PhSnCl]₂O,⁸ (ii) bridging oxygen atom and carbonate groups, [{2-(Me₂NCH₂)C₆H₄}₂Sn]₂(μ-O)(μ-CO₃),⁹ (iii) bridging hydroxy and CF₃CO₂⁻ groups, [{2-(Me₂NCH₂)C₆H₄}SnPh{O(O)CCF₃}]₂(μ-OH)(μ-O₂CCF₃),¹⁰ (iv) two bridging hydroxy groups, [{2-(Me₂NCH₂)C₆H₄}SnBu{O(O)CCF₃}]₂(μ-OH)₂,¹⁰

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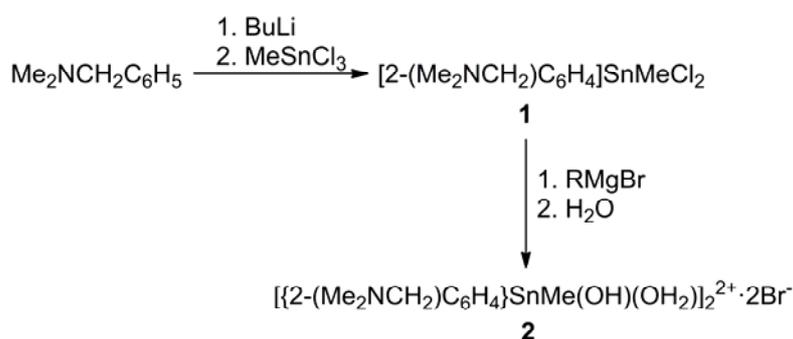
- *trinuclear species* with a (i) six-membered Sn_3O_3 core, $\text{cyclo-}[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_2\text{SnO}]_3$,¹¹ (ii) four-membered Sn_3O core, $\text{cyclo-L}_5\text{Sn}_3(\mu\text{-OH})$ [$\text{L} = 2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$],¹² or

- *tetranuclear species* with (i) cyclic structure, $\text{cyclo-}[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_2\text{SnO}]_4$,¹¹ and (ii) ladder-like structure, $[(\text{LSnPhCl})_2(\text{H}^+\text{LSnPh})_2(\text{OH})_2(\text{O})_2]^{2+} \cdot 2\text{Cl}^- \cdot 10\text{CDCl}_3$ [$\text{L} = 2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$].¹³

We report here on the synthesis, the solution behavior and solid state structure of $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{SnMeCl}_2$ (**1**) as well as the solid state structure of its ionic hydrolysis product $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}\text{SnMe}(\text{OH})(\text{OH}_2)]_2^{2+} \cdot 2\text{Br}^-$ (**2**).

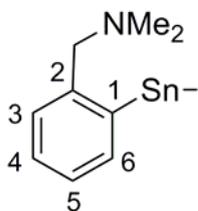
RESULTS

The diorganotin(IV) dichloride $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{SnMeCl}_2$ (**1**) was obtained from the reaction of MeSnCl_3 and the lithium salt of the organic ligand. The compound was previously prepared by reacting $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Cu}$ with methyltin trichloride.⁶ The ionic compound $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}\text{SnMe}(\text{OH})(\text{OH}_2)]_2^{2+} \cdot 2\text{Br}^-$ (**2**) was isolated after the workup, in open atmosphere, of the reaction mixture obtained by treatment of **1** with $[2-\{(\text{CH}_2\text{O})_2\text{CH}\}\text{C}_6\text{H}_4]\text{MgBr}$ as result of a hydrolysis process (Scheme 1).



Scheme 1

Compound **1** was investigated by multinuclear (^1H , ^{13}C , ^{119}Sn) NMR spectroscopy in solution at room temperature. The assignment of the ^1H and ^{13}C resonances was based on the reported data,⁶ on 2D NMR (HSQC and COSY) correlation spectra and tin–carbon coupling constants, according to the numbering scheme depicted in Scheme 2:



Scheme 2

The solution NMR spectra of the isolated product, recorded in CDCl_3 , are consistent with the formation of the title compound. The ^1H and ^{13}C NMR spectra showed the expected resonances in the alkyl as well as in the aryl regions for the organic groups attached to tin atom. Most ^{13}C resonances are surrounded by the satellites

corresponding to tin–carbon couplings. Compound **2** is insoluble in common solvents and has a low solubility in water and acetone. This behavior only allowed the recording of a low quality ^1H NMR spectrum in D_2O which confirms the presence of the organic groups on tin atom. In the APCI+ mass spectrum of **1** the pseudomolecular $[\text{M} + \text{H}]^+$ ion was observed [m/z (%) 339.39 (0.52)] and the base peak was assigned to the $[\text{R}\text{SnMeCl}]^+$ ion (m/z 303.99). For compound **2**, the base peak in the ESI+ mass spectrum was assigned to the $[2-(\text{Me}_2\text{N})\text{C}_6\text{H}_4\text{SnMeBr}]^+$ fragment (m/z 347.94), but the $[2-(\text{Me}_2\text{N})\text{C}_6\text{H}_4\text{SnMe}(\text{OH})]^+$ ion also gave an intense peak [m/z (%) 286.02 (49)].

Single crystals of **1** were grown from a $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ solvent mixture using the slow diffusion technique. Crystals of **2** were obtained from a diluted acetone solution by slow evaporation of the solvent. Selected bond distances and angles are listed in Tables 1 and 2. Fig. 1 shows the ORTEP-like view of the molecular structure of **1** and **2**, respectively, with the atom numbering scheme.

Table 1

Selected interatomic distances (Å) and angles (°) in [2-(Me ₂ NCH ₂)C ₆ H ₄]SnMeCl ₂ (1)			
Sn(1)–C(1)	2.112(4)	Sn(1)–C(10)	2.108(5)
Sn(1)–Cl(1)	2.450(2)	Sn(1)–Cl(2)	2.361(2)
Sn(1)–N(1)	2.405(4)		
N(1)–Sn(1)–Cl(1)	172.81(9)	N(1)–Sn(1)–C(1)	76.08(14)
Cl(1)–Sn(1)–C(1)	96.76(12)	N(1)–Sn(1)–C(10)	92.06(18)
Cl(1)–Sn(1)–C(10)	93.81(16)	N(1)–Sn(1)–Cl(2)	88.30(10)
Cl(1)–Sn(1)–Cl(2)	93.41(6)		
C(1)–Sn(1)–C(10)	138.6(2)		
C(1)–Sn(1)–Cl(2)	107.81(12)	C(10)–Sn(1)–Cl(2)	111.37(15)

Table 2

Selected interatomic distances (Å) and angles (°) in [{2-(Me ₂ NCH ₂)C ₆ H ₄ }SnMe(OH)(OH ₂) ₂] ²⁺ ·2Br [−] (2) ^a			
Sn(1)–C(1)	2.111(4)	Sn(1)–C(10)	2.103(4)
Sn(1)–O(1)	2.099(3)	Sn(1)–O(2)	2.480(4)
Sn(1)–O(1')	2.140(3)	Sn(1)–N(1)	2.410(4)
N(1)–Sn(1)–O(1')	160.26(12)	O(1)–Sn(1)–O(2)	155.60(12)
C(1)–Sn(1)–C(10)	157.67(19)	N(1)–Sn(1)–C(1)	76.64(15)
O(1')–Sn(1)–C(1)	97.92(14)	N(1)–Sn(1)–C(10)	92.81(17)
O(1')–Sn(1)–C(10)	98.18(17)	N(1)–Sn(1)–O(1)	88.27(12)
O(1')–Sn(1)–O(1)	73.91(13)	N(1)–Sn(1)–O(2)	116.13(13)
O(1')–Sn(1)–O(2)	81.91(12)	C(10)–Sn(1)–O(2)	81.19(17)
C(1)–Sn(1)–O(1)	100.44(14)	O(2)–Sn(1)–C(1)	85.88(14)
O(1)–Sn(1)–C(10)	98.82(17)		
Sn(1)–O(1)–Sn(1')	106.09(13)		

^a Symmetry equivalent atoms ($I-x, -y, -z$) are designated with a "prime" symbol.

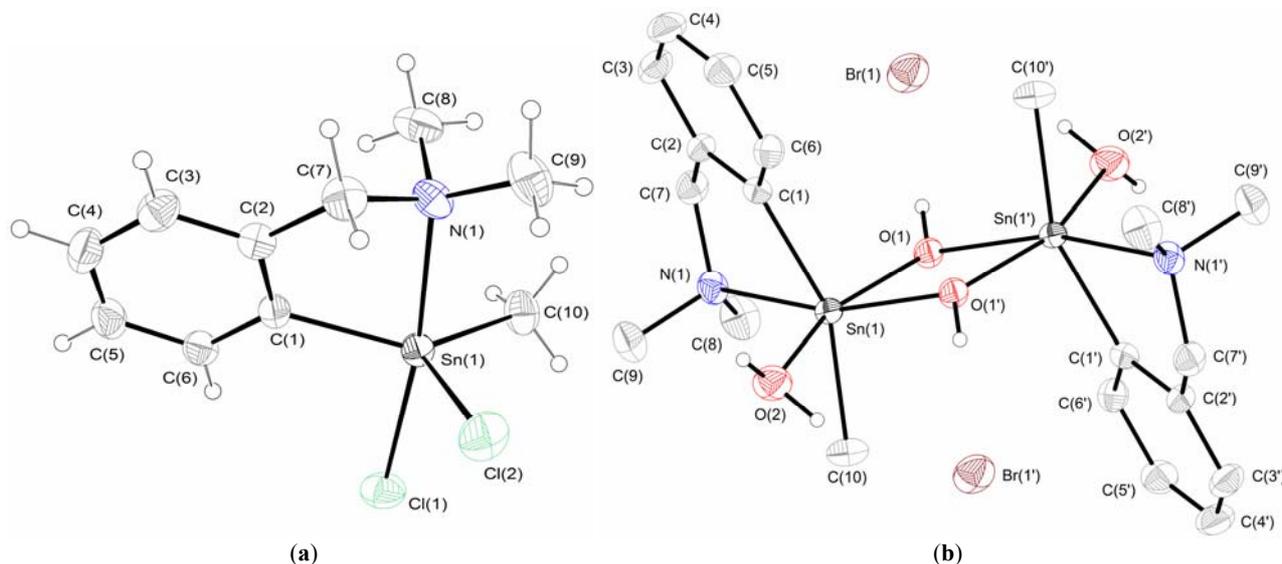


Fig. 1 – ORTEP representation at 30% probability and atom numbering scheme for (a) [2-(Me₂NCH₂)C₆H₄]SnMeCl₂ (**1**) and (b) [{2-(Me₂NCH₂)C₆H₄}SnMe(OH)(OH₂)₂]²⁺·2Br[−] (**2**) (hydrogen atoms are removed for clarity, except for water and hydroxy group).

DISCUSSION

Solution behavior

The ¹H NMR spectra of both compounds show all the expected resonance signals of the organic

groups bonded to tin. In the aliphatic region, the resonance signals corresponding to the methylene and the methyl groups bonded to the nitrogen atom from the pendant arm appear as singlet resonances. This is consistent with either (i) the lack of N→Sn intramolecular coordination, or (ii) a fast dynamic

behavior at NMR time scale, in solution. The later involves combined processes which consist in N→Sn dissociation / configuration inversion at nitrogen / N→Sn re-coordination (resulting in equivalent methyl groups on nitrogen) and alternating coordination of nitrogen *trans* to one of the chlorine atoms from the molecular unit (resulting in equivalent methylene protons of the pendant arm). Such a dynamic behavior is supported by the magnitude of the ^{119}Sn chemical shift observed at room temperature for compound **1** ($\delta = -97.4$ ppm, in CDCl_3) which is typical for pentacoordinate diorganotin(IV) species in solution (cf. $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{BuSnCl}_2$:¹ $\delta = -103.0$ ppm, in CDCl_3 ; $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{PhSnCl}_2$:⁵ $\delta = -170$ ppm, in CDCl_3). The increase of the tin coordination number to five is also supported by the upfield shift of the ^{119}Sn chemical shift for **1** with respect to the related tetrahedral PhMeSnCl_2 species ($\delta = 55.1$ ppm, in CDCl_3).¹⁴

Solid state structure

For both compounds the crystals contain molecular units in which the metal centers are strongly coordinated by the nitrogen atom from the pendant arm *trans* to one of the Cl atoms in **1** [$\text{N}(1)\text{--Sn}(1)\text{--Cl}(1) = 172.81(9)^\circ$] and to a OH group in **2** [$\text{N}(1)\text{--Sn}(1)\text{--O}(1) = 160.26(12)^\circ$]. This results in different coordination environments around the metal center, *i.e.* highly distorted trigonal bipyramidal geometry with $(C,N)\text{CSnCl}_2$ core in **1** and distorted octahedral geometry with $(C,M)\text{CSnO}_3$ core in **2**, respectively. The equatorial sites in **1** are occupied by the remaining Cl atom and the two carbon atoms from the organic ligands. The $\text{C}(1)\text{--Sn}(1)\text{--C}(10)$ angle [$138.61(19)^\circ$] in the equatorial plane of **1** is even larger than the equatorial C--Sn--Cl angle [$134.26(8)^\circ$] found in $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{SnCl}_3$.¹⁵ The Sn(1) atom is displaced from the C_2Cl equatorial plane towards the axial Cl(1) atom, by 0.181 Å.

The interatomic N→Sn distances in both compounds (Tables 1 and 2) exceed the sum of the covalent radii [$\Sigma r_{\text{cov}}(\text{Sn},\text{N}) 2.1$ Å] but are shorter than the sum of the van der Waals radii [$\Sigma r_{\text{vdw}}(\text{Sn},\text{N}) 3.74$ Å] of the corresponding atoms.¹⁶ The Sn(1)–N(1) distance in compound **1** [2.404(4) Å] is longer than the one found in $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{SnCl}_3$ [2.391(3) Å], but shorter than in related pentacoordinated $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{RSnCl}_2$ [R = Bu, 2.458(5) Å;¹

R = Ph, 2.444(5) Å⁵], $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{R}_2\text{SnCl}$ [R = Me, 2.488(7) Å,³ 2.485(3) Å,² 2.488(3) Å;² R = Ph, 2.519(2) Å,¹⁷ 2.538(4) Å and 2.509(3) Å for two independent molecules which are present in the unit cell²]. This is consistent with a stronger Lewis acid character of the Sn center in **1** with respect to these related diorganotin(IV) dichlorides or the triorganotin(IV) chlorides with trigonal bipyramidal geometry.

The crystal of compound **2** contains a mixture of $[\{\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}\text{SnMe}(\text{OH})(\text{OH}_2)]_2^{2+}$ dications and $[\text{Br}]^-$ anions. The dication consists of two distorted octahedral $(C,N)\text{CSnO}_3$ cores bridged slightly unsymmetrically by two hydroxy groups [$\text{Sn}(1)\text{--O}(1) = 2.099(6)$ Å and $\text{Sn}(1)\text{--O}(1') = 2.140(3)$ Å, respectively; symmetry equivalent position given by “prime”: ($1-x, -y, -z$)]. The result is a planar Sn_2O_2 ring with the pendant arm ligands from the two metal centers placed on opposite sides of the ring. The sixth coordination site of the octahedral $(C,M)\text{CSnO}_3$ core is occupied by a water molecule in *trans* to one of the OH groups, leading to a *trans*- SnC_2 fragment, while the two OH groups and the N atom and the H_2O molecule are in *cis* positions, respectively. The Sn(1)–N(1) distance of 2.410(3) Å in **2** is shorter than the similar interactions found in the related organotin hydroxides *cyclo*- $\text{L}_5\text{Sn}_3(\mu\text{-OH})$ [L = $\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$] [2.542(6), 2.638(6) Å],¹² $[\{\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_2\text{Sn}(\text{OH})_2\text{O}]$ [2.542(6) Å],⁷ $[\{\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}\text{SnBu}\{\text{O}(\text{O})\text{CCF}_3\}]_2(\mu\text{-OH})_2$ [2.520(3) Å],¹⁰ and $[\{\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}\text{SnMe}_2]_2(\mu\text{-OH})\text{T}^+$ [2.470(3) Å],¹⁸ probably due to the lower electron density at the tin atom.

The magnitude of the Sn–OH distances in **2** (Table 2) are comparable with values found for other organotin(IV) hydroxides containing $\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ groups on tin atom, *i.e.* 2.146(1) Å in $[\{\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_2\text{SnMe}_2]_2(\mu\text{-OH})\text{T}^+$,¹⁸ 2.094(3) and 2.106(3) Å in $[\{\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}\text{SnBu}\{\text{O}(\text{O})\text{CCF}_3\}]_2(\mu\text{-OH})_2$,¹⁰ 2.207(4) and 2.110(4) Å in *cyclo*- $\text{L}_5\text{Sn}_3(\mu\text{-OH})$ [L = $\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$],¹² or 2.036(3) in $[\{\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_2\text{Sn}(\text{OH})_2\text{O}]$.⁷

As a result of the intramolecular N→Sn coordination a five-membered SnC_3N ring is formed. This ring is folded along the $\text{Sn}(1)\cdots\text{C}_{\text{methylene}}$ axis [SnC_3/SnCN dihedral angle of $40.5(2)^\circ$ for **1** and $31.7(3)^\circ$ for **2**], with the nitrogen atom out from the best plane of the rest of the atoms by 0.731 Å for **1** and 0.579 Å for **2**,

respectively. The deviations of the bond angles at the metal atom from the ideal values, are mainly due to the constraints imposed by the small bite of the *C,N*-bidentate ligand (Tables 1 and 2) and crystal packing.

The folding of the five-membered C_3SnN chelate ring induces planar chirality (with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively; isomers given as S_N and R_N).¹⁹ In compound **1** the two chlorine atoms are non-equivalent (being placed in apical and equatorial positions, respectively, of the overall metal coordination core), while in compound **2** the octahedral core is unsymmetrical and therefore a second type of chirality is induced at the tin atom, described in term of C_{Sn} and A_{Sn} isomers.²⁰ Indeed, as seen for related organotin(IV) compounds,^{1-3,15,21,22} the crystals of the title compounds contain a 1:1 mixture of (S_N, A_{Sn}) and (R_N, C_{Sn}) isomers for **1**, while the dinuclear dication of **2** contains tin atoms with both (S_N, A_{Sn}) and (R_N, C_{Sn}) chirality, respectively.

In crystals of **1** pairs of (S_N, A_{Sn}) and (R_N, C_{Sn}) isomers are connected into dimer associations through intermolecular interactions between the axial Cl atom and an aromatic hydrogen atom [$Cl(1) \cdots H(5') = 2.874 \text{ \AA}$; symmetry equivalent position given by “prime”: ($I-x, -y, -z$)]. No further inter-dimer interactions are established (Fig. 2).

In solid state, the two Br^- anions are linked to one [$\{2-(Me_2NCH_2)C_6H_4\}SnMe(OH)(OH_2)\}_2^{2+}$ dication through two strong hydrogen bonds with the bridging OH group and the water molecule [$Br(1) \cdots H(20) = 2.404 \text{ \AA}$ and $Br(1) \cdots H(22') = 2.484 \text{ \AA}$; *c.f.* $\sum r_{vdw}(Br, H)$ ca. 3.15 \AA]. Furthermore, strong hydrogen bonds between the Br^- anions and water molecules from neighboring dication units [$Br(1) \cdots H(21'') = 2.470 \text{ \AA}$; symmetry equivalent position given by “second”: ($I+x, y, z$)] lead to the formation of a ribbon-like polymer along the *a* axis (Fig. 3).

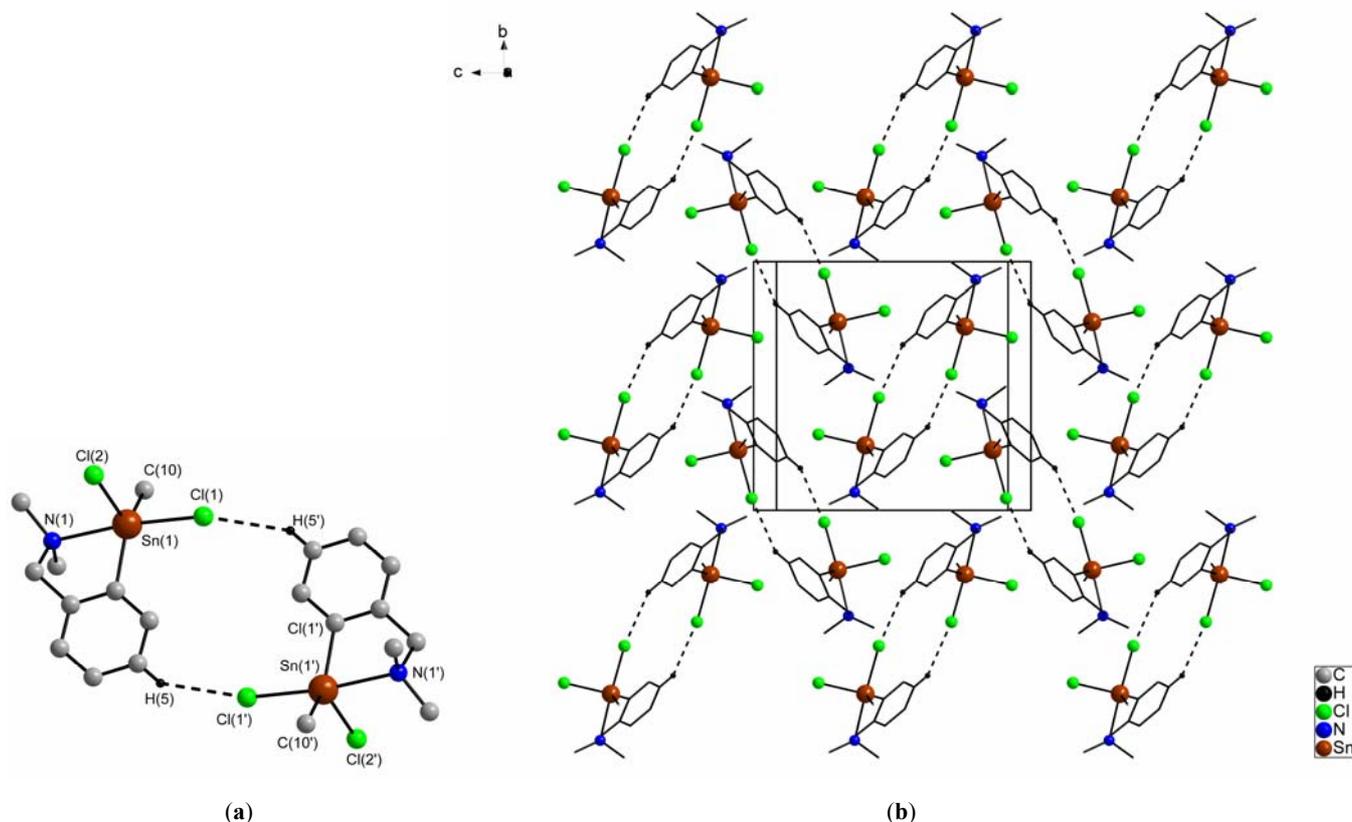


Fig. 2 – View of the (a) dimer, and (b) packing in the crystal of **1** based on intermolecular $Cl \cdots H$ interactions [only hydrogens involved in interactions are shown; symmetry equivalent positions given by “prime”: ($I-x, -y, -z$)].

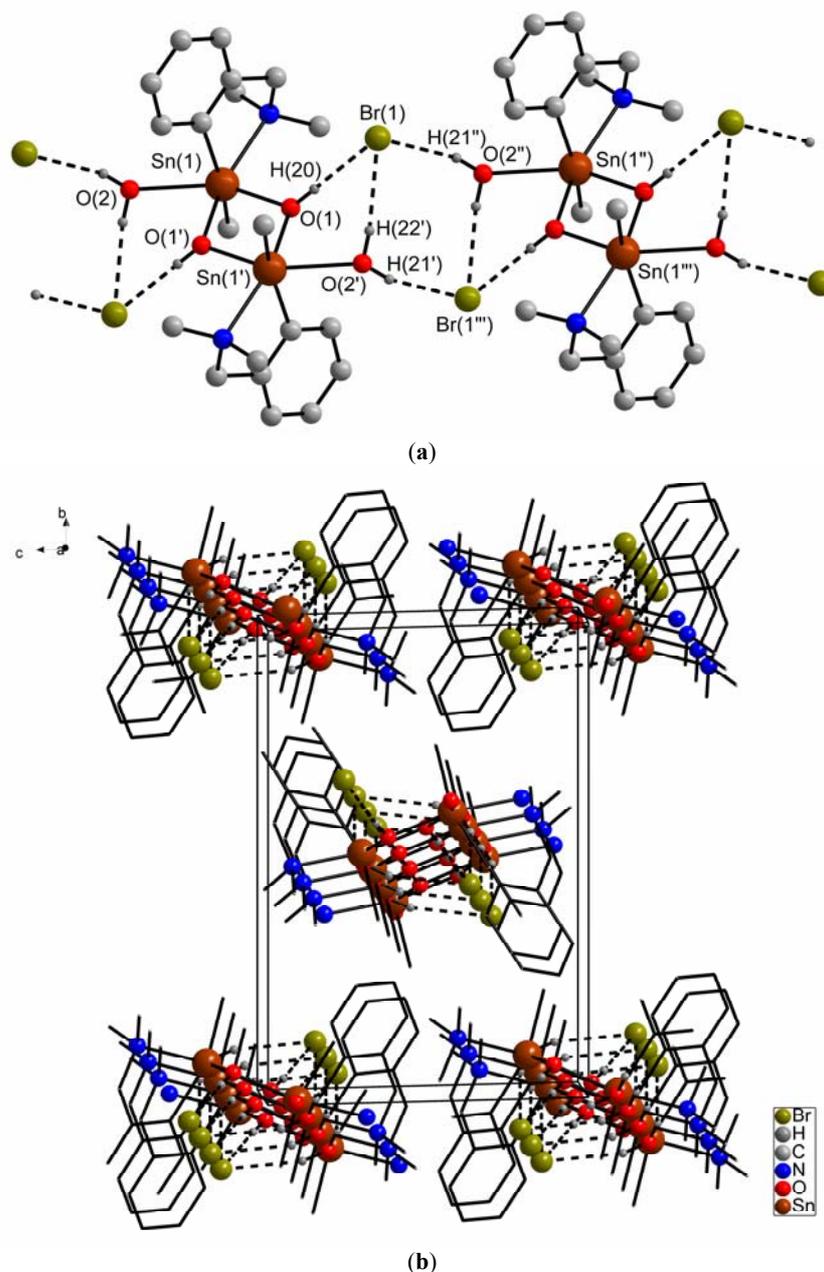


Fig. 3 – View of the (a) ribbon-like supramolecular arrangement, and (b) packing in the crystal of **2** based on intermolecular Br \cdots H interactions [only hydrogens involved in interactions are shown; symmetry equivalent positions given by “prime”: ($I-x$, $-y$, $-z$); “second”: ($I+x$, y , z), and “third”: ($2-x$, $-y$, $-z$)].

EXPERIMENTAL

Most of the syntheses were carried out in argon atmosphere using Schlenk techniques. Solvents were dried and freshly distilled prior to use. Multinuclear NMR spectra (^1H , ^{13}C , ^{119}Sn and 2D) were recorded at room temperature on a Bruker Avance 300 (**1**) and a Bruker Avance III 400 (**2**) instrument. The ^1H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. CDCl_3 : ^1H 7.26 ppm, D_2O : 4.79 ppm). The ^{13}C chemical shifts are reported in δ units (ppm) relative to the peak of the solvent (ref. CDCl_3 : ^{13}C 77.17 ppm). For the ^{119}Sn NMR spectra the chemical shifts are reported in ppm relative to SnMe_4 . The NMR spectra were processed using

the *MestReNova* software.²³ Mass spectra were recorded with an Applied Biosystems (Type Mariner) (ESI/APCI-TOF) instrument. Melting points were measured with an Electrothermal 9200 apparatus and are not corrected. Starting materials such as MeSnCl_3 , *N,N*-dimethylbenzylamine and *n*-butyllithium were commercially available. $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Li}$ was prepared according to the literature method.²⁴

Synthesis of $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{SnMeCl}_2$ (**1**)

A suspension of $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Li}$ (2.94 g, 20.83 mmol) in 50 mL anhydrous toluene was added dropwise under stirring to a cooled ($-78\text{ }^\circ\text{C}$) solution of MeSnCl_3 (5 g, 20.82 mmol) in 100 mL of dry toluene. The reaction mixture was stirred for 1 h

at $-78\text{ }^{\circ}\text{C}$ and then allowed to reach the room temperature overnight. The reaction mixture was filtered and the obtained solution was stored into the freezer. Colorless crystals were obtained (5.1 g, 72%), mp 125–127 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz, 20 $^{\circ}\text{C}$): 1.23 (s, 3H, SnCH_3 , $^2J_{117/119\text{SnH}}$ 77.5 / 81.1 Hz), 2.41 (s, 6H, NCH_3), 3.74 (s, 2H, CH_2), 7.20 (m, 1H, H -3), 7.41 (m, 2H, H -4, H -5), 8.14 (m, 1H, H -6, $^3J_{\text{SnH}}$ 91.8 Hz) ppm. ^{13}C NMR (CDCl_3 , 75.4 MHz, 20 $^{\circ}\text{C}$): 7.87 (SnCH_3 , $^1J_{117/119\text{SnC}}$ 658.6 / 689.7 Hz), 44.96 (NCH_3 , $^5J_{\text{SnC}}$ 8.5 Hz), 63.17 (CH_2 , $^3J_{\text{SnC}}$ 39.4 Hz), 127.49 (C-3, $^3J_{117/119\text{SnC}}$ 76.2 / 79.2 Hz), 128.77 (C-5, $^3J_{117/119\text{SnC}}$ 91.2 / 94.5 Hz), 131.28 (C-4, $^4J_{\text{SnC}}$ 16.0 Hz), 137.15 (C-6, $^2J_{117/119\text{SnC}}$ 65.0 / 67.7 Hz), 138.37 (C-1), 141.08 (C-2, $^2J_{\text{SnC}}$ 51.2 Hz) ppm. ^{119}Sn NMR (CDCl_3 , 111.9 MHz, 20 $^{\circ}\text{C}$): -97.34 ppm. MS (APCI $^+$), m/z (%): 339.39 (0.52) $[\text{M}+\text{H}]^+$, 303.99 (100) $[\text{RSnMeCl}]^+$.

$[\{2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\}\text{SnMe(OH)(OH)}_2\text{]}^{2+}\cdot 2\text{Br}^-$ (**2**)

A solution of 2- $[(\text{CH}_2\text{O})_2\text{CH}]\text{C}_6\text{H}_4\text{Br}$ (1.51 g, 6.59 mmol) in THF (50 mL) was added dropwise, under stirring, to magnesium filings (0.17 g, 6.99 mmol, 6% excess) activated with 1,2-dibromoethane (0.3 mL). The reaction mixture was stirred for 2 h under reflux and then it was cooled to room temperature and the unreacted Mg was separated. The Grignard solution was added dropwise, under stirring, to a

solution of $2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{[SnMeCl}_2$ (2.14 g, 6.31 mmol) in THF (30 mL) at $-78\text{ }^{\circ}\text{C}$, the reaction mixture was stirred at this temperature for 30 min, and then for 12 h at room temperature. The solvent was removed under vacuum and the oily residue was dissolved in CH_2Cl_2 . The solution was filtered and the solvent was removed under vacuum. The obtained white solid was insoluble in common solvents and just slightly soluble in acetone and water. Repeated extraction with acetone resulted in isolation of **2** as colorless crystals (0.5 g, 21% based on **1**), mp 128–130 $^{\circ}\text{C}$. ^1H NMR (D_2O , 400 MHz, 20 $^{\circ}\text{C}$): 0.98 ppm (s, 6H SnCH_3 , $^2J_{\text{SnH}}$ 91.7 Hz), 2.48 (s, 12H, NCH_3), 3.87 (s, 4H, CH_2), 7.30 (m, 4H, H -3, H -4), 7.44 (t, 2H, H -5, $^3J_{\text{HH}}$ 7.3 Hz), 7.65 (d, 2H, H -6, $^3J_{\text{HH}}$ 7.1 Hz, $^3J_{\text{SnH}}$ 91.7 Hz). MS (ESI $^+$), m/z (%): 347.94 (100%) $[\text{2-(Me}_2\text{N)C}_6\text{H}_4\text{SnMeBr}]^+$, 286.02 (49%) $[\text{2-(Me}_2\text{N)C}_6\text{H}_4\text{SnMe(OH)}]^+$.

Crystal structure determination

Crystallographic data for the structural analysis of compounds **1** and **2** have been collected on a Bruker SMART APEX system (Babes-Bolyai University, Cluj-Napoca) using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$). Cell constants are given in Table 3, along with other experimental parameters and relevant information pertaining to structure solution and refinement.

Table 3

Crystallographic data for $2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{[SnMeCl}_2$ (**1**) and $[\{2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\}\text{SnMe(OH)(OH)}_2\text{]}^{2+}\cdot 2\text{Br}^-$ (**2**)

Compound	1	2
Molecular formula	$\text{C}_{10}\text{H}_{15}\text{NSnCl}_2$	$\text{C}_{20}\text{H}_{36}\text{Br}_2\text{N}_2\text{O}_4\text{Sn}_2$
M	338.82	765.73
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Temperature (K)	297(2)	297(2)
$a/\text{\AA}$	9.123(5)	9.3009(13)
$b/\text{\AA}$	12.165(6)	14.614(2)
$c/\text{\AA}$	12.520(6)	10.7840(15)
$\alpha/^\circ$	90	90
$\beta/^\circ$	106.320(8)	113.522(2)
$\gamma/^\circ$	90	90
$V/\text{\AA}^3$	1333.5(11)	1344.0(3)
Z	4	2
$D_{\text{calc}}/\text{gcm}^{-3}$	1.688	1.892
$F(000)$	664	744
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	2.283	4.857
Crystal size (mm^3)	0.26 x 0.23 x 0.21	0.28 x 0.23 x 0.20
θ range for data collection ($^\circ$)	2.38 to 25.01	2.45 to 25.00
Reflections collected	9244	12714
Independent reflections	2344 [$R_{\text{int}} = 0.0394$]	2363 [$R_{\text{int}} = 0.0463$]
Absorption correction	Multi-Scan ²⁵	Multi-Scan ²⁵
Maximum and minimum transmissions	0.6457 and 0.5883	0.4433 and 0.3433
Data / restraints / parameters	2344 / 0 / 130	2363 / 3 / 151
Goodness-of-fit on F^2	1.136	1.029
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0363$ $wR_2 = 0.0822$	$R_1 = 0.0308$ $wR_2 = 0.0705$
R indices (all data) ^a	$R_1 = 0.0428$ $wR_2 = 0.0851$	$R_1 = 0.0380$ $wR_2 = 0.0728$
Largest difference peak and hole (e \AA^{-3})	0.314 and -1.001	0.735 and -0.896

^a Definition of the R values: $R_1 = (\sum |F_o| - |F_c|) / \sum |F_o|$; $wR_2 = \{[w\sum(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

The structures were refined with anisotropic thermal parameters. All C-bound H atoms were placed in calculated positions (C–H = 0.93–0.97 Å) and treated using a riding model with $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for the rest. The methyl group was allowed to rotate, but not to tip, to best fit the electron density. The hydrogen atom from the OH and water in compound **2** was found in the difference map and refined with a restrained distance of 0.870(19) Å, 0.865(19) Å and 0.875(19) Å, respectively. For structure solving and refinement the software package SHELX-97 was used.²⁶ The drawings were created with the ORTEP-3²⁷ and Diamond programs.²⁸

CONCLUSIONS

A new diorganotin(IV) derivative containing one 2-(Me₂NCH₂)C₆H₄ pendant arm ligand was prepared and characterized both in solution and in solid state. The tin atom is pentacoordinated with highly distorted trigonal bipyramidal geometry. Single-crystal X-ray diffraction reveals the formation of dimers in crystal through hydrogen bond-type intermolecular interactions. Hydrolysis of **1** resulted in an ionic compound, [$\{2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\}\text{SnMe(OH)(OH}_2\text{)}_2\}^{2+} \cdot 2\text{Br}^-$ (**2**), featuring a Sn₂O₂ planar core with hexacoordinated metal centers. Strong intra- and intermolecular hydrogen bond-type interactions link the anions and the dications in a ribbon-like supramolecular arrangement.

Supplementary material

CCDC-1019241 (**1**) and -1019240 (**2**) contain the supplementary crystallographic data for this paper. These data have been deposited with the Cambridge Crystallographic Data Centre. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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