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Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

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Synthesis and Spectroscopic Studies (Mössbauer, IR and NMR) of Biologically Active Organotin(IV) Complexes of Schiff Bases Derived from 2-Amino-5-phenyl-1,3,4oxadiazole

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SYNTHESIS AND SPECTROSCOPIC STUDIES (MÖSSBAUER, IR AND NMR) OF BIOLOGICALLY ACTIVE ORGANOTIN(IV) COMPLEXES OF SCHIFF BASES DERIVED FROM 2-AMINO-5-PHENYL-1,3,4-OXADIAZOLE

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ABSTRACT

A few new organotin(IV) complexes of tridentate ONN donor Schiff bases of salicylaldehyde, 4-hydroxybenzaldehyde, 2-hydroxyacetophenone, 4-hydroxyacetophenone with 2-amino-5-phenyl-1,3,4-oxadiazole have been synthesised and characterised by elemental analyses. ¹H NMR, UV, IR and Mössbauer spectroscopic studies show hexa-coordination about the tin atom which is arranged in a distorted octahedral geometry. Representative complexes have been screened for their fungicidal as well as bactericidal activity and found to be quite active.

INTRODUCTION

The biological importance of organotin(IV) halides and their complexes have been recently reviewed¹. Since organotin compounds first appeared in a report on the antitumour activity and cancer chemotherapy^{2,3} of such compounds in 1980, over 2000 tin compounds have been tested by the U.S. National Cancer Institute (NCI)⁴ - more than of any other element. Dialkyltin(IV) dihalides have also been shown to be active against P388 lymphocytic leukaemia^{5,6}.

The biological importance of organotin species^{5,6} and the oxadiazole nucleus⁷ has created considerable interest in their coordination chemistry. A number of transition metal complexes containing substituted oxadiazoles have been synthesised and their antifungal activity has been evaluated^{8,9}, but only limited information on the bonding and structural features is available on the complexing behaviour of organotin(IV) complexes with the oxadiazole moiety¹⁰. Our continuing interest in chelated tin compounds^{11,12} has led us to synthesise organotin(IV) complexes of tridentate ONN donor Schiff bases derived from salicylaldehyde, 4-hydroxybenzaldehyde, 2-hydroxyacetophenone, 4-hydroxyacetophenone and 2-amino-5-phenyl-1,3,4-oxadiazole (Fig. 1) and to study their stereochemistry along with their biological activity. Furthermore, these systems serve as important models for understanding the general toxicology of organotin compounds.

RESULTS AND DISCUSSION

The reaction of tributyltin oxide with the Schiff bases proceeds smoothly, but slowly, with the elimination of water, which was removed azeotropically with benzene.

 $\frac{C_6H_6}{(Bu_3Sn)_2O + 2 HONN} \xrightarrow{-----> 2 Bu_3SnONN} + H_2O$

HONN = Tridentate Schiff bases of salicylaldehyde, 4-hydroxybenzaldehyde, 2-hydroxyacetophenone, 4-hydroxyacetophenone with 2-amino-5-phenyl-1,3,4-oxadiazole.



where X = H (2-Hydroxybenzaldehyde Schiff base): L¹H
H (4-Hydroxybenzaldehyde Schiff base): L²H
= CH₃ (2-Hydroxyacetophenone Schiff base): L³H
= CH₃ (4-Hydroxyacetophenone Schiff base): L⁴H
Fig. 1. Structural Formulae of Schiff Bases HONN

The reaction of equimolar amounts of triphenyltin chloride with the sodium salt of the Schiff bases can be depicted by the following equation.

$$CH_{3}OH$$
Ph_{3}SnCl + NaONN ------> Ph_{3}SnONN + NaCl

The resulting new derivatives are coloured solids which are soluble in DMF, DMSO, CHCl₃. The molar conductance of 10^{-3} M solutions in DMF lies in the range of 8-14 ohm⁻¹ cm² mol⁻¹, indicating their non-electrolyte behaviour. Molecular weight determinations indicate their monomeric nature. Their physical properties and elemental analyses are recorded in Table I.

IR Spectra

A comparison of the characteristic IR absorption bands (Table I) of the ligands¹³ with those of the corresponding tin(IV) complexes reveals the following

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TABLE I

Physical Characteristics, Analytical Data and Infrared Absorption Frequencies of Tin(IV) Complexes.

SI. Compound	Yield <i>m</i>	M.P.	Colour		Analyses $\%$				Characte	ristic I.R.		
ó	%	ر		Sn Found (Calcd.)	C Found (Calcd.)	N Found (Calcd.)	H Found (Calcd.)	$\gamma^{L}(C = N)$ (azome- thine)	V(N-N)	$\eta_{\rm CC} = 0$ (OXD- ring)	$\mathcal{V}^{\mathcal{L}}_{(Sn-0)}$	V(Sn-N)
1. Bu ₃ SnL ¹	90	105	Yellow	21.28	58.22	7.46 7.53)	6.64 (5.73)	1570	1080	1630	556	425
2. Bu3SnL ²	88	115	Yellow	(21.40) 22.12 (21.40)	58.24 58.47)	(7.22) 7.38 (7.67)	(0.72) 6.26 (6.77)	1572	1080	1625	563	422
C2/H3/H3/L3/C25II 3. Bu3SnL ³ CarladNaOaSh	90	66	Yellow	(20.42 (20.87)	()00.47) 59.66 (59.14)	(7.02) 7.02 (7.43)	(0.72) 6.46 (6.01)	1575	1085	1630	565	420
4. Bu3SnL ⁴ CreHanNaO-Sn	85	95	Yellow	20.46	59.26 59.4)	7.14 7.43)	(6.44 (6.41)	1575	1085	1625	562	420
5. Ph3SnL ¹ CritHreNoOch	88	180	Yellowish White	(19.20 (19.31)	(64.12 (64.49)	(6.47 (6.88)	4.12 (4.10)	1572	1095	1605	565	422
6. Ph3SnL ² CasH5cNaO5Sn	92	195	Yellowish White	19.28 (19.31)	(64.49)	(6.88)	4.02 (4.10)	1570	1093	1600	560	425
7. Ph ₃ SnL ³ CatH77NaO2Sn	90	165	Yellowish White	18.46 (18.88)	(64.96) (64.96)	6.20 (6.72)	4.10 (4.32)	1575	1095	1602	563	423
8. Ph3SnL ⁴ C34H27N3O2Sn	85	172	Ycllowish White	18.42 (18.88)	64.80 (64.96)	6.24 (6.72)	4.08 (4.32)	1570	1090	1595	560	425

important features:

- (i) In the infrared spectra of the ligands, a relatively sharp band appearing at 3350 cm^{-1} can be assigned to the hydrogen bonded $\sqrt[7]{OH}$ vibrations. In the spectra of the metal complexes this band has disappeared, showing the chelation of the phenolic oxygen to the metal atom after deprotonation, suggesting the formation of an Sn-O bond.
- (ii) A strong band at 965-1020 cm⁻¹ due to the C-O-C linkage¹⁴ and a band at 1645 cm⁻¹ assignable to $\sqrt{(C-N)}$ (ring) as well as a band at ~1025 cm⁻¹ due to $\sqrt{(N-N)}$ are also observed in the spectrum of all ligands. The shifting of the $\sqrt{(C=N)}$ ring vibrations and $\sqrt{(N-N)}$ bands to lower and higher frequencies, respectively, has been observed in all metal complexes. The presence of this band clearly indicates that the resulting metal complexes show coordination through one of the N-atoms of the oxadiazole ring.
- (iii) A band of medium intensity at $1570 \pm 10 \text{ cm}^{-1}$ in the complexes may be assigned to the $\sqrt[4]{(C=N)}$ vibration which originally appears in the ligand at $1590 \pm 10 \text{ cm}^{-1}$. The shift of this band to lower energy is probably due to an increase in the C=N bond order, showing the coordination of the azomethine nitrogen to the tin atom¹⁵. Two bands at 600 and 510 cm⁻¹ are also observed, assignable to Sn-C asymmetric and symmetric modes, respectively, and this indicates the presence of a bent C-Sn-C moiety¹⁶.

Several new band at 565 cm⁻¹ and 425 cm⁻¹ may be attributed to $\sqrt{(\text{Sn-O})}$, $\sqrt{(\text{Sn} \leftarrow N)}$, respectively, and thus tend to support the proposed coordination in the complexes.

¹H NMR Spectral Studies

The mode of bonding discussed above is further supported by the proton magnetic resonance spectral data of these complexes which have been compiled in Table II.

The phenyl protons of the salicylaldehyde and 2-hydroxyacetophenone moieties are observed as broad signals at § 7.35 ppm in all the complexes. The signal at § 11.20 ppm assigned to phenolic OH protons in the ligands, has not been observed in the spectra of all complexes, clearly indicating deprotonation. The protons of the butyl group are found to appear in the range of § 0.5 to 1.9 ppm. The signals at § 8.65 ppm and § 2.56 ppm in the complexes are due to -CH and -CH₃ protons, respectively. They are shifted downfield as compared to their positions in the ligands, owing to the donation of a lone pair of electrons by the nitrogen of the C=N group to the central tin atom on account of the formation of a coordinate linkage^{12,17}.

Electronic Spectra

The UV and visible spectra of the Schiff bases show two intense maxima at 225nm, 280 nm due to $\pi_{-}\pi^{*}$ transitions within the benzene ring and the double bond of the azomethine group, respectively. The third band observed around 360 nm may be assigned to n- π^{*} transitions of the C=N chromophore. The first two bands remain unchanged in the corresponding complexes, whereas an appreciable hypsochromic shift is observed in the third band due to the polarisation in the C=N bond caused by tin-ligand π electron interaction¹⁸.

TABLE II

¹H NMR Data (6, ppm) of Ligands and Tin(IV) Complexes

Ligands and	-OH	-C-X	-C6H4	Sn(C4H9)
Complexes		X = H; CH	13	
$L^{1}H$	11.20 bs	8.45 s	7.25 bs	-
Bu3SnL ¹	-	8.54 s	7.30 bs	0.6-1.7 m
Ph ₃ SnL ¹	-	8.68 s	7.32 bs	-
L ² H	11.20 bs	8.42 s	7.28 bs	-
Bu3SnL ²	-	8.68 s	7.32 bs	0.7-1.75 m
Ph ₃ SnL ²	-	8.65 s	7.28 bs	-
L ³ H	11.40 bs	2.40 s	7.40 bs	-
Bu ₃ SnL ³	-	2.56 s	7.32 bs	0.7-1.86 m
Ph ₃ SnL ³	-	2.60 s	7.35 bs	-
L ⁴ H	11.40 bs	2.45 s	7.40 bs	-
Bu3SnL ⁴	-	2.56 s	7.32 bs	0.6-1.9 m
Ph3SnL ⁴	-	2.64 s	7.32 bs	-

s = singlet; bs - broad singlet; m = multiplet

Mössbauer Spectra

The Mössbauer I.S. values (Table III) are typical of tin(IV) in inorganic and organometallic derivatives¹⁹. The relatively low values of I.S. indicate the coordination number to be more than four. This is supported by the quadrupole splitting (QS) and P(QS/IS) values compared with those for tin derivatives having coordination numbers four or six^{19,20}. The newly synthesised compounds give a value of 2.3 indicating a coordination number greater than four and this is unambiguously indicative of an octahedral geometry. A decrease in the isomer shift always occurs as a result of interaction of tin(IV) with nitrogen donors in an octahedral field having two Sn —N bonds²¹ with sp³d² hybridisation²². Monomeric six-coordinate structures seem to be most probable for these compounds, as the isomeric shift and quadrupole splitting values are well within the range (1.06-2.60) prescribed for octahedral geometries^{17,19}.

Thus, the tridentate behaviour of the ligand moieties and the presence of two $Sn \ll N$ dative bonds show that the complexes are six- coordinated species. The complexes may adopt any of the two geometries, or both, as shown in Fig. 2. At the present stage of the investigations no unambiguous assignment to any of the two geometries can be made.

Fungicidal and Bactericidal Activity

The compounds were tested for their fungicidal and bactericidal activity (Table IV) and the results are quite consistent with earlier reports.^{11,12} Almost all the compounds tested are very effective bactericides against *S. aureus*. The compounds screened for fungicidal activity against *A. niger* show high activity even

TABLE III

119^m Sn Mössbauer Parameters (mms⁻¹) of the Tin(IV) Complexes

Complexes	IS	QS	P = QS/IS
Bu3SnL ¹	1.06	2.38	2.24
Bu ₃ SnL ²	1.08	2.50	2.31
Bu ₃ SnL ³	1.08	2.54	2.35
Bu ₃ SnL ⁴	1.10	2.52	2.29
Ph ₃ SnL ¹	1.12	2.60	2.32
Ph ₃ SnL ²	1.12	2.62	2.33
Ph ₃ SnL ³	1.08	2.54	2.35
Ph ₃ SnL ⁴	1.10	2.56	2.32





Fig. 2. Proposed Structures of Organotin(IV) Complexes

TABLE IV

Results of Antifungal and Antibacterial Activity (% Inhibition) of Ligands and

Ligands/	Bactericid	al Activity	Fungicida	l Activity
Complexes	S. aureus		A. niger	
	0.01%	0.1%	0.01%	0.1%
L ¹ H	76.60	85.48	86.40	88.52
L^2H	70.20	82.80	80.10	85.30
L ³ H	65.40	70.14	70.80	80.46
L ⁴ H	60.80	65.20	65.40	75.25
Bu3SnL ¹	90.20	92.45	96.18	98.40
Bu ₃ SnL ²	95.40	95.10	90.60	95.75
Bu3SnL ³	92.60	95.80	92.90	95.10
Bu3SnL ⁴	90.36	92.78	95.34	95.68
Ph3SnL ¹	80.90	90.12	90.56	92.78
Ph ₃ SnL ²	85.20	90.50	90.10	90.10
Ph ₃ SnL ³	85.10	85.10	92.20	93.10
Ph3SnL ⁴	80.20	90.45	90.80	90.30

their Organo Tin(IV) Complexes in Dimethyl Sulphoxide^a

^aDimethyl sulphoxide was used as solvent for preparing different concentrations (0.01%, 0.1%) of the ligand and organotin complexes.

at low concentrations. All complexes exhibited higher activity than the parent oxadiazole ligands.

The effectiveness of the tin compounds can be best explained on the basis of a triorganotin-ligand relationship which dictates that the function of an anionic group or groups is to aid the transport of the active organotin moiety to the site of the action. It seems almost certain that the anionic ligand is displaced from tin when the organometallic unit is bonded to the active site of a biological system¹. Alternatively, the anionic ligand may remain bonded to tin until it reaches its receptor site, where it is displaced by a suitable donor atom.

EXPERIMENTAL

The chemicals and solvents used were of analytical reagent chemically pure grade. 2-Amino-5-phenyl-1,3,4-oxadiazole was prepared by a literature method²³. The Schiff bases were prepared by the condensation of aldehydes/ketones with 2-amino-5-phenyl- 1,3,4-oxadiazole⁹.

Synthesis of Bu3SnL³ Schiff Base Complex (C28H39N3O2Sn)

The title complex (Bu₃SnL³) was prepared by mixing the ligand L³H (5.6 g, 2.2 mmole) in hot benzene (100 mL) and a solution of tributyltinoxide (6.1 g, 1.1 mmole) in dry benzene (10 mL). The liberated water was removed azeotropically with benzene. The mixture was refluxed for 6-8 h, excess of solvent removed under vacuum and a solid was obtained <u>in vacuo</u> at $60\pm5^{\circ}$ C after repeated washing with ethanol, followed by ether. The coloured solid was purified by recrystallization from benzene till the compound gave a sharp melting point. Yield = 5.05 g, 90%. Other tributyltin complexes were prepared similarly.

Synthesis of Ph3SnL¹ Schiff Base Complex (C33H25N3O2Sn)

The calculated amount of the sodium salt of the Schiff base ($L^{1}Na$) (2.88 g, 1.1 mmole) in dry methanol (25 mL) was added dropwise to the weighed amount of triphenyltin chloride (3.86 g, 1.1 mmole) in dry methanol (50 mL) with constant stirring. After about 2 h a clear supernatant solution along with the precipitate of sodium chloride was obtained. Further, to ensure completion of the reaction, the contents were refluxed for 5-6 h, and sodium chloride was filtered off. The filtrate was dried under reduced pressure and the resulting product washed repeatedly with dry <u>n</u>-hexane. The complex was purified by recrystallization from dry <u>n</u>-hexane till the compound gave a sharp melting point. Yield 5.42 g, 88%. Other triphenyltin complexes were prepared similarly.

Spectral Measurements

The complexes were analysed as reported earlier¹² and the infrared spectra in the region 4000-400 cm⁻¹ of all complexes were recorded on a Perkin-Elmer 577 grating spectrophotometer as Nujol mulls. ¹H NMR spectra were recorded on a Perkin Elmer spectrophotometer in CDCl₃ using TMS as an internal standard at 90 MHz. The electronic spectra were recorded in methanol on a Unicam Sp. 500 spectrophotometer. ¹¹⁹Sn Mössbauer spectra were recorded with a Ba¹¹⁹SnO₃ source at 77K and the isomer shift values are relative to SnO₂.

The determination of the biological activity was done by methods similar to those reported in our earlier communication¹².

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