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¹H NMR, Infrared and Mass Spectrometry of Di- and Tri-Organotin Derivatives of 1-Nitroso-2-Naphthol

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The di- and tri-organotin derivatives R_2SnL_2 and R_3SnL where $R = CH_3, n-C_4H_9, C_6H_5, C_6H_{11}$ and $C_6H_5CH_2$ and $L = 1$ -nitroso-2-naphthoxy were synthesized. These derivatives were characterized by elemental analysis, infrared, ¹H NMR and mass spectrometry.

Introduction

In recent years, considerable progress has been made in the synthesis, characterization and applications of organotin compounds¹. The whole field of organotin chemistry is based on the use of organotin halides as precursors². Previously, we synthesized a number of organotin derivatives of various donor ligands³⁻¹¹ and characterized them by different instrumental techniques. Biological activity^{12,13} for some compounds as well as crystal structures¹⁴⁻¹⁷ were reported. The present study, in which 1-nitroso-2-naphthoxy organotins such as R_3SnL and R_2SnL_2 where $R = CH_3, n-C_4H_9, C_6H_5, C_6H_{11}, C_6H_5CH_2$ and $LH = 1$ -nitroso-2-naphthol are reported, is a continuation of our previous work³. These compounds are characterized by elemental analysis, infrared, ¹H NMR and mass spectrometry.

Experimental

All chemicals were of analytical grade and used without further purification. Solvents were dried by conventional methods¹⁸.

Tribenzyltin chloride and dibenzyltin dichloride were prepared according to reported methods¹⁹.

Elemental analysis for CHN were obtained from the micro-analytical labs at the University of Science, Malaysia, while tin contents were measured on an atomic absorption spectrophotometer, model Z 8000, Hitachi, Japan.

Infrared studies were carried out on an infrared spectrophotometer, model 270-50, Hitachi, Japan. Proton NMR spectra were recorded on an NMR spectrometer, Model JNP-PMX-60, Jeol, Japan. Mass spectra were recorded on a mass spectrophotometer, MAT 112. 7, EI 80 eV.

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General Procedure for Synthesis

For the synthesis of these complexes, triorganotin and diorganotin halides were reacted with ligands in 1:1 and 1:2 molar ratios in dry chloroform, respectively. Et₃N was added in proper molar ratio to trap HCl produced during the reaction. Reactions were carried out in an inert atmosphere of helium. The contents were refluxed for 4 hours. The solvent was removed by rotary evaporation and the solid product was washed with methanol and crystallized from CH₂Cl₂. The purity of compounds were checked on TLC plates. The compounds prepared were:

1. 1-Nitroso-2-naphthoxy tribenzyltin (IV)

Crystallized from CH₂Cl₂ (Yield 60%) m.p. 95-97° C

Analysis: [C₁₀H₆NO₂Sn (C₆H₅CH₂)₃] % CHN Sn Found/Calc.

66.1/65.9, 5.0/4.7, 2.6/2.5, 21.5/21.0

Mass spectral data m/z, C₁₈H₁₆OSn⁺ 367 (100%), C₁₇H₁₃Sn⁺ 336 (48%), C₁₁H₁₀ OSn⁺ 277 (38%), C₁₀H₇Sn⁺ 246 (20%), C₇H₇⁺ 91 (32%).

2. 1-Nitroso-2-naphthoxy tricyclohexyltin (IV)

Crystallized from CH₂Cl₂ (Yield 72%). m.p. 59-61° C.

Analysis : [C₁₀H₆NO₂Sn (C₆H₁₁)₃] % CHN Sn Found/Calc.

62.5/62.2, 7.4/7.2, 2.9/2.6, 22.4/22.0

Mass spectral data m/z, C₂₂H₂₉Sn⁺ 412 (58%), C₁₈H₃₀OSn⁺ 381 (96%), C₁₃H₂₄Sn⁺ 299 (100%), C₉H₁₄Sn⁺ 241 (56%), C₃H₄Sn⁺ 159 (78%), C₆H₁₁⁺ 83 (24%).

3. Bis(1-nitroso-2-naphthoxy) diphenyltin (IV)

Crystallized from CH₂Cl₂ (Yield 63%) m.p. 70-72° C.

Analysis [(C₁₀H₆NO₂)₂ Sn (C₆H₅)₂] % CHN Sn Found/Calc.

62.6/62.2, 3.8/3.6, 4.9/4.5, 19.6/19.3.

Mass spectral data m/z, C₂₀H₁₂NO₃Sn⁺ 433 (36%) C₁₂H₆OSn⁺ 285 (0.5%), C₁₂H₁₀Sn⁺ 273 (1.3%), C₁₂H₆Sn⁺ 269 (2%), HNO₂Sn⁺ 166 (6%).

4. Bis(1-nitroso-2-naphthoxy) dibutyltin (IV)

Crystallized from CH₂Cl₂ (Yield 81 %) m.p. 90-92° C.

Analysis : [(C₁₀H₆NO₂)₂ Sn (C₄H₉)₂] % CHN Sn Found/Calc.

58.7/58.2, 5.3/5.2, 5.1/4.8, 20.9/20.6.

Mass Spectral data m/z, C₂₃H₂₆NO₂Sn⁺ 467 (10%), C₂₀H₂₃NOSn⁺ 412 (38%), C₁₅H₁₃Sn⁺ 312 (38%), C₈H₁₂Sn⁺ 227 (20%), C₈H₁₂⁺ 108 (10%), C₄H₉⁺ 57 (84%), C₃H₈⁺ 44 (100 %).

5. Bis(-1-nitroso-2-naphthoxy) dibenzyltin (IV)

Crystallized from CH₂Cl₂ (Yield 59%) m.p. 65-67° C.

Analysis: [(C₁₀H₆NO₂)₂ Sn (C₆H₅CH₂)₂] % CHN Sn Found/Calc.

63.6/63.2, 4.4/4.0, 4.8/4.3, 18.6/18.4.

Mass Spectral data m/z, C₁₉H₂₀N₂O₄Sn⁺ 459 (4 %), C₁₃H₉N₂O₄⁺ 257 (64%), C₉H₉O₂⁺ 149 (44%), C₃H₂O₂⁺ 70 (54%), C₂HO₂⁺ 57 (100%), CO₂⁺ 44 (82%).

6. Bis(1-nitroso-2-naphthoxy) dimethyltin (IV)

Crystallized from CH₂Cl₂ (Yield 67 %) m.p. 80-82° C.

Analysis : [(C₁₀H₆NO₂)₂ Sn (CH₃)₂] % CHN Sn Found/Calc.

53.8/53.5, 3.7/3.6, 5.9/5.6, 24.2/24.1.

Mass Spectral data m/z, C₁₇H₁₄N₂O₄Sn⁺ 429 (.4%), C₁₀H₁₁N₂O₄Sn⁺ 342 (2.5%), C₁₀H₉N₂O₃⁺ 205 (100%), C₉H₅N₂O₂⁺ 173 (44%), C₉H₅⁺ 113 (6 %), C₆H₄⁺ 76 (8%).

Result and Discussion

The analytical results and certain physical properties of the complexes are listed along each complex. These complexes are quite stable, having sharp melting points, and are soluble in most common organic solvents.

The infrared spectra of the synthesized complexes were recorded by KBr disc in the range of 4000-250 cm⁻¹. The important group frequencies of the ligand are C-H, C=C (aromatic), N=O and O-H stretching vibrations, although the last was not observed due to intramolecular hydrogen bonding²⁰. Bands significant as evidence of complexation are Sn-O, Sn-C and -N= O-Sn, as given in Table 1. There was no marked difference in the 1400-600 cm⁻¹ region in the ligand or in the complexes because of C=C skeletal vibrations²¹.

Table 1. Infrared Characteristics of Complexes and Ligand Band Position (ν)* in cm⁻¹

Compound No.	C=C (Ar)	N = O	Sn-C	Sn-O	-CH ₂
1.	1629 (m) 1599 (s) 1494 (s)	816 (s)	459 (s)	636 (m)	3058 (m) 3022 (m)
2.	1605 (m) 1569 (s) 1545 (m)	804 (s)	450 (s)	606 (m) 651 (m)	2914 (s) 2842 (s)
3.	1590 (s) 1520 (s)	830 (s)	440 (m)	580 (m)	-
4.	1620 (s) 1595 (s) 1522 (s)	835 (s)	496 (s)	650 (s)	-
5.	1590 (m) 1524 (m) 1482 (m)	840 (s)	480 (m)	625 (s)	3040 (s) 2950 (m)
6.	1650 (m) 1630 (s) 1600 (s)	840 (s)	440 (m)	620 (s)	-
LH**	1623 (s) 1524 (s) 1452 (m)	852 (s)	-	-	-

*s, sharp; m, medium

**LH = 1-nitroso-2-naphthol.

The most important band confirming complexation through oxygen is - N=O of the ligand at 852 cm⁻¹, which shifts to a lower-frequency region in complexes. Complexation is evidenced by the Sn-O band in our complexes, which appears at 650-600 cm⁻¹. Different authors have reported this band at 675-560 cm⁻¹ 22-25. The absence of the Sn-Cl band in organotin derivatives is further evidence of complexation.

¹H NMR spectra were recorded in CDCl₃ and the data is given in Table 2. In 1-nitroso-2-naphthol the multiplet signal at 7-8.5 ppm is assigned as six protons of aromatic rings where the -OH proton resonates at high frequency and low field (9.5 ppm).

Table 2. ¹H NMR Characteristics of Complexes and Ligand

Compound No.	Chemical Shift (ppm)	Assignment
1.	7-8 multiplet	Fifteen proton of phenyl ring and six protons of naphthyl ring.
	2.6-2.8	Six methylene protons
2.	7-8 multiplet	Six protons of naphthyl ring.
	1.7-1.9 multiplet	Cyclohexyl ring.
3.	6-9 multiplet	Twelve protons of naphthyl ring and ten protons of phenyl ring.
4.	6-9 multiplet	Twelve protons of naphthyl ring.
	1.23-2.13 multiplet	Twelve protons of methylene group.
	0.9 multiplet	Six protons of methyl group.
5.	7-8.2 multiplet	Twelve protons of naphthyl ring and ten protons of phenyl ring.
	0.8-1.3 multiplet	Four protons of methylene group.
6.	6-7.9 multiplet	Twelve protons of naphthyl ring.
	1.2 singlet	Six protons of methyl groups.
LH*	7-8.5 multiplet	Six protons of naphthyl ring.
	9.5	One proton of hydroxy group.

*LH = 1-nitroso-2-naphthol.

We observed different multiplet signals in the 6-9 ppm range for different complexes which are assigned as aromatic protons of the ligand and in some cases phenyl groups. For complexes having benzyl groups, multiplet signals were observed at 2.6-2.8 ppm for -CH₂ groups, where as for the n-C₄H₉ group the multiplet was obtained at 1.23-2.13 ppm. For the -CH₃ group the signal was recorded at 1.2 ppm.

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