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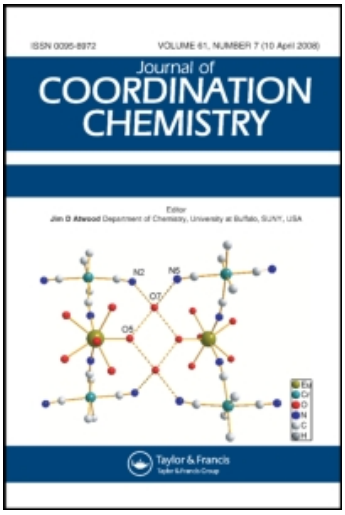

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The chemistry, properties, and characterization of organotin(IV) complexes of 2-(N-naphthylamido)benzoic acid

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The chemistry, properties, and characterization of organotin(IV) complexes of 2-(N-naphthylamido)benzoic acid

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2-(N-naphthylamido)benzoic acid was synthesized by the reaction of phthalic anhydride with naphthylamine in glacial acetic acid at room temperature. Complexes **1**–**9** were synthesized under reflux in good yield with general formula $R_{4-n}SnL_n$ (R = Me, *n*-Bu, Ph, *n*-Oct, Bz and $n = 2, 3$), which were studied by microanalysis, IR, NMR (^{1}H, ^{13}C, ^{119}Sn), and mass spectrometry. Cytotoxicity of the synthesized compounds was checked against Brine-shrimp larvae. *In vitro* activities against some Gram-positive and Gram-negative bacteria and fungi were also determined. Antimicrobial activities show that species with tetrahedral geometry in solution are more toxic.

Keywords: 2-(N-naphthylamido)benzoic acid; Organotin(IV) complexes; NMR; IR; Mass spectrometry; Antimicrobial activity

1. Introduction

The exponential increase in industrial, agricultural, and biological applications of organotin(IV) compounds has led to their accumulation in the environment and biological systems [1–5]. In addition, many organotin compounds have been tested for *in vitro* activity against a large variety of tumor lines and found to be more effective than traditional heavy metal anticancer drugs such as *cis*-platin [6]. The coordination chemistry of tin is extensive with various geometries and coordination numbers known for both inorganic and organometallic complexes [7]. Higher coordination numbers can be generated either by inter- or intramolecular interaction, especially in complexes where tin bonds to electronegative atoms such as oxygen, nitrogen, and sulfur. Organotin compounds are the active components in a number of biocidal formulations, finding applications in such diverse areas as fungicides, miticides, molluscicides, marine antifouling paints, surface disinfectants, and wood preservatives [8]. In general, the biochemical activity of organotin(IV) carboxylates is greatly influenced by the structure and coordination number of tin [9]. 2-(N-naphthylamido)benzoic acid was used for complexation with the expectation that they will show significant antimicrobial activities and will be used as drugs.

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As continuation of our studies of biologically active organotin(IV) derivatives [10–12], we have studied the di- and triorganotin derivatives of 2-(N-naphthylamido)benzoic acid (figure 1). The synthesized compounds were characterized by ^{1}H, ^{13}C, ^{119}Sn NMR, and FTIR spectroscopy, as well as by elemental and mass spectrometric analyses. The synthesized complexes and the ligand acid (**HL**) have been tested for *in vitro* biological activity.

2. *Experimental*

Di- and triorganotin(IV) chlorides/oxide were purchased from Aldrich, Fluka, or Alfa-Aesar Chemicals and used without purification. Organic solvents were purchased from Merck (Germany) and dried *in situ* using standard procedures [13]. Di- and tribenzyltin chlorides were prepared by the methods reported in [14]. Melting points were determined in capillaries using an electrothermal melting point apparatus, model MPD Mitamura Riken Kogyo (Japan). Infrared (IR) spectra of 4000–400 cm^{-1} were recorded using KBr pellets on a Bio-Rad *EXCALIBER* FT-IR, model FTS 300 MX spectrometer (USA). The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Bruker ARX 250 FT-NMR spectrometer (Switzerland) using $CDCl_3$ as an internal reference. ^{119}Sn NMR spectra were obtained with Me_4Sn as an external reference. Elemental analyses were carried out with a Perkin-Elmer 2400 Series II instrument. Mass spectral data were recorded on a MAT 8500 Finnigan mass spectrometer (Germany).

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2.1. *Synthesis of* 2-(*N-naphthylamido*)*benzoic acid* (*HL*)

A solution of phthalic anhydride (10 g, 6.75 mmol) in HOAc (300 mL) was added to a solution of naphthyl amine (9.66 g, 6.75 mmol) in HOAc (150 mL) and the mixture was stirred at room temperature overnight. The light purple precipitate was filtered, washed with cold distilled H_2O (200 mL), and air dried.

2.2. *General procedure for synthesis of organotin(IV) complexes*

2-(N-naphthylamido)benzoic acid (1 g, 3.43 mmol) was suspended in dry toluene (100 mL) and treated with triethylamine (0.48 mL, 3.43 mmol). The mixture was refluxed for 2–3 h, diorganotin dichloride (1.71 mmol) or triorganotin chloride (3.43 mmol) was added as solid with constant stirring and refluxed for an additional 8–10 h.

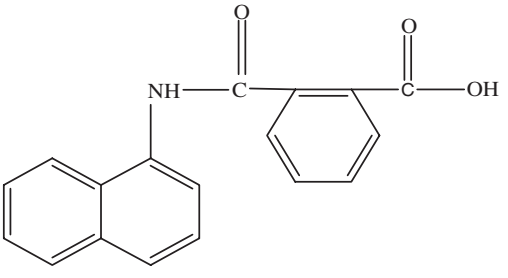

Figure 1. Chemical structure of 2-(N-naphthylamido)benzoic acid (**HL**).

The reaction mixture containing Et_3NHCl was filtered such that filtrate contained the organotin(IV) derivative. The solvent was removed through rotary evaporator and the solid was recrystallized from $CHCl_3$ and *n*-hexane (1 : 1). In the case of Oct_2SnO, 2-(N-naphthylamido)benzoic acid (3.43 mmol) was suspended in dry toluene (100 mL), solid Oct_2SnO (1.71 mmol) was added with constant stirring and the reaction was refluxed for 8–10 h. Water formed was removed *via* Dean and Stark trap. After cooling to room temperature, solvent was evaporated under reduced pressure.

3. Results and discussion

All compounds were prepared by reaction of 2-(N-naphthylamido)benzoic acid with R_2SnCl_2 (2 : 1) or R_3SnCl (1 : 1) in the presence of triethylamine as base or Oct_2SnO (2 : 1) by esterification. The general reactions are given in as follows.

$$R_2SnCl_2 + 2HL \xrightarrow{2Et_3N} R_2SnL_2 + 2Et_3NHCl$$

$$R_3SnCl + HL \xrightarrow{Et_3N} R_3SnL + Et_3NHCl$$

$$n\text{-}Oct_2SnO + 2HL \longrightarrow n\text{-}Oct_2SnL_2 + H_2O$$

All the complexes are purple, have sharp melting points, and are soluble in most organic solvents. Physical data for the compounds are given in table 1.

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3.1. *Infrared spectral data*

The infrared spectra were recorded as KBr discs and data are given in table 2 The disappearance of a broad band in the range of 2900–2500 cm^{-1}, in the spectra of all the compounds indicates deprotonation of –COOH and formation of a new Sn–O bond. The $\nu C=O$ in all the compounds shifts to slightly higher frequency thereby showing no coordination to tin(IV). The carboxylate group generally adopts a bridged structure in the solid state unless the organic substituents at the tin atom are bulky or the carboxylate group is branched at the α-carbon [15]. The $\nu_{asym}(COO)$ values (1535–1585 cm^{-1}) and $\nu_{sym}(COO)$ values (1390–1462 cm^{-1}) reveal strong interactions

Table 1. Physical data for compounds of 2-(N-naphthylamido)benzoic acid.

Compound No.	Molecular formula	M.W.	Melting point (°C)	% Yield	Elemental analysis Calcd (found)		
					% C	% H	% N
HL	$C_{18}H_{13}NO_3$	291.3	145	80	74.22 (74.25)	4.50 (4.54)	4.81 (4.86)
(1)	$C_{38}H_{30}N_2O_6Sn$	729.36	128	90	62.58 (65.62)	4.15 (4.18)	3.84 (3.89)
(2)	$C_{44}H_{42}N_2O_6Sn$	813.52	160	75	64.96 (64.99)	5.20 (5.24)	3.44 (3.50)
(3)	$C_{48}H_{34}N_2O_6Sn$	853.5	118	84	67.55 (67.49)	4.02 (3.96)	3.28 (3.22)
(4)	$C_{50}H_{38}N_2O_6Sn$	881.56	95	67	68.12 (68.06)	4.34 (4.31)	3.18 (3.22)
(5)	$C_{52}H_{58}N_2O_6Sn$	925.74	125	80	67.47 (67.51)	6.32 (6.37)	3.03 (3.07)
(6)	$C_{21}H_{21}NO_3Sn$	454.11	122	60	55.54 (55.50)	4.66 (4.62)	3.08 (3.13)
(7)	$C_{30}H_{39}NO_3Sn$	580.35	105	72	62.09 (62.12)	6.77 (6.73)	2.41 (2.36)
(8)	$C_{36}H_{27}NO_3Sn$	640.31	121	78	67.53 (67.57)	4.25 (4.19)	2.19 (2.14)
(9)	$C_{39}H_{33}NO_3Sn$	682.39	111	58	68.64 (68.58)	4.87 (4.83)	2.05 (2.09)

Table 2. IR spectral data for compounds of 2-(N-naphthylamido)benzoic acid (cm^{-1}).

Compound No.	$\nu C=O$	$\nu_{asym}(COO)$	$\nu_{sym}(COO)$	$\Delta\nu$	$\nu Sn–O$	$\nu Sn–C$
HL	1702	1591	1426	165	–	–
1	1712	1585	1462	123	420	522
2	1716	1545	1410	135	416	515
3	1713	1541	1401	140	441	–
4	1717	1560	1412	148	418	529
5	1712	1550	1390	160	431	520
6	1708	1538	1405	133	426	531
7	1710	1535	1408	127	437	528
8	1716	1578	1420	158	422	–
9	1714	1555	1402	153	435	532

between oxygen and tin. The magnitude of the $(\nu_{asym} - \nu_{sym})COO = (\Delta\nu)$ separation lies in the range of 123–160 cm^{-1}, confirming the bidentate nature of the ligand [16]. Medium to weak bands in the region 416–441 cm^{-1} are assigned to Sn–O, whereas those in the region 515–532 cm^{-1} indicate Sn–C bonds [17].

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3.2. *Mass spectrometry*

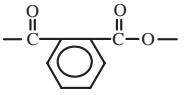
The 70 eV mass fragments of **1**–**9** are reported in "Supplementary material". For organotin(IV) derivative the spectra are easily interpreted in terms of fragmentation patterns (Supplementary material). The fragmentation patterns follow established routes described in earlier reports [18, 19]. Molecular ion peak is observed for trimethyl, tributyl, triphenyl, and tribenzyl, while none of the rest exhibits the molecular ion. The most frequent fragmentation route is elimination of R, and to a lesser extent tin–oxygen. However, secondary fragmentation is a consequence of loss of CO_2 or the R group, the former being the most probable and frequent pathway [20, 21]. The successive loss of R groups and loss of remaining ligand give Sn^+/SnH^+.

3.3. *NMR spectroscopy*

The ^1H NMR spectra of **1**–**9** recorded in $CDCl_3$ are given in table 3. All the protons have been identified and the total number of protons calculated from integration tallies with expected molecular formulas. The aromatic proton resonances were assigned by comparing experimental chemical shifts with those calculated by the incremental method [22]. Naphthyl protons are in the range of 7.92–7.79 ppm and –NH shows a singlet at 9.90–9.20 ppm. CH_3 protons of both di-*n*-butyl- and tri-*n*-butyltin(IV) of **2** and **7** are a triplet at 0.75 and 0.89 ppm with $^3J[^1H, ^1H] = 6.6$ and 8.7 Hz, respectively; the α-CH_2, β-CH_2, and γ-CH_2 protons are multiplets.

The most important information obtained from ^1H NMR values is $^2J[^{119}Sn–^1H]$ coupling constant values. Coupling values in the range of 79 Hz in **1** demonstrate coordination number greater than four, probably five or six in non-coordinating solvents. The 51 Hz in **6** shows distorted tetrahedral geometry [23, 24] in solution. The results of ^{13}C and ^{119}Sn NMR spectra are given in "Supplementary material". The chemical shift of C-12 in the compounds depends on the coordination of –COO to the tin. C-7 (–C=O) gives a signal in the range 168.90–167.27 ppm. C-8 and C-9 appear at 131.10–128.10 ppm and 130.80–130.00 ppm, respectively. The coupling

Table 3. ^{1}H NMR[a] data for compounds of 2-(N-naphthylamido)benzoic acid.

Compound No.		–NH		R
HL	7.50m	9.72s	7.27m	–
1	7.80–7.82m	9.70s	7.24m	1.20s [79]
2	7.82–7.84m	9.40s	7.25m	0.75t [6.6], 1.28m, 1.56m, 0.88m
3	7.83–7.85m	9.53s	7.20–7.24m	7.93–7.99m
4	7.79–7.82m	9.20s	7.23–7.40m	1.25s, 7.95–7.99m
5	7.86–7.88m	9.63s	7.29m	0.81–0.84m
6	7.84–7.89m	9.69s	7.50–7.64m	0.49s [51]
7	7.86–7.88m	9.59s	7.25–7.30m	0.89t [8.7], 1.21m, 1.33m, 1.54m
8	7.89–7.92m	9.48s	7.21–7.22m	7.76–7.79m
9	7.79–7.83m	9.90s	7.09–7.19m	1.28s, 7.99–8.02m

[a]Chemical shifts (δ) in ppm. $^{n}J[^{119}\mathrm{Sn}, ^{1}\mathrm{H}]$ in Hz are listed in square brackets.

Table 4. C–Sn–C angles (°) estimated from NMR.

Compound	^{1}J [^{119}Sn–^{13}C] (Hz)	^{2}J[^{119}Sn–^{1}H] (Hz)	C–Sn–C angles (°) calculated from	
			^{1}J	^{2}J
1	–	79	–	129.6
6	377	51	107.9	109.8
7	358	–	117.2	–

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constants, $^{n}J[^{119}\mathrm{Sn}, ^{13}\mathrm{C}]$, are important for structure characterization of organotin(IV) compounds. For **6**, the magnitude of $^{1}J[^{119}\mathrm{Sn}, ^{13}\mathrm{C}]$ is 377 Hz, suggesting typical tetrahedral geometry around tin in solution [25]. The geometry of the diorganotin dicarboxylates in non-coordinating solvents is not defined with certainty because of the fluxional behavior of the carboxylate oxygen in coordination with tin, e.g. ^{1}J for **3**. C–Sn–C angles calculated by the use of the Holecek and Lycka's equation [26] are summarized in table 4. The geometric data calculated are consistent with tetrahedral geometries for the triorganotin(IV) species, i.e. monomer in solution. For the diorganotin(IV) species, the calculated C–Sn–C angles are consistent with the skew-trapezoidal bipyramidal geometries, with the lower apparent coordination number arising from the asymmetric coordination mode of the carboxylate.

The chemical shifts $\delta(^{119}\mathrm{Sn})$ vary over a wide range from −46.1 to +149.7 ppm. Diorganotin compounds have $\delta(^{119}\mathrm{Sn})$ values in the range from −136.4 to +49.1 ppm suggesting the coordination number greater than five, but triorganotin carboxylate $\delta(^{119}\mathrm{Sn})$ are in the range from +149.7 to −46.1 ppm showing tetrahedral geometry. ^{119}Sn chemical shifts move to higher field as electron-releasing power of the alkyl group increases and tin becomes progressively more shielded [27].

3.4. *Biological activity*

LD_{50} values for the synthesized compounds were determined by a Brine-Shrimp method [28] (table 5). Compound **9** shows the highest toxicity with LD_{50} of 4.6331 μg mL^{-1},

Table 5. Brine shrimp (*Artemia salina*) lethality bioassay for compounds of 2-(N-naphthylamido)benzoic acid.[a]

Compound No.	Dose ($\mu g\,mL^{-1}$)	No. of shrimps	No. of survivors	LD_{50} ($\mu g\,mL^{-1}$)
HL	100	30	10	–
	10	30	10	
	1	30	10	
1	100	30	0	–
	10	30	10	
	1	30	10	
2	100	30	0	<1
	10	30	0	
	1	30	0	
3	100	30	0	3.2481
	10	30	2	
	1	30	10	
4	100	30	0	3.3141
	10	30	3	
	1	30	27	
5	100	30	0	–
	10	30	30	
	1	30	30	
6	100	30	0	4.3362
	10	30	4	
	1	30	29	
7	100	30	0	3.3141
	10	30	1	
	1	30	10	
8	100	30	10	–
	10	30	10	
	1	30	10	
9	100	30	2	4.6331
	10	30	4	
	1	30	28	

[a]Etoposide has a LD_{50} ($\mu g\,mL^{-1}$) of 7.4625.

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Table 6. Antibacterial activity for compounds of 2-(N-naphthylamido)benzoic acid (standard drugs are Ampicilline $(H_2O)_3$ and Cephalexin Na).

	Inhibition zone diameter (mm)									
Name of bacteria (ATCC No.)	HL	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Escherichia coli	–	–	10	10	12	–	12	12	–	9
Bacillus subtilis (11774)	–	20	–	16	12	–	17	14	20	21
Shigella flexenari (700390)	12	–	9	11	–	–	–	12	10	13
Staphlyococcus aureus (25923)	15	13	10	13	15	11	17	17	18	13
Pseudomonoas aeruginosa (10145)	9	11	10	15	10	10	9	10	12	10
Salmonella typhi (10749)	9	12	–	13	–	–	–	16	14	20

while **1**, **5**, and **8** do not show toxicity; the reference drug Etoposide's LD_{50} value is $7.4625\,\mu g\,mL^{-1}$. All the synthesized compounds were screened for antibacterial activity using the agar well diffusion method [28] at $100\,mg\,mL^{-1}$ in DMSO solution; susceptibility zones were measured in millimeters (table 6). All compounds show significant antibacterial activity against all test bacteria, but lesser antibacterial activity than standard reference drugs Ampicilline $(H_2O)_3$ and Cephalexin Na.

Table 7. Antifungal activity for compounds of 2-(N-naphthylamido)benzoic acid.

	Inhibition (%)										
Name of fungi (ATCC No.)	HL	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	Standard drug
Trichophyton longifusus (22397)	0	60	0	0	0	0	10.5	94.7	84.2	45	Miconazole Ketoconazole
Candida albicans (2192)	0	0	0	40	0	0	0	0	47.3	0	Miconazole Ketoconazole
Aspergillus flavis (1030)	0	0	0	0	0	0	35	89.4	88.8	65	Amphotericin-B Flucytosine
Microsporum canis (9865)	0	60	0	80	0	45	89.4	94.7	85	60	Miconazole Ketoconazole
Fusarium solani (11712)	0	0	0	0	0	0	0	94.7	70	0	Miconazole
Candida glaberata	0	0	0	0	0	0	0	0	0	0	Miconazole

The reported compounds were screened against different fungal strains using the tube diffusion test [28]. Compounds **6–8** showed significant antifungal activity and the rest of the compounds were active against these fungi with a few exceptions (table 7). From the antimicrobial activities, tetrahedral complexes in solution are more toxic.

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4. Conclusion

Organotin(IV) complexes of 2-(N-naphthylamido)benzoic acid were synthesized in quantitative yield and their structures studied in solid and solution state by FTIR, multinuclear (^{1}H, ^{13}C, and ^{119}Sn) NMR spectroscopy, and mass spectrometry. Elemental analyses showed good agreement between calculated and observed percent of C, H, and N. Solid state studies show coordination number greater than four in diorganotin(IV) dicarboxylates, while four is observed in triorganotin(IV) complexes in solution. Antimicrobial activities show that tetrahedral species in solution are more toxic.

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