

Rapid Communication

Uwe Böhme* and Gisela Weling

Synthesis and crystal structure of an ionic phenyltin(IV) complex of *N*-salicylidene-valine

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Abstract: Triethylammonium dichloro[*N*-[(2-oxyphenyl)methylidene]valinato]-phenyl-tin(IV) was prepared and characterized by spectroscopic methods and single crystal X-ray crystallography. The compound consists of a triethylammonium cation and a tin complex as anion. The tin complex is composed of a tridentate *O,N,O*-Schiff base ligand coordinated to a SnCl_2Ph unit. The tin atom is in distorted octahedral coordination geometry. NMR spectroscopic studies have shown that the unusual hexa-coordinated tin complex was formed as a kinetically controlled product. Storage of the solid product for several years led to a transformation into a thermodynamically stable penta-coordinated tin complex.

Keywords: organotin, alkyltin complex, *N*-salicylidene-valine, crystal structure

Organotin complexes of Schiff bases are a fast-developing field of research due to their various possible applications which were covered in a review until 2011 (Nath and Saini, 2011). These complexes can exhibit anti-tumor, anti-microbial, anti-nematicidal, anti-insecticidal, anti-inflammatory properties (Amin et al., 2019; Bhatra et al., 2016; Kobakhidze et al., 2010; Shah et al., 2020; Sharma et al., 2016; Yao et al., 2017; Wang et al., 2022), and might be useful as highly selective sensor molecules for hydrogen sulfide (Basu Baul et al., 2020). We are interested in chiral complexes of group 14 elements. For that purpose, we have explored several chiral ligand types (Böhme et al., 2006; Böhme and Fels, 2013; Schwarzer et al., 2015, 2018; Warncke et al., 2012, 2016).

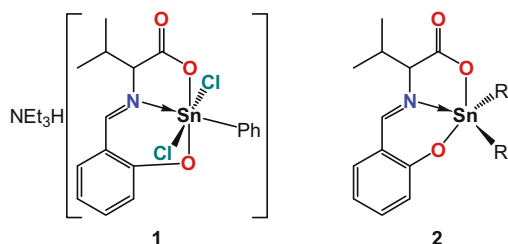
The present work describes the synthesis and crystal structure of the title compound triethylammonium dichloro[*N*-[(2-oxyphenyl)methylidene]valinato]-phenyl-tin(IV) (**1** in Scheme 1). Several related dialkyltin complexes of *N*-salicylidene-valine have been already prepared and were structurally characterized (**2** in Scheme 1). These were derivatives with $\text{R} = \text{Me}$ (Tian et al., 2020), Ph (Beltran et al., 2003; Yin and Wang, 2004a), *n*-Bu (Beltran et al., 2003; Smith et al., 1992; Yin et al., 2004b), 2-fluorobenzyl (Ding et al., 2007), cyclohexyl (Shi et al., 2016), and *tert*-butyl (Ding et al., 2006). These contain the same chelate ligand, but different substituents of tin. None of these complexes crystallize as anion like the title compound.

Compound **1** crystallizes in the monoclinic space group *Cc* with cation and anion in the asymmetric unit. The space group *Cc* (containing a glide plane) indicates that both enantiomers of the title compound are present in the crystal (Suh et al., 1997). The value of optical rotation of the batch product was determined to be $[\alpha]_D^{20} = 0^\circ$, which confirms the presence of the racemate. Initially the *S*-isomer of the ligand molecule, (*S*)-*N*-[(2-hydroxyphenyl)methylidene]valine-methylester, was used for the synthesis. Apparently, a racemization of the ligand system took place during the formation of the complex. This is associated with cleavage of the carboxylic acid ester, as has already been observed in other cases (Belokon et al., 1981; Warncke et al., 2012). Another special feature of the title compound is its crystallization as an ionic compound composed of a triethylammonium cation (NEt_3H^+) and an organostannate anion (tin complex). This leads to a six-fold coordination of the tin complex (Figure 1). The tin atom is in a distorted octahedral coordination geometry (see bond angles in Table 1).

The tridentate Schiff-base ligand is coordinated meridionally to the central atom. The chlorine atoms are in *trans* position to each other. The phenyl group C13 to C18 is in *trans* position to the Schiff-base nitrogen atom N1. The O1-Sn1-O3 angle of $161.3 (1)^\circ$ deviates strongly from 180° . The Cl1-Sn1-Cl2 and C13-Sn1-N1 angles are $170.47 (5)^\circ$ and $173.2 (2)^\circ$, respectively. The interatomic Sn-O and Sn-N distances are similar as in comparable hexa-coordinated tin complexes (Paul et al., 2014; Schwarzer

* Corresponding author: Uwe Böhme, Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Str. 29, 09599 Freiberg, Germany, e-mail: uwe.boehme@chemie.tu-freiberg.de

Gisela Weling: Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Str. 29, 09599 Freiberg, Germany



Scheme 1: Title compound **1** (left) and dialkyltin complexes of *N*-salicylidene-valine (**2**, right).

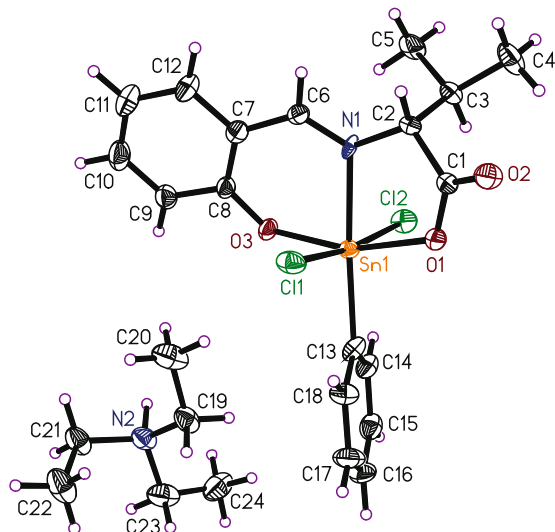


Figure 1: Diagram of the title molecule showing the atom-labeling scheme. Atomic displacement parameters are at the 50% probability level.

Table 1: Selected bond lengths (Å) and angles (°) for compound **1**

Parameter	Value	Parameter	Value
Sn1–O3	2.050 (4)	Sn1–N1	2.224 (5)
Sn1–O1	2.134 (4)	Sn1–Cl2	2.4620 (13)
Sn1–Cl3	2.178 (6)	Sn1–Cl1	2.5132 (16)
O3–Sn1–O1	161.28 (13)	C13–Sn1–Cl2	95.48 (16)
O3–Sn1–Cl3	100.49 (19)	N1–Sn1–Cl2	87.88 (13)
O1–Sn1–Cl3	98.11 (18)	O3–Sn1–Cl1	91.39 (12)
O3–Sn1–N1	85.42 (15)	O1–Sn1–Cl1	85.33 (12)
O1–Sn1–N1	75.89 (15)	C13–Sn1–Cl1	93.48 (17)
C13–Sn1–N1	173.2 (2)	N1–Sn1–Cl1	82.88 (11)
O3–Sn1–Cl2	90.17 (12)	Cl2–Sn1–Cl1	170.47 (5)
O1–Sn1–Cl2	90.19 (12)		

et al. 2018). The Sn–Cl1 and Sn–Cl2 distances are 2.513 (2) and 2.462 (1) Å, respectively. These are longer than the sum of the covalent radii of Sn and Cl with 2.39 Å (Pauling, 1962). However, anionic tin complexes with the same coordination geometry at tin containing a tridentate O,N,O-ligand, two

chlorine atoms, and one alkyl or aryl substituent show similar Sn–Cl distances. The Sn–Cl bond lengths in such complexes range from 2.429 to 2.600 Å (Böhme and Dittrich, 2020; Hong et al., 2010; Jimenez-Perez et al., 2000). The elongation of the Sn–Cl distances is caused by the six-fold coordination.

A bifurcated intermolecular N–H···O interaction is observed at N2–H2 with O1 and O2 (Table 2 and Figure 2). Furthermore, there are short contacts between the chlorine atom Cl1 and C–H bonds from the neighboring molecules (C2–H2···Cl1 and C6–H6···Cl1).

A ^{119}Sn NMR spectrum at room temperature of complex **1** in CDCl_3 solution showed two resonances at δ –337.1 (35.6%) and –507.2 ppm (64.4%), respectively,

Table 2: H-bonding geometry parameters (Å and °) for compound **1**

D–H···A	D–H	H···A	D···A	D–H···A
N2–H2A···O1 ⁱ	1.05(6)	2.55(6)	3.326(6)	130(5)
N2–H2A···O2 ⁱ	1.05(6)	1.80(6)	2.840(6)	170(5)
C2–H2···Cl1 ⁱⁱ	1.00	2.80	3.700(5)	150
C6–H6···Cl1 ⁱⁱ	0.95	2.81	3.713(5)	160

Symmetry codes: (i) $x + 1/2, -y + 1/2, z + 1/2$; (ii) $x, -y, z - 1/2$.

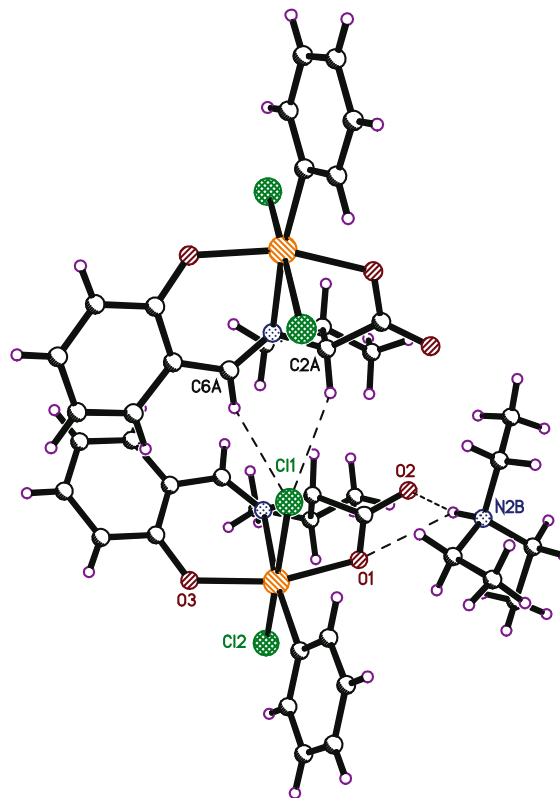
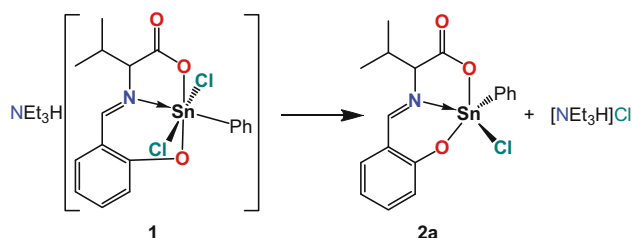


Figure 2: Relevant intermolecular interactions.

which are typical for penta- and hexa-coordinated mono-organotin compounds (Schwarzer et al., 2018). Both ^1H and ^{13}C NMR spectra of the same solution revealed two sets of signals (NMR spectra are presented in Appendix). These data suggest that complex **1** might be involved in an equilibrium. However, this is not the case. The product was stored as a solid for 6 years. A renewed examination of a solution of this solid in chloroform showed that the hexa-coordinated compound (**1**) was only present in the sample in a proportion of approx. 7%, whereas 93% of the sample was present as penta-coordinated compound (**2a**) (Scheme 2).



Scheme 2: Transformation of the hexa-coordinated into the penta-coordinated tin complex.

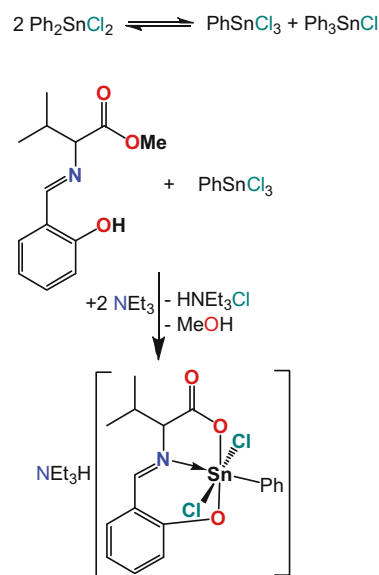
Triethylammonium chloride in chloroform was added to this NMR sample. However, this did not change the ratio of the two compounds. After 68 h, the two compounds were still present in the same ratio (see Appendix). From this we conclude with caution that initially the hexa-coordinated compound crystallized out as a kinetically controlled product. During the long storage time, this transformed into the penta-coordinated compound.

In summary, an unusual ionic tin complex was obtained. The crystal structure analysis proved the formation of the hexa-coordinated complex. Storage of the solid product for several years led to a transformation into the thermodynamically stable penta-coordinated complex. This also explains why such an unusual ionic tin complex has not been described in the literature so far.

Experimental

Synthesis of **1**

The synthesis of the title compound is shown in Scheme 3. Dichlorodiphenylstannane was used as a starting material for the synthesis. Surprisingly, the crystal structure proved the formation of a product containing just one phenyl group at the tin atom. Therefore, a redistribution reaction



Scheme 3: Reaction scheme for the synthesis of the title compound.

as shown in Scheme 3 must be assumed taking place during the reaction. This redistribution reaction of organic groups is commonly known in tin(IV) compounds and is used for the preparation of different organotin halides in industrial scale (Davies and Smith, 1982; Schwarzer et al., 2013). The used starting material was checked with ^{119}Sn NMR. It contains only Ph_2SnCl_2 with ^{119}Sn NMR shift of $\delta = -26.4$ ppm (Casas et al., 1996).

(S)-N-[(2-hydroxyphen-1-yl)methylidene]valine-methylester (1.0 g, 4.2 mmol) was dissolved in 40 mL tetrahydrofuran and triethylamine (0.86 g, 8.4 mmol) was added via syringe. The yellow solution was then cooled down to 273 K. Dichlorodiphenylstannane (1.46 g, 4.2 mmol) was added to the solution. Immediately, a white precipitate of triethylamine hydrochloride was formed. After 30 min the mixture was warmed up to room temperature and stirred for 72 h at room temperature. Triethylamine hydrochloride was collected via suction filtration, washed with 10 mL tetrahydrofuran, and the solvent was removed completely under reduced pressure. The residue was dissolved in chloroform. For crystallization, *n*-hexane was added, the crystals collected via suction filtration and dried *in vacuo*.

Yield: 0.9 g (37%); m.p. 475 K. NMR (CDCl_3 , TMS, δ , ppm); ^{119}Sn : -337.1 (35.6%, penta-coordinated Sn), -507.2 (64.4%, hexa-coordinated Sn).

^1H : 0.77 (d, $\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}} = 5$ Hz), 0.86 (d, $\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}} = 5$ Hz), 1.07 (t, CH_3 , Et_3NH^+ , $^3J_{\text{HH}} = 7.5$ Hz), 2.17 (m, $\text{CH}(\text{CH}_3)_2$), 2.81 (q, CH_2 , Et_3NH^+ , $^3J_{\text{HH}} = 7.5$ Hz), 3.66 (d, $\text{CH}-\text{COO}$, $^3J_{\text{HH}} = 5$ Hz), 3.86 (d, CHCOO , $^3J_{\text{HH}} = 5$ Hz), 6.66–8.0 (mm, H_{Ph}), 8.1 (s, $\text{HC}=\text{N}$), 8.23 (s, $\text{HC}=\text{N}$).

^{13}C : 7.6 (CH_3 , Et_3NH^+), 17.9, 19.7 (2CH_3), 32.2, 33.9 ($\text{CH}(\text{CH}_3)_2$), 45.0 (CH_2 , Et_3NH^+), 72.2, 73.0 ($\text{CH}-\text{COO}$), 116.3,

Table 3: Crystal data and structure refinement of 1

Parameter	Value
Chemical formula	C ₁₈ H ₁₈ Cl ₂ NO ₃ Sn·C ₆ H ₁₆ N
Formula weight	588.12
Crystal dimensions (mm)	0.16 × 0.22 × 0.45
Crystal system	Monoclinic
Space group	Cc
<i>a</i> (Å)	16.8326 (6)
<i>b</i> (Å)	16.2397 (8)
<i>c</i> (Å)	9.7225 (3)
β (°)	97.651 (3)
<i>V</i> (Å ³)	2,634.05 (18)
<i>Z</i>	4
<i>D</i> _{calc} (g·cm ^{−3})	1.483
μ (mm ^{−1})	1.20
<i>F</i> (000)	1,200
<i>T</i> (K)	153
λ (Å)	Mo K α (0.71073)
θ range (°)	2.9–28.0
Measured reflections	29,165
Unique reflections	6,077
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	5,787
No. of parameters refined	297
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.028, 0.0591
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.032, 0.0618
Goodness-of-fit on <i>F</i> ²	1.27
Largest peak and hole (e·Å ^{−3})	2.38–0.84

116.6, 117.0, 121.9, 122.3, 127.9, 128.2, 129.6, 129.8, 134.3, 134.5, 135.0, 135.2, 135.5, 135.6, 137.1 (C_{Ph}), 168.5, 166.9 (C=N), 176.1, 172.0 (COO).

IR (KBr pellets, cm^{−1}): 1,670 ν (C(O)O)asym, 1,614 ν (C=N), 1,538 ν (C(O)O)sym. UV–Vis (*c* = 1.72 mmol·L^{−1} in CHCl₃): $\lambda_{\max}$ (ϵ , L·mol^{−1}·cm^{−1}) = 379 (5,116), 285 (13,799) nm, $[\alpha]_{\text{D}}^{20}$ = 0°.

X-ray crystallography

Single-crystal X-ray diffraction data was obtained using a STOE IPDS 2T diffractometer equipped with an image plate detector with graphite monochromated MoK α radiation (λ = 0.71073 Å). Software for data collection: X-Area, cell refinement: X-Area, and data reduction: X-RED (Stoe, 2009). The structure was solved by direct methods using SHELXT (Sheldrick, 2015a) and refined by full matrix least squares with SHELXL2018 (Sheldrick, 2015b), refining on *F*². Molecule graphics was generated with ORTEP-3 (Farrugia, 1997). Hydrogen atoms bonded to C were positioned geometrically and allowed to ride on their parent atoms. The hydrogen atom at N2 was localized from residual electron density maps and was freely refined. The

absolute structure was determined as absolute structure parameter x = −0.047(6), also denoted as Flack-parameter (Parsons et al., 2013). Detailed crystal data and structure refinement are listed in Table 3. Crystallographic data has been deposited with the Cambridge Crystallographic Centre as supplementary publication number CCDC-2234038.

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Author contributions: Uwe Böhme: writing – original draft, writing – review and editing, formal analysis, visualization, project administration, investigation, and data curation; Gisela Weling: methodology, formal analysis, investigation, and data curation.

Conflict of interest: The authors state no conflict of interest.

Data availability statement: NMR spectra are available in Appendix.

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Appendix

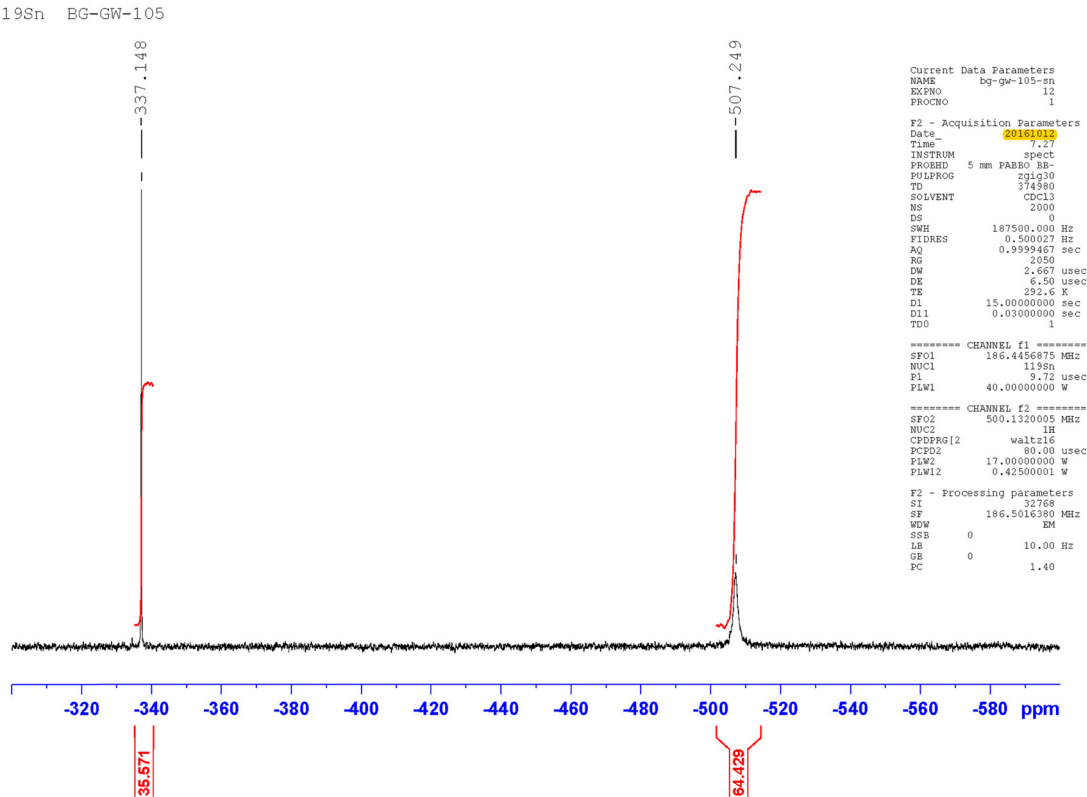


Figure A1: ¹¹⁹Sn NMR spectrum – initial sample after synthesis (2016).

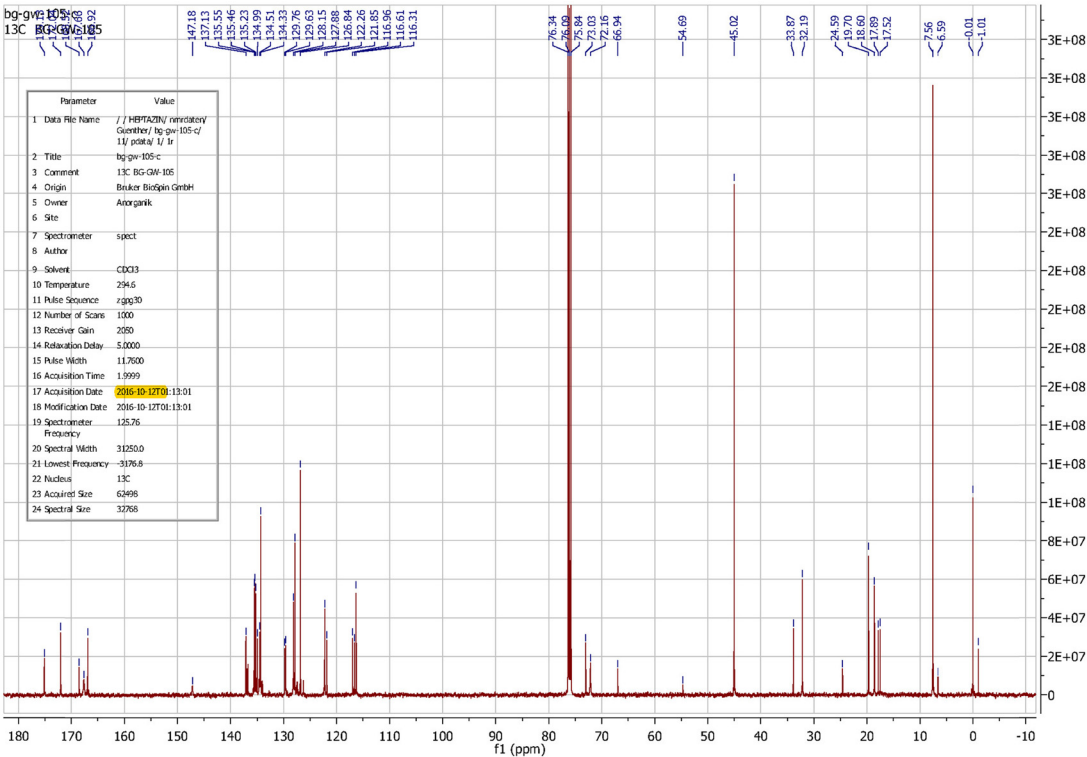
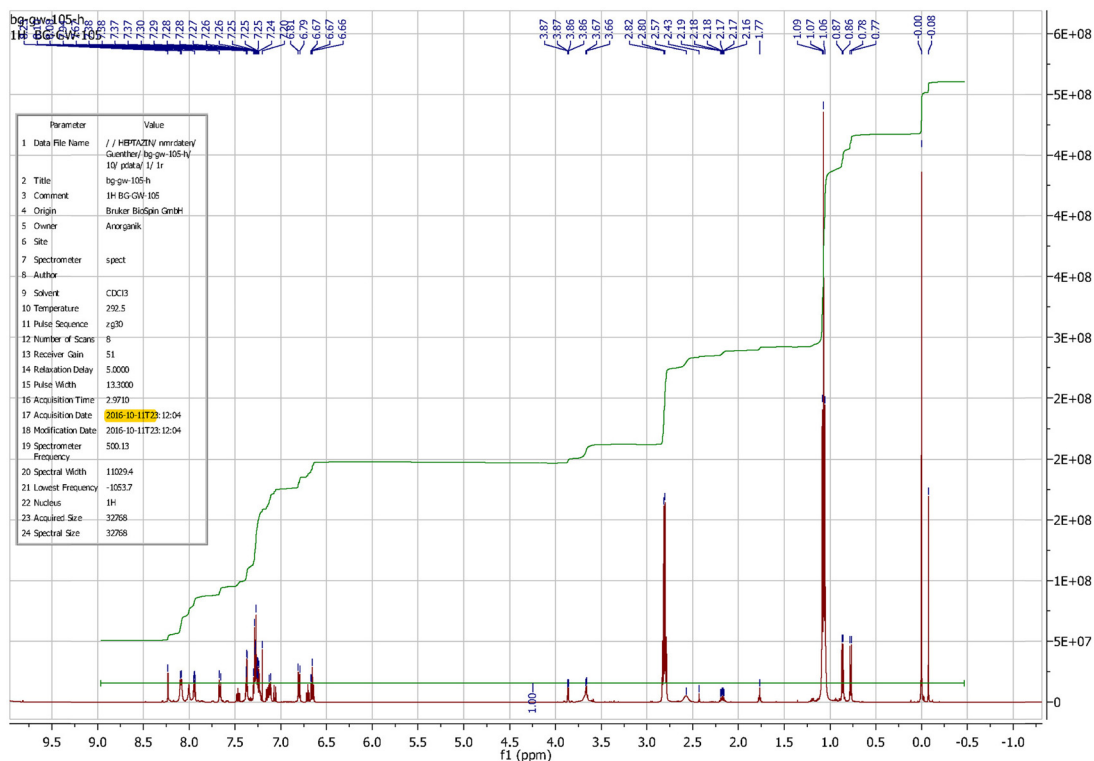
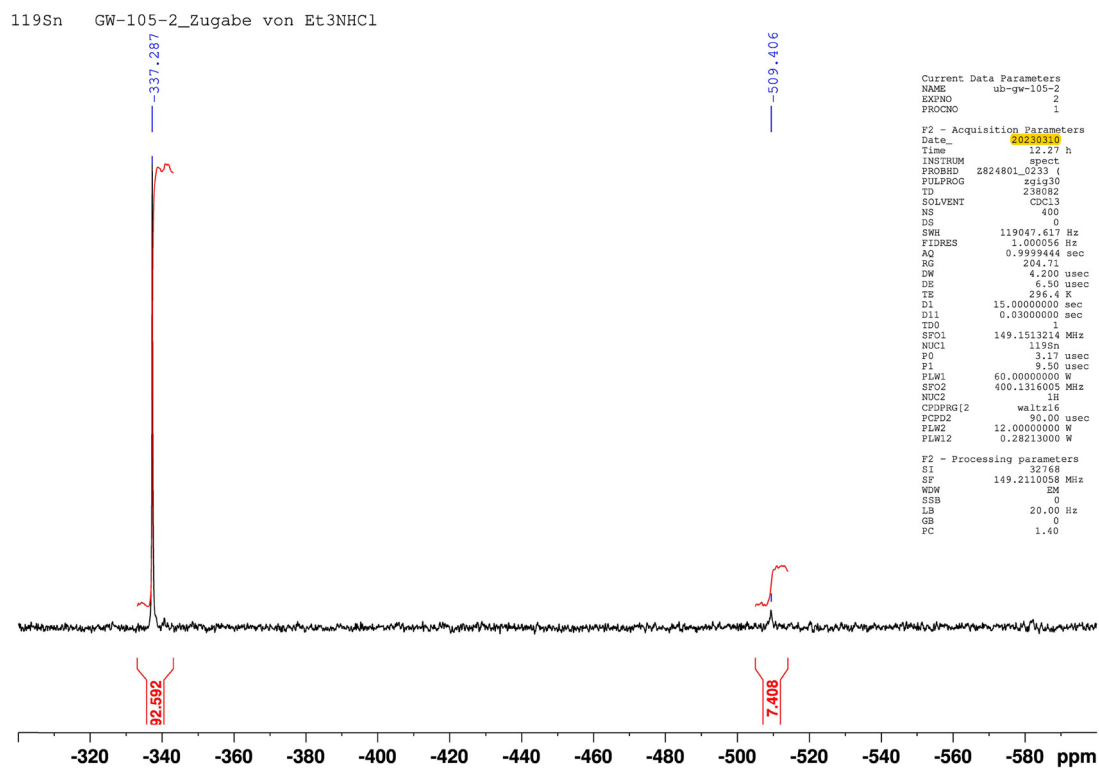


Figure A2: ¹³C NMR spectrum – initial sample after synthesis (2016).

Figure A3: ^1H NMR spectrum – initial sample after synthesis (2016).Figure A4: ^{119}Sn NMR spectrum – after 6 years (2023).

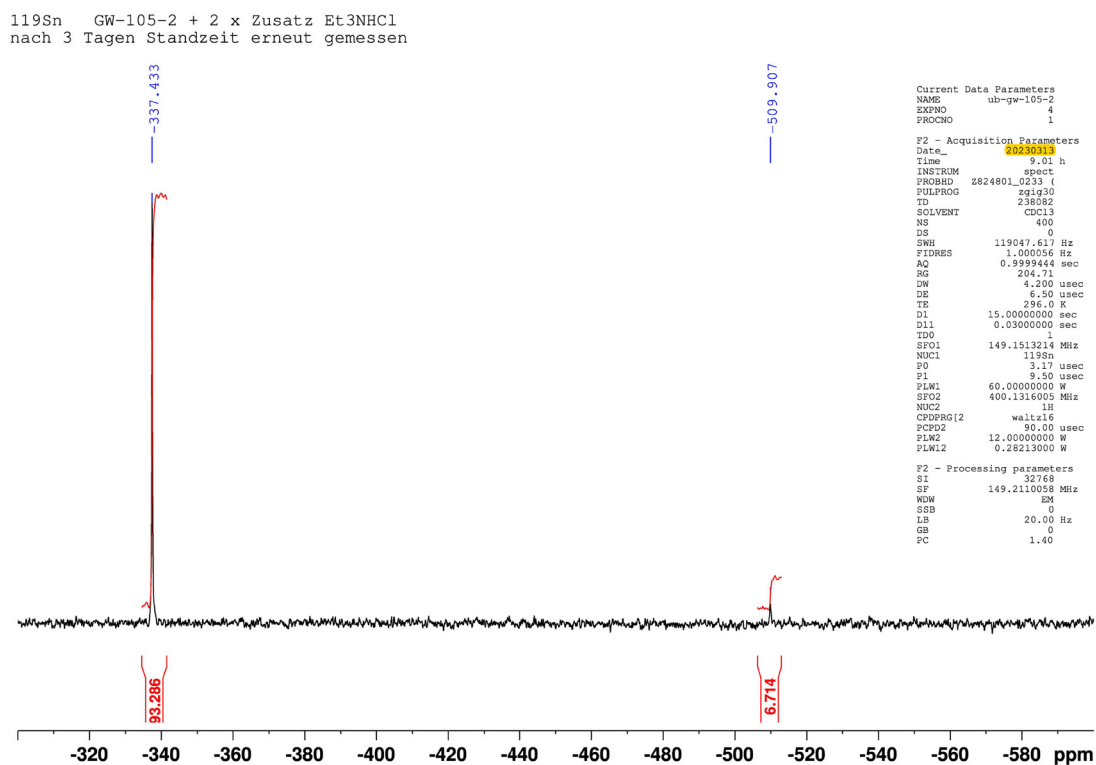


Figure A5: ^{119}Sn NMR spectrum – after 6 years (2023) with added HNEt_3Cl and standing for 68 h.