

Synthesis and Spectroscopic Characterization of Organotin(IV) Complexes Containing Schiff Bases

Avadhesh Pratap Singh and Raj Kumar Dubey

Synthetic Inorg. and Metallo-organic Research Laboratory

Department of Chemistry, University of Allahabad

Allahabad-211002, India

Email: rajalkoxy@yahoo.com

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Abstract: Reactions of $n\text{-Bu}_2\text{SnCl}_2$ with sodium salts of Schiff bases in different molar ratio in tetrahydrofuran-benzene solution afforded complexes of the types $[(n\text{-Bu})_2\text{Sn}(\text{sb})\text{Cl}]$ and $[(n\text{-Bu})_2\text{Sn}(\text{sb})_2]$, respectively, [where sb= Schiff bases: salicylidene-1-aminobenzene (sabH), salicylidene-3-nitro-1-aminobenzene (snabH), and salicylidene-2-amino-4-picoline(sapicH)]. All these coloured solid complexes are soluble in common organic solvents and were characterized by elemental (C, H, N, Cl and Sn) analysis and spectral [IR, (^1H , ^{13}C and ^{119}Sn) NMR] and mass studies. On the basis of spectroscopic studies plausible structures have been proposed tentatively.

Keywords: Schiff bases; organotin(IV) complexes; ^{119}Sn NMR; antimicrobial activity.

1. Introduction

The studies of organotin(IV) complexes have gained considerable interest due to their various biological and industrial applications^{1, 2}. The organotin(IV) complexes have been extensively studied because of its versatile chemistry and its potential as biological activity. The chemistry of organotin(IV) complexes³ of Schiff bases has been extensively studied due to its thermal stability, structural variety, and important antitumor, antimicrobial, antifungal, antibacterial, antioxidant or anti-inflammatory properties. However, the mode of biological activities of the organotin(IV) compounds is not completely known. The structure of the organotin(IV) complexes, its coordination number, the extent of alkylation and the nature of the organic groups attached to the tin atom are the main factors deciding the biological activities of the tin complexes⁴⁻⁶. As part of our investigations on organotin(IV) complexes containing, N-arylsalicylaldiminate⁷⁻¹¹ Schiff bases, we report in this paper synthesis and physicochemical

characterization studies of di-*n*-butyltin(IV) complexes derived from Schiff bases such as sab \mathbf{H} , snab \mathbf{H} and sapic \mathbf{H} .

2. Experimental

2.1. Materials and Physical Measurements

All the chemicals used throughout the present course of experimental work were of G.R/Analar grade. Di-*n*-butyltin(IV)dichloride (Fluka), *m*-nitroaniline, aniline, Salicyldehyde (Loba), 2-amino-4-picoline (Merck) were used without further purification. Benzene (AR Merck), tetrahydrofuran (AR Merck), *n*-hexane (AR Merck) were dried according to standard literature procedures¹². Elemental analyses were performed with a Haraeus Carlo Erba 1108 elemental analyzer. Chlorine was estimated volumetrically by using Volhard method¹³. Tin was estimated gravimetrically as SnO₂. Infrared spectra were recorded on a Perkin-Elmer 100 FT-IR spectrometer in the range 4000-400 cm⁻¹. ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on Bruker DRX-300 spectrometer in CDCl₃ / DMSO-d₆ solvent and chemical shifts were given in ppm relative to tetramethyl silane for carbon, hydrogen and tetramethyltin for tin. A mass spectrum was recorded on TOF MS MS spectrometer.

2.2. Synthesis of Schiff bases

The Schiff bases were prepared according to the method described in some of our earlier publications⁹.

2.3. Synthesis of complexes

Similar procedure was used for the synthesis of the complexes (**1-6**), therefore, general synthetic details are given below: To a benzene (~ 20 ml) solution of *n*-Bu₂SnCl₂, sodium salt of Schiff base [prepared by the reaction of equimolar amounts of sodium metal and a Schiff base (**HL**) in tetrahydrofuran (~ 30 ml)] in appropriate (1:1 and 1:2) molar ratios was added dropwise with constant stirring. The reaction mixture was refluxed for ~ 5 h. The precipitated NaCl was removed by filtration. The solvent was removed by distillation. The solid products were dried under reduced pressure and recrystallized from a mixture of THF/*n*-hexane (20:80) at -20°C.

[(*n*-Bu)₂Sn(sab)Cl](**1**): Yield: 78%, yellow solid, m.p. 78-79 °C. Anal. Found: C, 51.55; H, 5.82; N, 5.98; Cl, 7.52; Sn, 25.36% Calc. For C₂₁H₂₈ClNOSn: C, 54.29; H, 6.07; Cl, 7.63; N, 3.01; Sn, 25.55. ¹H NMR (CDCl₃) (ppm): 8.61 (1H, s, CH=N), 6.35-7.84 (m, 8H, Ar-H) 1.25-1.68 (12H, m, Sn-(CH₂)₃-), 0.86-0.81 (6H, m, CH₃). ¹³C NMR (CDCl₃) (ppm):

163.62 (s, CO), 160.19 (s, CN), 146.64-118.64, (s, Ar-C, Py-C), 26.73, 20.92, 20.35, 12.86 (s, Sn-Buⁿ). ¹¹⁹Sn NMR (DMSO-d₆) (ppm): -148.62. IR (KBr, cm⁻¹) 1617 (ν_{C=N}), 1276 (ν_{C-O}), 671 (ν_{Sn-C}), 528 (ν_{Sn-O}), 407 (ν_{Sn-N}).

[(*n*-Bu)₂Sn(sab)₂](**2**): Yield: 80%. dark yellow solid, m.p. 126-127 °C. Anal. Found: C, 61.23; H, 5.72; N, 8.88; Sn, 18.86% Calc. For C₃₄H₃₈N₂O₂Sn: C, 65.30; H, 6.12; N, 4.48; Sn, 18.98. ¹H NMR (CDCl₃) (ppm): 8.66 (2H, s, CH=N), 6.45-7.86 (m, 16H, Ar, Py) 1.32-1.59 (12H, m, Sn-(CH₂)₃-), 0.84-0.71 (6H, m, CH₃). ¹³C NMR (CDCl₃) (ppm): 164.72 (s, CO), 161.74 (s, CN), 148.52-117.69 (s, Ar-C, Py-C), 25.53, 25.13, 25.71, 13.56 (s, Sn-Buⁿ). ¹¹⁹Sn NMR (DMSO-d₆) (ppm): -359. IR (KBr, cm⁻¹) 1622 (ν_{C=N}), 1274 (ν_{C-O}), 668 (ν_{Sn-C}), 524, (ν_{Sn-O}), 412 (ν_{Sn-N}).

[(*n*-Bu)₂Sn(snab)Cl](**3**): Yield: 79%, yellow solid, m.p. 76-78 °C. Anal. Found: C, 55.17; H, 6.28; N, 2.90; Cl, 7.38; Sn, 24.76% Calc. For C₂₁H₂₇ClN₂O₃Sn: C, 49.49; H, 5.34; Cl, 6.96; N, 5.50; Sn, 23.29. ¹H NMR (CDCl₃) (ppm): 8.74(1H, s, CH=N), 6.78-7.61(m, 8H, Ar-H), 1.22-1.69(12H, m, Sn-(CH₂)₃-), 0.93-0.81(6H, m, CH₃). ¹³C NMR (CDCl₃) (ppm): 165.73 (s, CO), 162.46 (s, CN), 143.83-118.46, (s, Ar-C), 28.54, 27.65, 26.19, 13.42 (s, Sn-Buⁿ). ¹¹⁹Sn NMR (DMSO-d₆) (ppm): -142.64. IR (KBr, cm⁻¹) 1616 (ν_{C=N}), 1277 (ν_{C-O}), 659 (ν_{Sn-C}), 518 (ν_{Sn-O}), 416 (ν_{Sn-N}).

[(*n*-Bu)₂Sn(snab)₂](**4**): Yield: 80%, yellow solid, m.p. 116-119 °C. Anal. Found: C, 66.13; H, 6.42; N, 4.22; Sn, 18.17% Calc. For C₃₄H₃₆N₄O₆Sn: C, 57.08; H, 5.07; N, 7.83; Sn, 16.59. ¹H NMR (CDCl₃) (ppm): 8.80 (2H, s, CH=N), 6.54-7.21(m, 16H, Ar-H), 1.24-1.44 (12H, m, Sn-(CH₂)₃-), 0.78-0.90 (6H, m, CH₃). ¹³C NMR (CDCl₃) (ppm): 165.32 (s, CO), 162.52 (s, CN), 148.28-118.43 (s, Ar-C), 26.18, 25.73, 25.14, 13.28 (s, Sn-Buⁿ). ¹¹⁹Sn NMR (DMSO-d₆) (ppm): -377. IR (KBr, cm⁻¹) 1618 (ν_{C=N}), 1278 (ν_{C-O}), 624 (ν_{Sn-C}), 519 (ν_{Sn-O}), 409 (ν_{Sn-N}).

[(*n*-Bu)₂Sn(sapic)Cl](**5**): Yield: 80%, brown solid, m.p. 87-88 °C. Anal. Found: C, 51.55; H, 5.82; N, 5.98; Cl, 7.52; Sn, 25.36% Calc. For C₂₁H₂₉ClN₂OSn: C, 52.59; H, 6.09; Cl, 7.39; N, 5.84; Sn, 24.75. ¹H NMR (CDCl₃) (ppm): 9.90(1H, s, CH=N), 8.51(d, 1H, Py-H), 6.34-7.67(m, 7H, Ar, Py) 1.31-1.68 (12H, m, Sn-(CH₂)₃-), 0.87-0.81(6H, m, CH₃). ¹³C NMR (CDCl₃) (ppm): 164.35 (s, CO), 162.12 (s, CN), 145.84-116.17, (s, Ar-C, Py-C), 26.73, 24.87, 24.64, 13.32 (s, Sn-Buⁿ). ¹¹⁹Sn NMR (DMSO-d₆) (ppm): -143 IR (KBr, cm⁻¹) 1622 (ν_{C=N}), 1280 (ν_{C-O}), 674 (ν_{Sn-C}), 532 (ν_{Sn-O}), 413 (ν_{Sn-N}).

[(*n*-Bu)₂Sn(sapic)₂](**6**): Yield: 84%. dark brown solid, m.p. 146-147 °C. Anal. Found: C, 61.23; H, 5.72; N, 8.88; Sn, 18.86% Calc. For C₃₄H₄₀N₄O₂Sn: C, 62.31; H, 6.15; N, 8.55; Sn, 18.11. ¹H NMR (CDCl₃)

(ppm): 9.93 (2H, s, CH=N), 8.52 (d, 2H, Py-H), 6.38-7.84 (m, 14H, Ar, Py) 1.26-1.46 (12H, m, Sn-(CH₂)₃-), 0.78-0.71 (6H, m, CH₃). ¹³C NMR (CDCl₃) (ppm): 165.32 (s, CO), 161.42 (s, CN), 149.89-116.54 (s, Ar-C, Py-C), 25.53, 25.51, 25.43, 12.14 (s, Sn-Buⁿ). ¹¹⁹Sn NMR (DMSO-d₆) (ppm): -356 IR (KBr, cm⁻¹) 1615 (ν_{C=N}), 1282 (ν_{C-O}), 673 (ν_{Sn-C}), 529, (ν_{Sn-O}), 407 (ν_{Sn-N}).

3. Results and Discussion

Organotin(IV) complexes (**1-6**) have been synthesized by the reactions of di-*n*-butyltin(IV)dichloride with sodium salts of Schiff bases in 1:1 and 1:2 molar ratios in THF-C₆H₆ mixture (Scheme 1). All these complexes are coloured solids, soluble in polar solvents (e. g. methanol, ethanol, THF, DMF and DMSO).

3.1. Infrared spectral studies

The following salient features appear to be significant from the point of view of structural elucidation: The disappearance of stretching vibration band of phenolic (O-H) group in the region 3436-3350 cm⁻¹, may be assigned to be due to replacement of phenolic proton by the metal [4a]. The metallation of phenolic proton is also supported by shifting of ν_{C-O} toward higher frequency in the region 1282-1274 cm⁻¹ with respect to that observed in Schiff bases⁹ and appearance of new bands in the region 532-518 cm⁻¹ which are assignable to ν_{Sn-O}. In complexes the ν(C=N), occurring between 1622-1615 cm⁻¹, is considerably shifted towards lower frequencies with respect to that of the parent Schiff bases 1638-1635 cm⁻¹, confirming the coordination of the azomethine nitrogen to dibutyltin(IV) moiety⁹. The weak intensity bands observed in the 416-407 cm⁻¹ region may be due to ν(Sn-N) vibration¹¹. The ν(Sn-C) bands were observed at 673-624 cm⁻¹. On the basis of the observations the structures of the complexes displayed in Scheme 1 are more acceptable.

3.2. ¹H NMR spectral studies

The bidentate (O, N) connectivity⁷⁻¹¹ of the Schiff bases to Bu₂Sn-moiety in complexes (**1-6**) is consistent with the (i) The ¹H NMR spectra of tin(IV) complexes exhibit an absence of signal due to OH group of Schiff bases in the region 13.18-12.40 ppm, which is indicative of metallation of the OH group, (ii) The presence of signals in the region 9.93-8.61 ppm for azomethine hydrogen, which is shifted down field, compared to the parent Schiff bases (9.37-8.40 ppm) is supportive of the coordination of azomethine nitrogen to tin atom. The butyl group attached to tin showed two broad peaks in the 0.93-0.71 and 1.69-1.22 ppm regions, respectively due to

$-\text{CH}_3$ and $(-\text{CH}_2)_3$ groups of butyl chain.

3.3. ^{13}C NMR spectral studies

The azomethine carbon signals which are observed in the region 159.93-158.70 ppm for free Schiff base ligands, are present in the region 162.52-160.19 ppm for tin (IV) complexes such downfield shift is in support of coordination of azomethine nitrogen to the tin atom¹¹. The signals for phenolic carbon in the region 150.83-148.26 ppm for free Schiff base ligands are shifted downfield 165.72-163.62 ppm in the complexes, supporting the bonding through phenolic oxygen and the formation of metal-oxygen bond¹¹.

3.4. ^{119}Sn NMR spectral studies

The organotin(IV) complexes (**1**, **3**, **5**) and (**2**, **4**, **6**) exhibit a single sharp ^{119}Sn resonance (see Experimental Section) in the -148 to -143 and -377 to -356 ppm regions consistent with penta- and hexa- coordinated tin atoms, respectively².

3.5. Mass spectral studies

The mass spectral data for the complex $[(n\text{-Bu})_2\text{Sn}(\text{sab})\text{Cl}]$ (**1**) was recorded and different fragmentation patterns has been suggested (Schemes 2). For complex (**1**) most of the fragment ions were observed in the form of group of peaks due to the presence of various isotopes of tin⁷⁻¹¹. In the spectra of (**1**) (Figure 1) the molecular ion peaks are observed at m/z 465.8573 (calculated mass = 465.0881]. In spectrum of the complex (**1**), the base peak was observed due to the formation of phenoxy cation $[\text{C}_6\text{H}_5\text{O}]^+$ at m/z 93.0461, and other important peaks were also observed at m/z 408.0177, 388.0490, 362.0459, 350.9473, 315.9784, 304.9755, 247.9051, 238.9393, 212.9362 and 119.9022 due to the formation of various radicals $^n\text{Bu}^\bullet$, Cl^\bullet , $\text{C}_6\text{H}_5^\bullet$, CHN , $\text{C}_6\text{H}_5\text{O}^\bullet$, Sn^\bullet in complex (**1**).

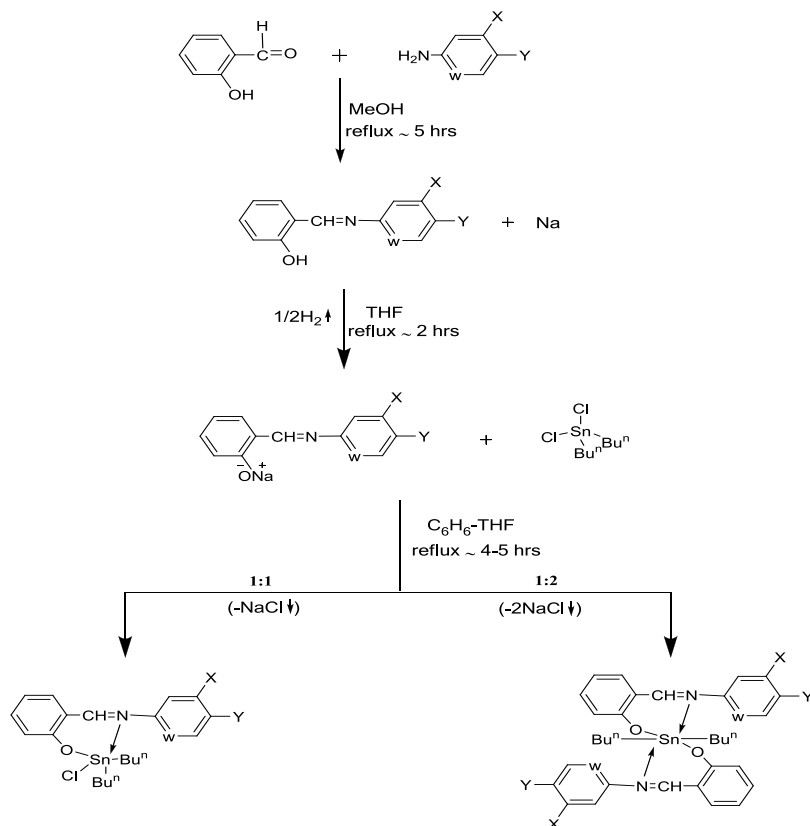
4. Conclusion

Synthesis of five- and six- coordinate di-*n*-butyltin(IV) complexes have been achieved by the reactions of di-*n*-butyltin(IV)dichloride with appropriate sodium salt of Schiff base ligands in 1:1 and 1:2 molar ratios, respectively and investigated by a variety of physicochemical methods.

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Complex	W	X	Y
1	C	H	H
2	C	H	H
3	C	NO_2	H
4	C	NO_2	H
5	N	H	CH_3
6	N	H	CH_3

Scheme 1. General method for synthesis of Schiff bases and di-*n*-butyltin(IV) complexes

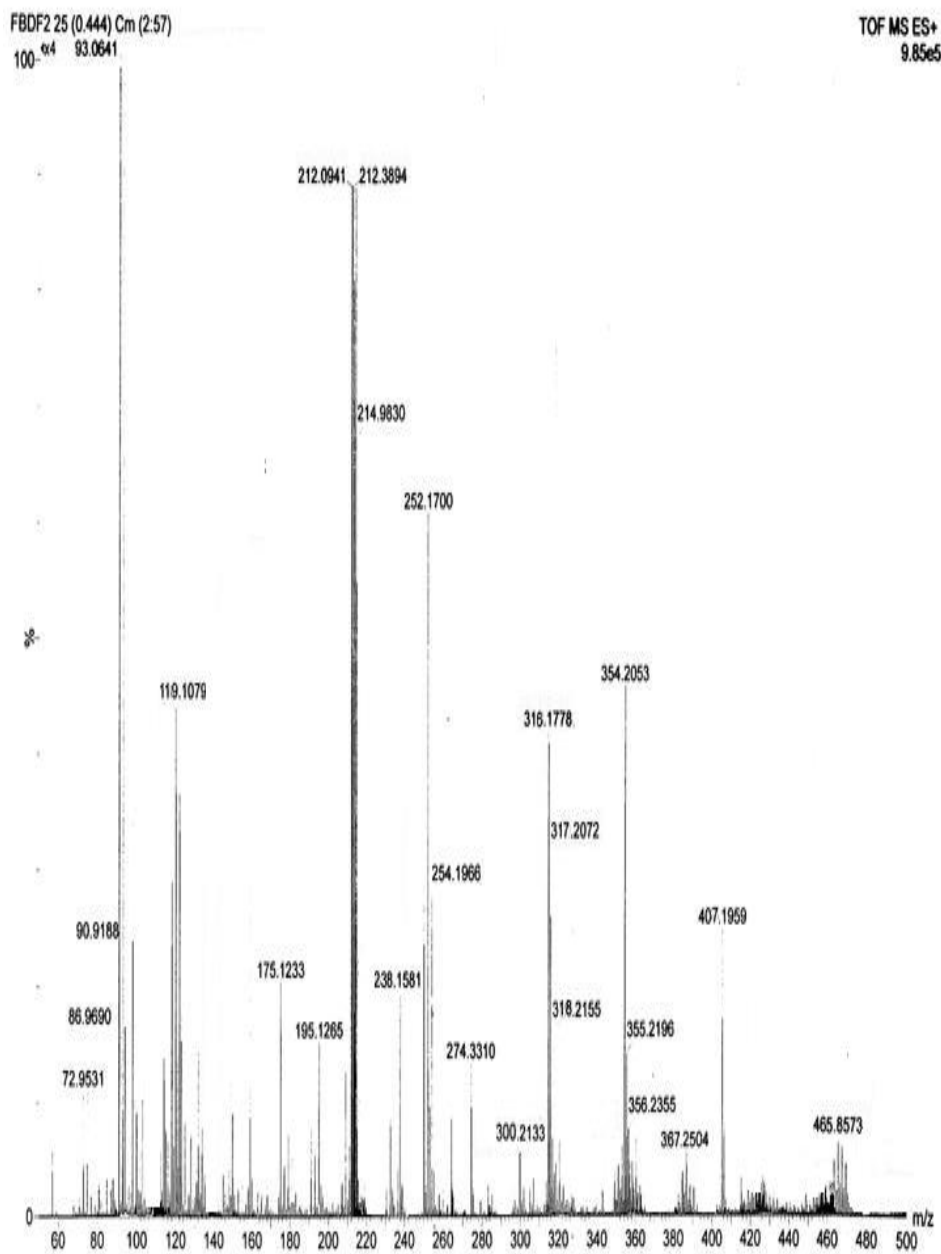
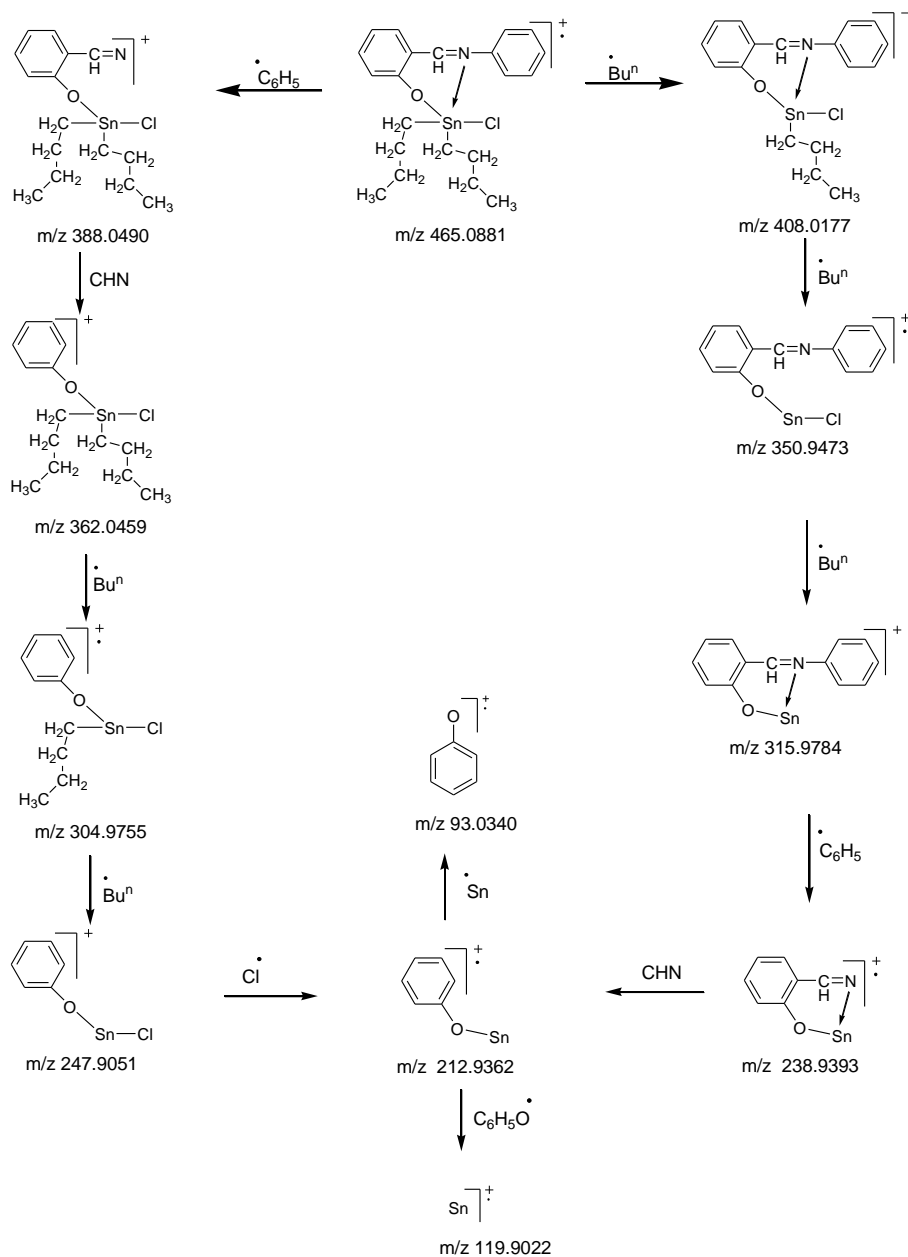


Fig. 1. TOF-MS spectrum of complex $[(n\text{-Bu})_2\text{Sn}(\text{sab})\text{Cl}]$ (1)



Scheme 2. Fragmentation pattern of complex $[(n\text{-Bu})_2\text{Sn}(\text{sab})\text{Cl}]$ (1)

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