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Microwave-assisted synthesis, characterization and biological screening of nitrogen–sulphur and nitrogen–oxygen donor ligands and their organotin(IV) complexes

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Abstract

Series of new trigonal bipyramidal and octahedral complexes of tin(IV) have been synthesized by the reaction of dimethyltin(IV) dichloride with 4-nitro-benzanilidethiosemicarbazone (L^1H), 4-chlorobenzanilidethiosemicarbazone (L^2H), 4-nitrobenzanilidesemicarbazone (L^3H) and 4-chlorobenzanilidesemicarbazone (L^4H). The unimolecular and bimolecular reactions of dimethyltin(IV) dichloride and monobasic bidentate ligands were carried out using microwave irradiations as the thermal energy source and the complexes so formed were characterized by elemental analysis, conductance measurements, molecular weight determinations and spectral data, viz. IR, UV–vis, ^1H and ^{13}C NMR. The complexes have also been prepared by the general thermal methods for comparison purposes. The comparison data support the synthesis using the microwave route, i.e. green chemistry route. The tin(IV) complexes show penta-coordinated structure for 1:1 complexes and hexa-coordinated for 1:2 complexes. The antifungal, antibacterial and antifertility activities have been examined and the results were indeed very encouraging.

Keywords: Thiosemicarbazone; Semicarbazone; Spectral; Antimicrobial; Organotin(IV)

1. Introduction

Microwave synthesis represents one of the important dimensions of modern chemistry attracting a considerable amount of attention. The main advantage of microwave heating is the almost instantaneous 'in-core' heating of materials in a homogenous and selective manner, coupled with the significantly shorter reaction times that can be achieved. This implies a considerable saving in energy [1,2]. The synthesis of a number of tin metal compounds has been accomplished in pressure vessels similar to those used in high-pressure organic synthesis. Organotin compounds have been found to possess usage in wide range of products as stabilizers for PVC [3,4], efficient fungicides [5] and agrochemicals [5,6], treatment of bacterial infections [7,8], because of their low phytotoxicity and favorable environmental degradation to non-toxic inorganic tin residues [8,9]. Semicarbazones [10,11] and thiosemicarbazones [12,13] are biologically important nitrogen and oxygen/sulphur donor ligands and their organotin(IV) complexes show significant activity [14,15]. In the present study we report the synthesis, spectral characterization and the antimicrobial screening of the organotin(IV) complexes derived from the thiosemicarbazones and semicarbazones, derived from 4-nitrobenzanilide and 4-chlorobenzanilide.

2. Experimental

2.1. Analytical methods and physical measurements

All the reagents used were of AR grade and the solvents used were dried, distilled and purified by the standard methods. The dimethyltin(IV) dichloride was purchased from Alfa

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aesar. The reactions were carried out under strict anhydrous conditions and adequate care was taken to keep the organotin(IV) complexes, chemicals and glass apparatus free from moisture. The electronic spectra were recorded on Hitachi-U-2000 spectrophotometer. IR and far IR spectra were recorded on a Perkin-Elmer 577 grating spectrophotometer and FTIR spectrophotometer 8400S as Nujol mulls using KBr optics. The ^{13}C and ^{1}H NMR spectra were recorded on a JEOL AL 300 FT NMR using TMS as an internal standard. Nitrogen and sulphur were determined by the Kjeldahl's and Messenger's methods, respectively. Molecular weights were determined by the Rast Camphor method. Tin was estimated gravimetrically as SnO_2.

2.2. Antimicrobial studies

2.2.1. Antifungal studies

The linear growth method was followed wherein the ligands and their corresponding tin complexes were screened against the three pathogenic fungi, *Helminthosporium graminium*, *Rhizopus oryzae* and *Aspergillus flavus*. Methanol was used as the solvent for preparing different concentrations (0.01% and 0.1%). The growth inhibition percentage was calculated on the basis of the average diameter of the fungal colony, percentage inhibition $= (C - T) \times 100/C$, where C is the diameter of the fungus colony in the control plate after 96 h and T is the diameter of the fungus colony in tested plates after the same period.

2.2.2. Antibacterial activity

For the evaluation of antibacterial activity, the paper disc plate method was followed. A nutrient media containing 0.5% peptone, 0.15% yeast, 0.15% beef extract, 0.35% sodium chloride and 0.13% KH_2PO_4 in distilled water (1000 cm^3) was autoclaved for 20 min at 15 psi before inoculation. The compounds were dissolved in DMF at 500 and 1000 ppm concentrations. The 5 mm diameter Whatman No. 1 paper discs were soaked in different solutions of the compounds dried and then placed in petriplates previously seeded with the test organism. The plates were incubated for 24 h at 28 °C and the inhibition zone around each disc was measured.

2.2.3. Antifertility activity

The described experiments have been carried out under the approval of the Departmental Ethics Committee. The antifertility activity in male rats was carried out by using the following method. One hundred and thirty adult male Wistar rats (body weight 180–200 g) were divided into 13 groups of 10 animals each. The animals were maintained and fed with balanced pallet diet and tap water was provided *ad libitum.* One group was used as a control, and each animal of this group received 0.5 ml olive oil per day orally. The ligands (L^1H, L^2H, L^3H and L^4H) and their dimethyltin(IV) complexes were suspended in olive oil separately and given to animals orally at dose level of 2 mg day^{-1} kg^{-1} body weight for 60 days. At 24 h after the last administration of the compound, the animals were autopsied and the reproductive tract was dissected out and the mortality and the sperm counts were measured.

2.3. Preparation of the ligands

Two different routes were employed for the synthesis of the ligands for comparison purposes. These are the microwave-assisted synthesis and the thermal method. A comparison between thermal method and microwave method has been given in Table 1.

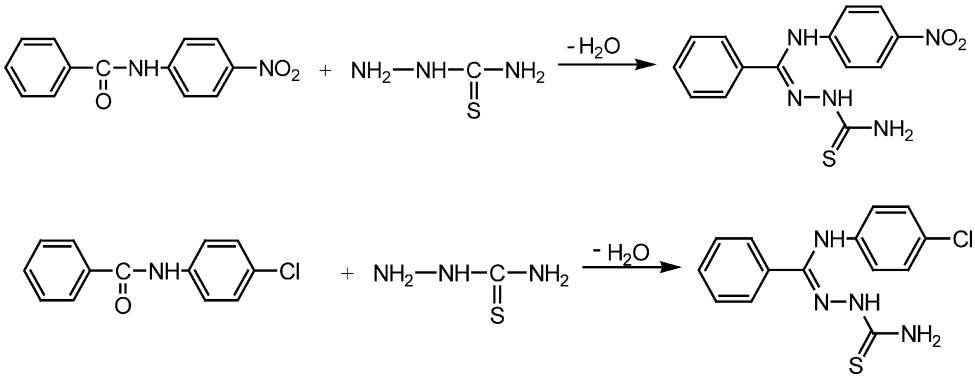
2.3.1. Microwave-assisted synthesis of L^1H and L^2H

The ligands were prepared by the condensation of thiosemicarbazide (2.0 g, 2.2 mmol) with 4-nitrobenzanilide (5.3 g, 2.2 mmol) in case of (L^1H) and 4-chlorobenzanilide (5.0 g, 2.2 mmol) in case of (L^2H) in presence of a few drops of ethanol (~3.0 ml), respectively, and irradiated by the microwave irradiation for nearly ~6 min. The resulting precipitate was then recrystallized with alcohol and dried under vacuum. The analytical results came in good consistence with the proposed formulas as follows:

Table 1
Comparison between conventional and microwave methods of synthesis

Compound	Yield (%)		Solvent (ml)		Time	
	Thermal	Microwave	Thermal	Microwave	Thermal (h)	Microwave (min)
L^1H	83	90	100	3	4.5	5
L^2H	80	90	100	3	4	4
L^3H	82	88	100	2	4	6
L^4H	82	89	100	3	4	4
$Me_2Sn(L^1)Cl$	75	82	40	2	15	3
$Me_2Sn(L^1)_2$	72	86	30	1	15	6
$Me_2Sn(L^2)Cl$	70	89	30	1	14	5
$Me_2Sn(L^2)_2$	73	87	50	2	13	5
$Me_2Sn(L^3)Cl$	71	85	40	1	16	4
$Me_2Sn(L^3)_2$	69	88	50	2	13	6
$Me_2Sn(L^4)Cl$	74	80	30	1	14	6
$Me_2Sn(L^4)_2$	70	84	30	2	15	4

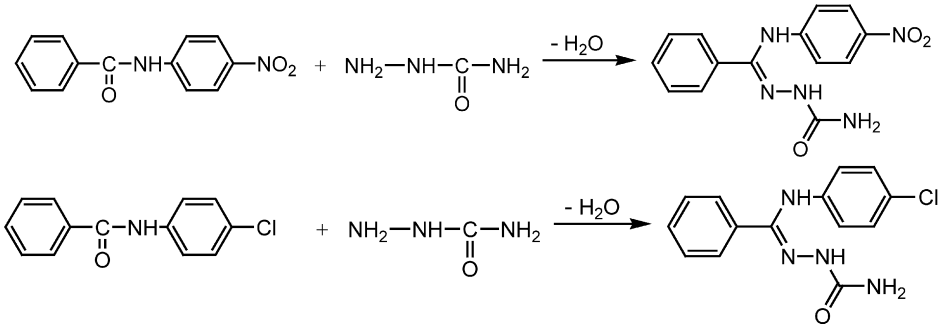
L[1]*H*. ($C_{14}H_{13}N_5O_2S$, 315.355); mustard yellow; M. Pt., 136–138; yield = 83%; C, 53.32 (52.98); H, 4.15 (3.85); N, 22.20 (21.99); S, 10.16 (9.88).
L[2]*H*. ($C_{14}H_{13}N_4ClS$, 304.803); creamy white; M. Pt., 126–131; yield = 80%; C, 55.16 (55.90); H, 4.29 (3.90); N, 18.38 (17.98); S, 10.51 (10.07); Cl, 11.63 (11.15).



2.3.2. Microwave-assisted synthesis of L^3H and L^4H

The ligands were prepared by the condensation of semicarbazide hydrochloride (2.7 g, 2.4 mmol) and sodium acetate (2.0 g, 2.4 mmol) with 4-nitrobenzanilide (5.8 g, 2.4 mmol) in case of (L^3H) and 4-chlorobenzanilide (5.6 g, 2.4 mmol) in case of (L^4H), respectively, in presence of few drops of ethanol (∼4.0 ml) and irradiated by microwave irradiation for ∼4 min. The resulting precipitate were recrystallized with alcohol and dried under vacuum.

L[3]*H*. ($C_{14}H_{13}N_5O_3$, 299.290); turmeric yellow; M. Pt., 130–135; yield = 82%; C, 56.18 (55.88); H, 4.37 (3.96); N, 23.40 (23.03).
L[4]*H*. ($C_{14}H_{13}N_4OCl$, 288.738); off-white; M. Pt., 118–123; yield = 82%; C, 58.23 (57.96); H, 4.53 (4.02); N, 19.40 (19.06); Cl, 12.27 (11.94).

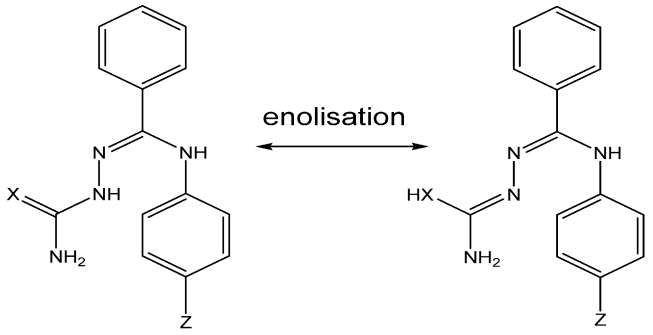


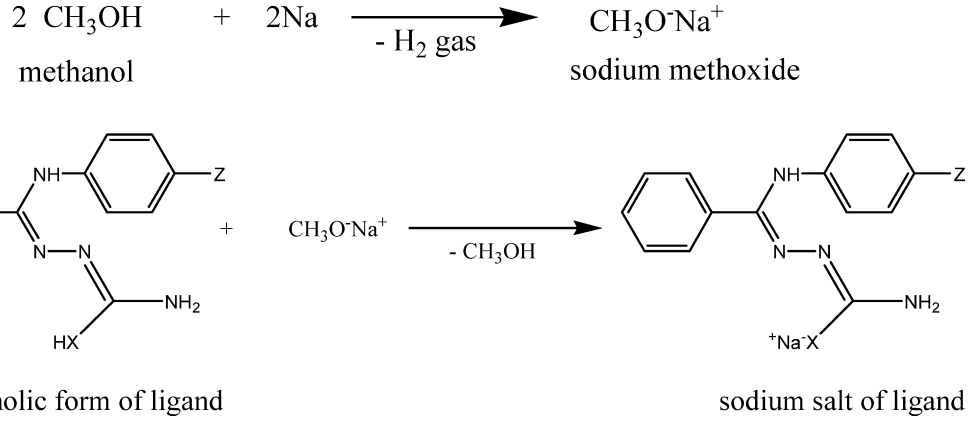
2.3.3. Conventional thermal method

Similar procedure was followed for synthesis by the thermal method where instead of few drops of alcohol the starting materials of the ligands were dissolved in minimum amount of alcohol ∼100 ml and the contents were refluxed for nearly 4.5 h. The solution was then concentrated under reduced pressure, which on cooling gave white or yellow crystalline precipitate. These were recrystallized twice in alcohol.

2.3.4. Preparation of the sodium salts of the ligands

Sodium metal was taken in equimolar ratio of the ligand. Now sodium metal and ligand were dissolved in minimum amount of methanol separately. Ultimately these two solutions had been dissolved to prepare sodium salt of the ligand. In this process the sodium metal first react with methanol and form sodium methoxide and hydrogen gas removed. This sodium methoxide in the next step reacts with the ligand and replace acidic proton from the enolic form of the ligand with sodium metal and form salt of the particular ligand. We can use the ligand as such but the rate of reaction will be slow as compare to the sodium salt. Removal of chloride from the metal chloride is easy with sodium as compare to hydrogen.





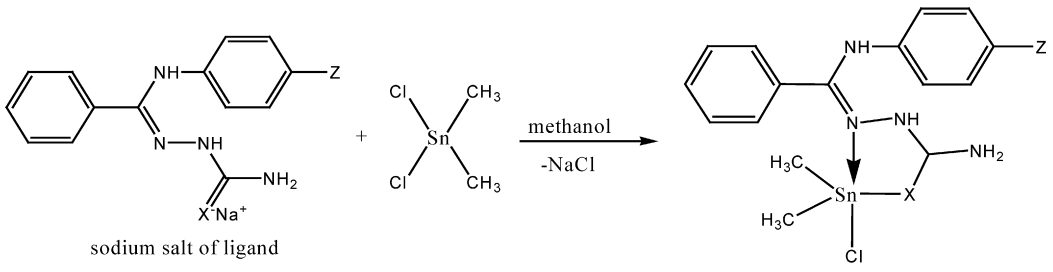
2.4. Preparation of the complexes

2.4.1. Microwave method

The reaction of dimethyltin(IV) dichloride with the corresponding sodium salt of the ligands (L^1H, L^2H, L^3H and L^4H) was carried out in equimolar and bimolar ratios, using 1–2 ml of methanol as a solvent in a microwave oven for ~6 min. The product recovered from the microwave oven and dissolved in few milliliters of dry methanol; the white precipitate of NaCl formed during the course of the reaction was removed by filtration and the filtrate was dried under reduced pressure. The resulting products were repeatedly washed and dried with *n*-hexane and petroleum ether and finally dried at 40–60 °C/0.5 mmHg for3–4 h.

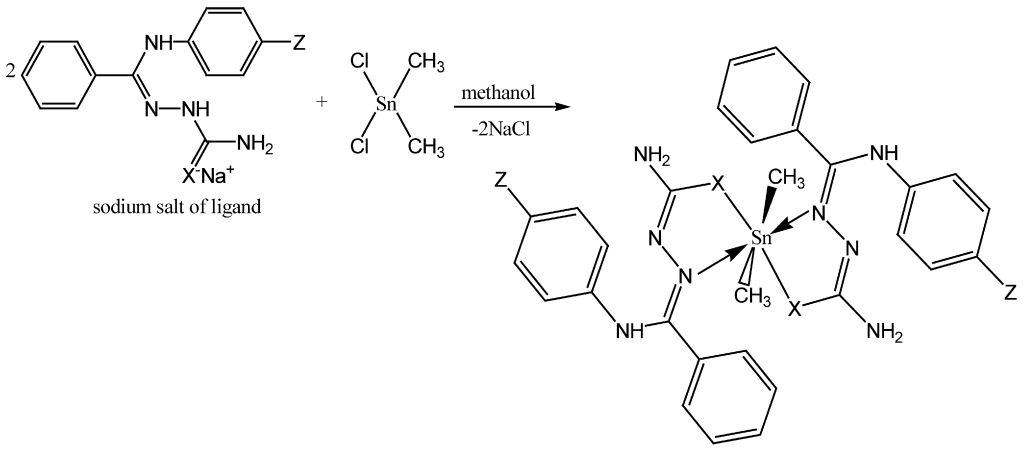
2.4.2. Thermal method

In the thermal method instead of 3–6 min reactions were completed in 13–15 h and the reaction mixture was refluxed for about 14–17 h over a distillation assembly fitted with quick fit interchangeable joints, and the white precipitate of sodium chloride obtained, was removed by filtration. The mother liquor was concentrated by removing the excess of solvent. Compounds were dried under reduced pressure for 3–4 h. These were purified by the same process as described in the above method. The purity was further checked by thin-layer chromatography using silica gel-G.



sodium salt of ligand

1:1 complex



sodium salt of ligand

1:2 complex

where,

	X	Z
L^1 =	S	NO_2
L^2 =	O	Cl
L^3 =	S	NO_2
L^4 =	O	Cl

3. Results and discussion

3.1. Elemental analysis and electronic spectra

The resulting coloured complexes were found to be monomeric in nature as evidenced by their molecular weight determinations. All the complexes are soluble in most of the common organic solvents and showed sharp melting points. The physical properties and analytical data of the organotin(IV) complexes are enlisted in Table 2. The UV spectra of the ligands (L^1H, L^2H, L^3H and L^4H) exhibit three intense maxima at ca. 43478, 37037 and 31250 cm^{-1}. The maxima at ca. 43478 and 37037 cm^{-1} are due to π–π* (benzenoid) electronic transitions. Another band at 31250 cm^{-1} may be due to n–π* transitions of the azomethine group. This band undergoes a blue shift on complexation due to the coordination of nitrogen atom to the central metal atom.

3.2. IR spectra

Table 3 lists the significant IR bands in the region 4000–200 cm^{-1} of organotin(IV) complexes that are useful for the establishment of the mode of the coordination of thiosemicarbazones and semicarbazones. The spectra of the free ligands display absorption bands at 3150–3250 cm^{-1}; 3360 cm^{-1}; 1680–1640 cm^{-1}; 1030 cm^{-1} and 1610 cm^{-1} due to ν(N–H); ν(–NH_2); ν(>C=O); ν(>C=S); and ν(>C=N), respectively. The IR spectra of the ligands L^1H and L^2H do not display ν(SH) band in 2600–2450 cm^{-1} region suggesting that in the solid state, Schiff base remain in thio-keto/keto form but in solution it may remain as an equilibrium mixture of both the thioketo and thiol/keto and enol tautomeric forms [16].

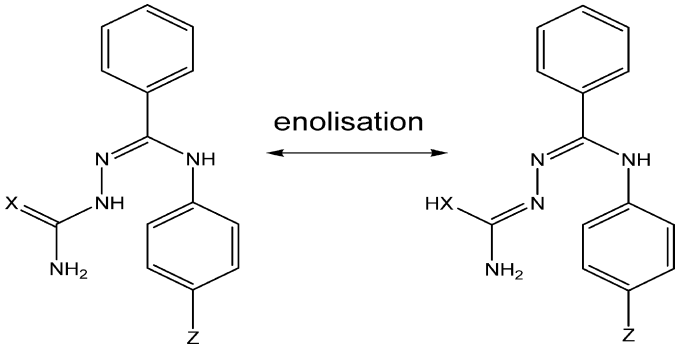
Several significant changes with respect to the ligand bands on complexation suggest coordination through the azomethine and oxygen and sulphur of the enolic or thiolic forms of the ligands, respectively. The ν(N–H), ν(>C=O) and ν(>C=S) absorption bands are absent in complexes, thereby indicating ligand enolization, followed by deprotonation during complexation to the metal atom. The sharp band at ∼1615 cm^{-1} due to ν(>C=N) shifts to the higher frequency (ca. 10 cm^{-1}) on complexation.

Table 2
Physical properties and analytical data of the ligands and their corresponding organotin(IV) complexes

Compound	Color	M. Pt. (°C)	Analysis (%) found (calculated)						M. Wt. found (calculated)
			C	H	N	S	Cl	Sn	
$Me_2Sn(L^1)Cl$	Pale yellow	210–215	37.85 (38.54)	3.38 (3.63)	13.82 (14.04)	6.18 (6.43)	6.80 (7.11)	22.80 (23.8)	469.32 (498.56)
$Me_2Sn(L^1)_2$	Yellow	218–221	45.78 (46.34)	3.52 (3.88)	17.82 (18.01)	7.97 (8.24)	–	14.97 (15.26)	751.48 (777.45)
$Me_2Sn(L^2)Cl$	Dirty white	206–208	38.87 (39.37)	3.48 (3.71)	11.18 (11.48)	6.24 (6.57)	13.26 (14.52)	24.01 (24.32)	463.36 (488.01)
$Me_2Sn(L^2)_2$	Creamy white	211–213	47.08 (47.64)	3.72 (3.99)	14.61 (14.81)	8.15 (8.47)	9.10 (9.37)	15.37 (15.69)	727.54 (756.35)
$Me_2Sn(L^3)Cl$	Light yellow	223–226	39.58 (39.82)	3.47 (3.76)	14.24 (14.51)		7.03 (7.34)	24.21 (24.59)	459.36 (482.49)
$Me_2Sn(L^3)_2$	Yellow green	207–229	47.88 (48.34)	3.75 (4.05)	18.44 (18.79)		–	15.69 (15.92)	718.42 (745.32)
$Me_2Sn(L^4)Cl$	Off white	214–218	40.15 (40.69)	3.64 (3.90)	11.63 (11.86)		14.76 (15.01)	24.83 (25.13)	449.86 (472.24)
$Me_2Sn(L^4)_2$	Off white	219–221	49.23 (49.75)	3.82 (4.17)	15.25 (15.47)		9.54 (9.79)	16.12 (16.38)	698.87 (724.22)

Table 3
IR spectral data (cm^{-1}) of the ligands and their organotin(IV) complexes

Compound	ν(>NH)	ν(C=N)	ν(NH_2)	ν(C=O)	ν(C=S)	ν(Sn–O)	ν(Sn–S)	ν(Sn ← N)	ν(Sn–Cl)
L^1H	3142–3246	1612	3355, 3431		1030				
L^2H	3150–3250	1620	3360, 3440		1044				
L^3H	3128–3224	1608	3340, 3418	1630, 1675					
L^4H	3135–3238	1615	3346, 3423	1640, 1680					
$Me_2Sn(L^1)Cl$		1622	3354, 3430				325	420	340
$Me_2Sn(L^1)_2$		1625	3355, 3432				328	420	
$Me_2Sn(L^2)Cl$		1630	3360, 3439				330	425	346
$Me_2Sn(L^2)_2$		1632	3360, 3440				334	425	
$Me_2Sn(L^3)Cl$		1619	3340, 3418			530		415	330
$Me_2Sn(L^3)_2$		1622	3341, 3418			535		415	
$Me_2Sn(L^4)Cl$		1625	3345, 3423			536		422	338
$Me_2Sn(L^4)_2$		1628	3446, 3424			540		422	



Several new bands observed in the far IR region of the tin complexes at ~530 cm^{-1}, ~420 cm^{-1}, ~325 cm^{-1} and ~340 cm^{-1} are assigned to ν(Sn–O), ν(Sn ← N), ν(Sn–S) and ν(Sn–Cl),respectively.

3.3. ^1H NMR spectra

The ^{1}HNMR spectral data of the ligands and their corresponding organotin(IV) complexes were recorded in d_6-DMSO taking TMS as an internal standard. The spectra of the ligands exhibit signals due to –CH aromatic protons (δ, 6.25–8.80 ppm), –NH (δ, 10.00–10.32 ppm) of semicarbazone and thiosemicarbazone. The disappearance of –NH signal of the semicarbazone and thisemicarbazone residue in the organotin(IV) derivatives indicate the coordination of azomethine nitrogen as well as covalent bond formation between metal and oxygen/sulphur due to deprotonation of enolic form of the ligands. The appearance of signals due to NH_2 group at nearly the same position (δ, 3.42–4.20 ppm) in ligands and their organotin(IV) complexes show the non-involvement of this group in coordination. The proton signals of the methyl groups appear at (δ, 1.12–1.34 ppm) in the organotin(IV) complexes. The ^{1}H NMR values for all the compounds are given in Table 4.

3.4. ^{13}C NMR spectra

^{13}C NMR spectral data (Table 5) also support the authenticity of the proposed structures. The considerable shifts in the positions of carbon atoms adjacent to the azomethine nitrogen (157.72–162.91 ppm) and thiolic sulphur/enolic oxy-

Table 4
^{1}HNMR spectral data (δ, ppm) of the ligands and their compounds

Compound	Ar–NH	–NH	Aromatic	$–NH_2$
L^1H	10.50 (bs)	10.32 (bs)	8.32–6.80 (m)	4.40 (bs)
L^2H	10.48 (bs)	10.32 (bs)	8.28–6.74 (m)	3.48 (bs)
L^3H	10.56 (bs)	10.00 (bs)	8.24–6.96 (m)	4.10 (bs)
L^4H	10.42 (bs)	10.00 (bs)	8.20–6.80 (m)	3.42 (bs)
$Me_2Sn(L^1)Cl$	10.88 (bs)		8.40–6.88 (m)	4.20 (bs)
$Me_2Sn(L^1)_2$	10.85 (bs)		8.46–6.94 (m)	4.20 (bs)
$Me_2Sn(L^2)Cl$	10.87 (bs)		8.38–6.79 (m)	3.48 (bs)
$Me_2Sn(L^2)_2$	10.83 (bs)		8.45–6.84 (m)	3.48 (bs)
$Me_2Sn(L^3)Cl$	10.80 (bs)		8.56–6.72 (m)	4.10 (bs)
$Me_2Sn(L^3)_2$	10.78 (bs)		8.60–6.84 (m)	4.10 (bs)
$Me_2Sn(L^4)Cl$	10.82 (bs)		8.51–6.64 (m)	3.42 (bs)
$Me_2Sn(L^4)_2$	10.80 (bs)		8.57–6.73 (m)	3.42 (bs)

Table 5
^{13}C NMR spectral data (δ, ppm) of the ligands and their corresponding organotin(IV) complexes

Compound	>C=S/>C=O	>C=N	Aromatic carbon
L^1H	175.82	162.91	158.2, 157.9, 132.4, 129.8, 127.9, 129.4, 124.3,118.4
L^2H	170.96	158.64	144.6, 132.4, 131.6, 129.8, 129.4, 127.9, 126.3, 118.2
L^3H	168.60	157.72	157.6, 156.8, 132.8, 129.4, 128.9, 127.9, 125.4, 119.1
L^4H	166.92	151.28	143.9, 132.4, 131.6, 130.4, 128.1, 127.9, 127.3, 119.1
$Me_2Sn(L^1)Cl$	165.78	155.76	158.2, 157.6, 132.4, 128.9, 128.8, 127.9, 124.3, 118.4
$Me_2Sn(L^1)_2$	165.78	155.76	157.6, 157.4, 132.4, 128.4, 127.9, 127.6, 125.2, 118.1
$Me_2Sn(L^2)Cl$	162.48	143.21	145.4, 132.4, 131.4, 129.8, 129.4, 127.8, 125.9, 118.2
$Me_2Sn(L^2)_2$	162.48	143.21	145.1, 131.4, 131.9, 129.8, 129.4, 127.8, 126.3, 118.2
$Me_2Sn(L^3)Cl$	161.5	149.82	157.9, 156.8, 133.4, 129.4, 128.9, 127.9, 125.4, 119.2
$Me_2Sn\ (L^3)_2$	161.5	149.82	156.9, 156.4, 132.8, 129.4, 128.9, 127.9, 125.4, 119.2
$Me_2Sn(L^4)Cl$	158.64	142.47	144.4, 132.4, 130.4, 128.1, 127.9, 131.6, 128.3, 119.4
$Me_2Sn(L^4)_2$	158.64	142.47	143.9, 132.8, 131.6, 130.4, 128.4, 128.1, 127.9, 119.4

Table 6
Fungicidal screening data of the ligands and their corresponding complexes

Compound	Average % inhibition after 96 h			
	Rhizopus oryzae		*Aspergillus flavus*	
	Concentration (0.01%)	Concentration (0.1%)	Concentration (0.01%)	Concentration (0.1%)
L^1H	38	50	45	56
L^2H	35	46	40	51
L^3H	36	47	42	53
L^4H	33	42	39	48
$Me_2Sn(L^1)Cl$	44	74	53	80
$Me_2Sn(L^1)_2$	56	85	60	77
$Me_2Sn(L^2)Cl$	40	68	48	70
$Me_2Sn(L^2)_2$	52	81	64	79
$Me_2Sn(L^3)Cl$	42	68	51	75
$Me_2Sn(L^3)_2$	50	76	57	80
$Me_2Sn(L^4)Cl$	46	59	48	60
$Me_2Sn(L^4)_2$	57	67	59	72

gen (δ, 168.60–175.82 ppm) support the proposed coordination in the complexes. The shifts in the positions of carbon atoms adjacent to the coordinating atoms clearly indicate the bonding of the azomethine nitrogen to the central metal atom.

3.5. Antimicrobial screening

3.5.1. Antifungal activity

Found values of the percentage inhibition of the ligands and their tin complexes are reported in Table 6. It is clear from the

Table 7
Bactericidal screening data of the ligands and their corresponding organotin(IV) complexes (concentration, ppm)

Compound	Diameter of inhibition zone (mm) after 24 h							
	Escherichia coli (−)		*Pseudomonas cepaciocola* (−)		*Klebsiclla acrogenons* (−)		*Staphylococcus aureus* (+)	
	500	1000	500	1000	500	1000	500	1000
L^1H	10	12	11	13	7	11	14	16
L^2H	7	10	9	11	10	13	11	14
L^3H	9	11	11	14	12	14	13	15
L^4H	7	9	10	13	9	11	10	13
$Me_2Sn(L^1)Cl$	12	14	13	15	12	7	15	18
$Me_2Sn(L^1)_2$	14	16	14	17	14	18	17	21
$Me_2Sn(L^2)Cl$	9	12	11	13	10	14	12	16
$Me_2Sn(L^2)_2$	10	11	12	14	11	13	14	19
$Me_2Sn(L^3)Cl$	11	13	12	15	13	14	14	17
$Me_2Sn\ (L^3)_2$	12	15	14	16	15	17	15	20
$Me_2Sn(L^4)Cl$	8	10	10	13	10	14	11	15
$Me_2Sn(L^4)_2$	10	13	13	14	11	16	13	18

Table 8
Effect of ligands and organotin(IV) complexes on sperm dynamics and fertility of male rats (values are expressed as mean ± S.E.M.)

Group	Treatment	Sperm molality (*Cauda epididymis*) (%)	Sperm density (million/ml)		Fertility %
			Testes	*Cauda epididymis*	
A	Control	86.85 ± 3.8	5.17, 0.63	63.26, 2.9	100(+)
B	L^1H	43.18[a] ± 3.2	3.69[a], 0.22	45.28[a], 2.9	60(−)
C	L^2H	45.98[a] ± 2.8	3.51[a], 0.51	48.19[a], 3.1	58(−)
D	L^3H	46.62[b] ± 2.9	3.86[b], 0.48	50.28[b], 3.6	55(−)
E	L^4H	61.50[b] ± 1.7	4.23[b], 0.41	53.25[b], 3.7	48(−)
F	$Me_2Sn(L^1)Cl$	25.17[a] ± 1.8	0.78[a], 0.11	21.11[a], 2.6	95(−)
G	$Me_2Sn(L^1)_2$	28.63[a] ± 2.2	0.95[a], 0.12	23.91[a], 2.1	90(−)
H	$Me_2Sn(L^2)Cl$	40.22[b] ± 2.5	3.16[b], 0.28	38.16[b], 2.8	78(−)
I	$Me_2Sn(L^2)_2$	38.48[a] ± 3.1	2.63[a], 0.22	34.41[a], 3.7	83(−)
J	$Me_2Sn(L^3)Cl$	26.53[a] ± 2.5	1.46[a], 0.25	22.76[a], 3.2	92(−)
K	$Me_2Sn(L^3)_2$	29.06[a] ± 1.8	0.99[a], 0.13	23.68[a], 2.9	90(−)
L	$Me_2Sn(L^4)Cl$	36.23[a] ± 3.1	2.32[a], 0.49	31.89[a], 3.3	85(−)
M	$Me_2Sn(L^4)_2$	39.91[a] ± 2.7	2.88[a], 0.38	36.55[a], 2.8	80(−)

Mean ± S.E.M. of 10 animals. [a]$p \leq 0.001$ highly significant; [b]$p \leq 0.01$ significant; [c]significant; dose = 2 mg/kg between day^{-1} for 60 days.

fungicidal screening data that the metal complexes are more fungitoxic than the ligands themselves. Further, it was noted that the lower concentrations of the compounds could check growth in the fungi and at higher concentration; the growth of the organisms is comparatively more inhibited.

3.5.2. Antibacterial activity

The bactericidal data reported in Table 7 indicate that the activity of the ligand was appreciably enhanced on complexation with organotin(IV) halide. This may be explained by chelation theory [17], according to which chelation reduces the polarity of the central metal atom because of partial sharing of its positive charge with the donor groups and possible π-electron delocalization within the whole chelate ring. This chelation increases the lipophilic nature of the central atom, which favors the permeation of the complexes through the lipid layer of the cell membrane. Compounds inhibit the growth of bacteria to greater extent as concentration is increased. Also, the complexes of 4-nitrobenzanilidethiosemcarbzone and 4-nitrobenzanilidesemicarbazone were found to possess higher activity than 4-chlorobenzanilidethiosemicarbazone and 4-chlorobenzanilidesemicarbazone.

From the bactericidal activity, it is apparent that the complexes were more toxic towards Gram (+) strains than Gram (−) strains. The reason is the difference in the structures of the cell walls. The walls of Gram (−) cells are more complex than those of Gram (+) cells. Lipopolysacharides form an outer lipid membrane and contribute to the complex antigenic specificity of Gram (−) cells.

3.5.3. Antifertility activity

The results reported in Table 8, reveal that there is a significant reduction ($p \leq 0.001$) in sperm motility from 86.85 ± 3.8 to 25.17 ± 1.8, in animals treated with $Me_2SnCl(L^1)$ complex; the testicular sperm density also diminished significantly ($p \leq 0.001$) from 5.17 ± 0.63 to 0.78 ± 0.11 in testes, and from 63.26 ± 2.9 to 21.11 ± 2.6 in cauda epididymis.

The fertility percent varied between 100% positive to 95% negative. These results may also be correlated with the well-known fact that sulphur-containing compounds produce infertility in male rats [18]. Thus, it can be postulated that coordination through sulphur atoms induces the sterilizing activity in the biological systems.

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