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SYNTHESIS AND CHARACTERIZATION OF SOME NEW ORGANOTIN(IV) COMPLEXES OF A SCHIFF BASE DERIVED FROM SALICYLALDEHYDE AND HYDRAZINE HYDRATE

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ABSTRACT

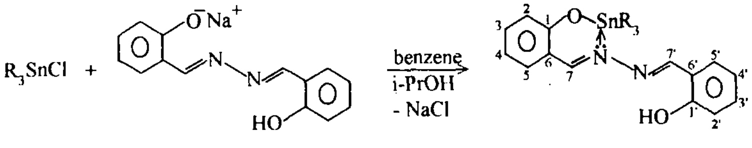
Herein are described the synthesis and characterization of the complexes of the formulae R_3SnL and $R_2SnL_nCl_{2-n}$ where R = Ph, n-Bu and L = N,N'-hydrazinebis(salicylideneimine). All the complexes have been characterized by elemental analyses, molecular weight determinations and spectroscopic (IR, ^1H, ^{13}C and ^{119}Sn NMR) studies.

INTRODUCTION

The most common form of tin in organotin compounds is tetravalent with sp^3 hybridization. The considerable developments over recent decades in the use of organotin compounds as reagents or intermediates in organic synthesis[1,2] has prompted the preparation of many new organotin compounds and the development of new rapid and convenient synthetic procedures. Organotin compounds having the general formulae R_nSnX_{4-n} are biologically active[3-8] and show maximum activity[3,4] when n = 3. Several reports have appeared on the complexes of di- and triorganotin halides with various nitrogen and oxygen/sulfur containing ligands.[9-12] Salen ligands give complexes which also hold promise as catalysts in enantioselective cyclopropanation of styrenes, asymmetric aziridination of olefins, asymmetric Diels-Alder cycloaddition and enantioselective ring opening of epoxides.[13] Generally, the electronic and structural properties of the ligands play an important role in the catalytic properties.[14] Thus, in view of the synthetic and biological importance of quadridentate ligands and in continuation of our studies on organotin(IV) derivatives,[15-19] we report here the synthesis and characterization of some new organotin(IV) complexes of an oxygen-nitrogen ligand containing the ONNO donor atoms.

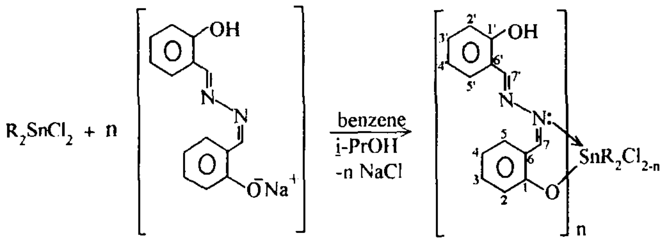
RESULTS AND DISCUSSION

The Schiff base N,N'-hydrazinebis(salicylideneimine) i.e. 1,4-bis(2-hydroxyphenyl)-2,3-diazabut-1,3-diene is prepared by the condensation of salicylaldehyde and hydrazine hydrate in 2:1 molar ratio in ethanol. Triorganotin(IV) and diorganotin(IV) derivatives of N,N'-hydrazinebis(salicylideneiminhave been synthesized by the reaction of corresponding triorganotin(IV) and diorganotin(IV) chlorides with the sodium salt of the ligand (prepared in situ) in desired molar ratios employing the following route.



(1)

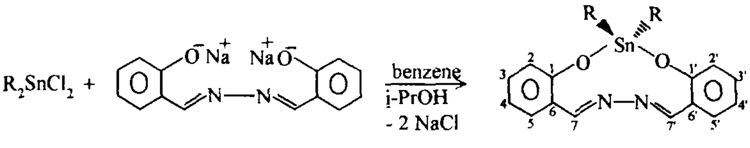
R = Ph, Compd.(1); R = n-Bu, Compd.(2)



(2)

n = 1, R = Me, Compd.(3); n = 1, R = n-Bu, Compd.(4); n = 2, R = Me, Compd.(5); n = 2, R = n-Bu, Compd.(6)

Further, diorganotin(IV) complexes of the type R_2SnL have been synthesized by the reaction of diorganotin(IV) dichloride with the disodium salt of the ligand.



(3)

R = Me, Compd.(7); R = n-Bu, Compd.(8)

This synthesis involves the initial formation of the dianion from sequential deprotonation of the ligand by sodium hydride. Intermolecular nucleophilic attack of the dianion on diorganotin(IV) chloride leads to the formation of compounds (7) and (8) with elimination of sodium chloride. All these compounds are characterized on the basis of satisfactory elemental analyses and spectral data. All these compounds are more or less soluble in common organic and coordinating solvents like C_6H_6, $CHCl_3$, CH_2Cl_2, CCl_4, DMF and DMSO. Molecular weight determinations in chloroform solution show a monomeric nature of these complexes.[19]

IR Spectral Data

The IR spectrum of the ligand shows bands at 3585-3270, 1585 and 985 cm^{-1} due to ν(OH), ν(C=N) and ν(N-N) modes, respectively. In the case of complexes **(1)** to **(6)**, two bands are observed around 1585 and 1540 cm^{-1} indicating the coordination of one of the nitrogen atoms of the two C=N groups, while in compounds **(7)** and **(8)**, only a single band around 1590 cm^{-1} is observed suggesting non-participation of both C=N groups in coordination. This is also apparent from the $\nu(Sn\leftarrow N)$ mode at 416-424 cm^{-1} in the spectra of the complexes.[20] The ligand ν(N-N) band at 985 cm^{-1} is shifted considerably ($\Delta\nu$ = 20 to 30 cm^{-1}) to lower frequencies in complexes **(1)** to **(6)** again suggesting coordination through one of the azomethine nitrogens.[21] New bands observed in all the complexes around 580 cm^{-1} may be assigned to the ν(Sn-O) mode.[19] The non-ligand band in the spectra of complexes **(3)** and **(4)** at 285 cm^{-1} may be due to the ν(Sn-Cl) vibration (Table I).

NMR Spectral Data

The ^1H NMR spectrum of the ligand displays a signal at δ 12.95 assignable to phenolic -OH protons. This signal disappears completely in the spectra of the complexes **(7)** and **(8)**, and appears in the region 12.66 - 12.80 ppm in the complexes **(1)** to **(6)**, showing integration for one to two protons, suggesting deprotonation of both -OH groups in complexes **(7)** and **(8)**, and deprotonation of only one -OH group in complexes **(1)** to **(6)**, consequently, forming tin-oxygen bond. One of the azomethine proton is deshielded and appears at ~ 8.70 ppm in the complexes **(1)** to **(6)**, indicating coordination of only one azomethine nitrogen to tin. Butyl protons exhibit a complex resonance pattern in the region 1.7-0.2 ppm. The resonance due to the phenyl moiety remains almost unaffected in all the complexes. The spectral features and integrations are consistent with the different stoichiometries and bonding sites as inferred from the infrared spectra.

^{13}C NMR spectra of some of the representative compounds were recorded in $CDCl_3$, and are a good diagnostic tool for determining the mode of bonding. On coordination, the resonances of the carbon atoms attached to the azomethine nitrogen and phenolic oxygen, shift some 15-20 ppm downfield, suggesting a bidentate character of the ligand and rendering the ligand unsymmetrical, exhibiting two resonances for two different C=N moieties as well as for the two different phenolic C-O ones. No significant change in ^{13}C chemical shifts in the spectra of compounds **(7)** and **(8)** compared to the free ligand clearly shows the absence of coordination of the azomethine nitrogens to tin. Compounds **(1)**, **(2)**, **(3)** and **(4)** show ^1J (^{119}Sn-^{13}C) values of 568, 619.2, 569.3 and 625.4 Hz, respectively, and these are characteristic of 5-coordinate tin. Whereas compounds **(5)** and **(6)** exhibit tin-carbon couplings ^1J (^{119}Sn-^{13}C) of 678 and 684 Hz, respectively, which are comparable to six-coordinated organotin(IV) derivatives. The values of the coupling constants for compounds **(7)** and **(8)** are strongly indicative of four-coordinated structures. As the complexes are monomeric, bridging of the ligand is ruled out. IR and ^{13}C NMR spectra of the complexes support the bidentate chelating nature of the ligand.

Table I. IR and NMR Spectral Data of the Compounds

Compd.	IR (cm^{-1})						NMR (δ, ppm)		
No.	ν(OH)	ν(C=N)	ν(N-N)	ν(Sn-O)	ν(Sn←N)	ν(Sn-Cl)	^{1}H	^{13}C	^{119}Sn
1.	3580 - 3270 br	1585 s 1535 vs	960 s	582 sh	420 m	—	6.56-7.98 (m, 23H, Ph), 8.66 (s, 2H, CH=N), 12.74 (br, s, 1H, OH).	158.6 (C-1), 160.2 (C-7), 174.6 (C-1'), 176.5 (C-7').	-173.8
2.	3565 - 3290 br	1580 s 1540 vs	965 vs	578 sh	422 m	—	6.64-7.52 (m, 8H, Ph), 8.60 (s, 2H, CH=N), 12.70 (br, s, 1H, OH), 0.2-1.7 (m, 27H, n-C$_4$H$_9$).	158.2 (C-1), 160.6 (C-7), 174.8 (C-1'), 176.8 (C-7').	-174.4
3.	3590 - 3295 br	1590 s 1550 vs	970 s	575 sh	418 m	285m	6.74-7.42 (m, 8H, Ph), 8.70 (s, 2H, CH=N), 12.84 (br, s, 1H, OH), 0.76 (s, 6H, SnCH$_3$).	157.6 (C-1), 159.4 (C-7), 173.9 (C-1'), 176.5 (C-7').	-176.2
4.	3570 - 3310 br	1585 s 1545 vs	965 s	580 sh	420 m	283m	6.58-7.60 (m, 8H, Ph), 8.56 (s, 2H, CH=N), 12.66 (br, s, 1H, OH), 0.36-1.60 (m, 18H, n-C$_4$H$_9$).	157.8 (C-1), 159.2 (C-7), 173.7 (C-1'), 177.1 (C-7').	-178.7
5.	3585 - 3305 br	1585 s 1535 vs	960 s	576 sh	416 m	—	6.70-7.52 (m, 16H, Ph), 8.68 (s, 4H, CH=N), 12.80 (br, s, 2H, OH), 0.78 (s, 6H, SnCH$_3$).	158.6 (C-1), 160.4 (C-7), 174.3 (C-1'), 176.7 (C-7').	-352.24
6.	3580 - 3295 br	1590 s 1545 vs	970 vs	578 sh	418 m	—	6.68-7.56 (m, 16H, Ph), 8.84 (s, 4H, CH=N), 12.76 (br, s, 2H, OH), 0.22-1.58 (m, 18H, n-C$_4$H$_9$).	157.2 (C-1), 159.7 (C-7), 173.8 (C-1'), 177.4 (C-7').	-354.36
7.	—	1585	965 s	585 sh	—	—	6.52-7.48 (m, 8H, Ph), 8.74 (s, 2H, CH=N), 0.72 (s, 6H, SnCH$_3$).	158.4 (C-1), 176.1 (C-7), 158.7 (C-1'), 176.5 (C-7').	134.64
8.	—	1590	960 s	582 sh	—	—	6.57-7.53 (m, 8H, Ph), 8.68 (s, 2H, CH=N), 0.31-1.63 (m, 18H, n-C$_4$H$_9$).	158.1 (C-1), 176.7 (C-7), 158.4 (C-1'), 176.3 (C-7').	132.4

s = strong, m = medium, vs = very sharp, sh = sharp

^{119}Sn NMR spectra of all compounds have been recorded and exhibit a sharp ^{119}Sn resonance in the region -354.36 to 134.64 ppm (Table I). The ^{119}Sn NMR spectra of the complexes **(1)** to **(4)** give signals in the region -178.7 to -173.8 ppm, and the complexes **(5)** and **(6)** show signals in the region -354.36 to -352.24 ppm, which suggest penta-coordinated[18] and hexa-coordinated[19] states around tin. Complexes **(7)** and **(8)** display a sharp ^{119}Sn resonances at δ 134.64 and 132.4 ppm, respectively, suggesting tetracoordinated tin[20].

So far, crystals suitable for X-ray diffraction have not been obtained, the actual structure can be elucidated only after an X-ray crystal structural study. Although, on the basis of above studies and reports already available in the literature, it becomes clear that the ligand is behaving in a bidentate manner coordinating through the azomethine nitrogen and phenolic oxygen. Therefore, tetra-, penta- and hexa-coordinated environments around tin in possibly tetrahedral, trigonal bipyramidal and octahedral geometries, respectively, tentatively may be proposed for the resulting complexes.

EXPERIMENTAL

All reactions were performed under a nitrogen atmosphere and with thoroughly dried solvents and glass ware. Solvents were purified and dried according to standard procedures[22]. Chemicals were obtained from Aldrich or Fluka and used without further purification. All melting points are uncorrected. The progress of the reactions were monitored by TLC on silica gel. The ligand was synthesized as previously described[21]. Elemental analyses were performed by the Central Drug Research Institute, Lucknow. Tin and chlorine in the complexes were determined by gravimetric and Messenger's method[23], respectively. Nitrogen was determined by Kjeldahl's method[23]. Infrared spectra were obtained on a model FTS 165 FTIR spectrometer. NMR spectra were recorded on a Bruker AC 200 MHz spectrophotometer at the National Chemical Laboratory, Pune. Chemical shifts are quoted in ppm relative to TMS for ^{1}H and ^{13}C, and relative to tetramethyl tin for the ^{119}Sn nucleus as an internal standard in $CDCl_3$.

Reaction Between Triphenyltin(IV) Chloride and the Sodium Salt of N,N'-Hydrazine bis(salicylideneimine) in 1:1 Molar Ratio

A quantity of 0.033 g (1.37 mmol) of sodium hydride and 20 mL of isopropanol were placed in a two necked round bottom flask fitted with a dried and cooled water condenser and addition funnel. The mixture was stirred for about half an hour till a clear solution of sodium isopropoxide was obtained. Then 0.329 g (1.37 mmol) of N,N'-hydrazinebis(salicylideneimine) was added and the mixture was refluxed. After half an hour a greenish yellow colour appeared which changed to dark yellow after two hours. After cooling, 0.528 g (1.37 mmol) of triphenyltin(IV) chloride was added slowly and the mixture was further refluxed for two hours to ensure the completion of the reaction. After filtering off the precipitated NaCl, removal of the solvent in vacuo afforded the desired compound as a yellow solid in stoichiometric yield which was recrystallized from a benzene-petroleum ether (40-60°) mixture

Table II. Synthetic, Physical and Analytical Data of the Compounds 1-8

Compd. No.	Reactants (g)			Molar ratio	Product / Mol.Wt. Found/(Calcd.)	Yield (%)	M.p. (°C)	Analysis : % Found / (Calcd.)				
	Organotin(IV) chlorides	Ligand	NaH					C	H	N	Sn	Cl
1.	Ph_3SnCl (0.528)	0.329	0.033	1:1:1	$C_{32}H_{26}N_2O_2Sn$ 567 (589)	70	202-204	65.34 (65.20)	4.22 (4.41)	4.70 (4.75)	20.47 (20.15)	—
2.	n-Bu_3SnCl (0.949)	0.700	0.070	1:1:1	$C_{26}H_{38}N_2O_2Sn$ 518 (529)	67	160-162	59.22 (58.98)	7.54 (7.18)	5.12 (5.29)	21.90 (22.44)	—
3.	Me_2SnCl_2 (0.604)	0.660	0.066	1:1:1	$C_{16}H_{17}N_2O_2SnCl$ 443 (423.5)	70	180-181	45.52 (45.34)	4.42 (4.01)	6.38 (6.61)	27.85 (28.06)	8.00 (8.38)
4.	n-Bu_2SnCl_2 (0.696)	0.550	0.055	1:1:1	$C_{22}H_{29}N_2O_2SnCl$ 527 (507.5)	72	203-205	52.37 (52.02)	5.67 (5.71)	5.29 (5.52)	23.12 (23.39)	6.88 (7.00)
5.	Me_2SnCl_2 (0.183)	0.400	0.040	1:2:2	$C_{30}H_{28}N_4O_4Sn$ 616 (627)	65	180-182	57.74 (57.42)	4.19 (4.47)	8.60 (8.93)	18.66 (18.93)	—
6.	n-Bu_2SnCl_2 (0.203)	0.320	0.032	1:2:2	$C_{36}H_{40}N_4O_4Sn$ 692 (711)	71	198-200	60.96 (60.76)	5.38 (5.63)	7.58 (7.88)	16.18 (16.69)	—
7.	Me_2SnCl_2 (0.298)	0.325	0.065	1:1:2	$C_{16}H_{16}N_2O_2Sn$ 366 (387)	70	190-192	49.98 (49.61)	4.52 (4.13)	7.02 (7.24)	30.45 (30.67)	—
8.	n-Bu_2SnCl_2 (0.462)	0.365	0.073	1:1:2	$C_{22}H_{28}N_2O_2Sn$ 452 (471)	68	174-176	56.47 (56.05)	5.73 (5.94)	5.62 (5.94)	25.57 (25.20)	—

L = [HOC_6H_4CH=N-N=CHC_6H_4OH]

(20 mL each). All other organotin(IV) derivatives of N,N'-hydrazinebis(salicylideneimine) were synthesized analogously. The pertinent data for this and other derivatives are given in Table II.

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