

Bioactive Versatile Azomethine Complexes of Organotin(IV) and Organosilicon(IV)

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Diorganotin(IV) and diorganosilicon(IV) derivatives of the types $R_2MCl(TSCZ)$ and $R_2M(TSCZ)_2$ (where TSCZ is the anion of a thiosemicarbazone ligand, $R=Ph$ or Me and $M=Sn$ or Si) have been synthesized and characterized by elemental analyses, molecular weight determinations and conductivity measurements. The mode of bonding has been established on the basis of IR and 1H , ^{13}C , ^{29}Si and ^{119}Sn NMR spectroscopic studies. Some of the representative complexes have also been evaluated for their antimicrobial effects on different species of pathogenic fungi and bacteria *in vivo* as well as *in vitro*. The results of these investigations are reported. © 1997 John Wiley & Sons, Ltd.

Appl. Organometal. Chem. **11**, 39–46 (1998)

Keywords: organotin(IV); organosilicon(IV) complexes; thiosemicarbazones; antimicrobial studies; NMR spectra

Received 28 January 1997; accepted 12 June 1997

INTRODUCTION

This work stemmed from our interest in the development of a systematic synthetic methodology for the preparation of new series of diorganotin and diorganosilicon complexes. Organotin and organosilicon compounds exhibit a broad spectrum of biological activity which includes bactericidal,^{1,2} fungicidal,³ antitumour⁴ and acaricidal effects. Our ongoing work with chelated tin(IV) derivatives⁶ involving such systems led us to describe the synthetic and

stereochemical features of some diorganotin dihalide complexes. The interest in organosilicon compounds is generated by the wide applicability of organosiloxane elastomers, resins and liquid polymers.^{7,8} The biochemistry of synthetic organometallics has generated active research relating to their biochemical significance.^{12–14} The importance of metal–nitrogen and metal–sulphur bonding and their prominence in agricultural, medicinal and industrial chemistry led us to screen the ligands and their organometallic compounds for their antifungal and antibacterial activities.

EXPERIMENTAL

All the chemicals used were dried and distilled before use. Glass apparatus fitted with Quickfit interchangeable standard ground joints was used throughout. Moisture was excluded from the apparatus by using calcium chloride drying tubes.

Preparation of ligands

The ligands were prepared by the condensation of heterocyclic ketones, i.e. 1,3-dihydro-3-(2-phenyl-2-oxoethylidene)-2H-indol-2-one, and 2-phenyl-3-(3-phenyl-3-oxoprop-1-enyl)indole with hydrazine carbothioamide in 1:1 molar ratio in absolute ethanol to give **L**₁ and **L**₂ respectively. These were purified by recrystallization from the same solvent and analysed before use. The deprotonated forms of the ligands can be represented by the structures **L**₁ and **L**₂.

A typical procedure was as follows. To a weighed amount of R_2MCl_2 (where $R=Ph$ or Me ; $M=Sn$ or Si) in dry methanol was added the sodium salt of the thiosemicarbazone ligand (TSCZH) (prepared by treating the ligand with sodium metal in dry methanol) in 1:1 and 1:2 molar ratios. The contents were refluxed for 5–6 h, filtered to remove sodium chloride, and

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the excess of the solvent was removed under reduced pressure. The complexes thus obtained were purified by repeated washing with dry n-hexane (Table 1).

Analytical methods and physical measurements

Nitrogen and sulphur were estimated by the Kjeldahl and Messenger methods, respectively. Tin and silicon were estimated gravimetrically.¹⁵ Molecular weights were determined by the Rast

camphor method and conductivity was measured at 32 ± 1 °C with a conductivity bridge (Type 304 Systronics model). Infrared spectra were recorded on an FTIR spectrophotometer in KBr pellets. ¹H, ¹³C, ¹¹⁹Sn and ²⁹Si NMR spectra were recorded on a JEOL FX 90Q spectrometer.

Microbial assays

Bioefficacies of the synthesized compounds were checked *in vitro* and *in vivo*. The *in vitro* antifungal activities of the ligands and their complexes have been evaluated against several fungi by the radial growth method.²¹ The compounds were directly mixed with the medium in different concentrations. Controls were also run and three replicates were used in each case. The linear growth of the fungus was obtained by measuring the diameter of the fungal colony after four days. The amount of growth inhibition in each of the replicates was calculated by Eqn [1], (see top of next page) where C is the diameter of the colony on the control plate and T is the diameter of the fungal colony on the test plate.

Determination of antibacterial activity was carried out by the inhibition zone technique. All the compounds were dissolved in methanol; paper discs of Whatman No. 1 paper with a

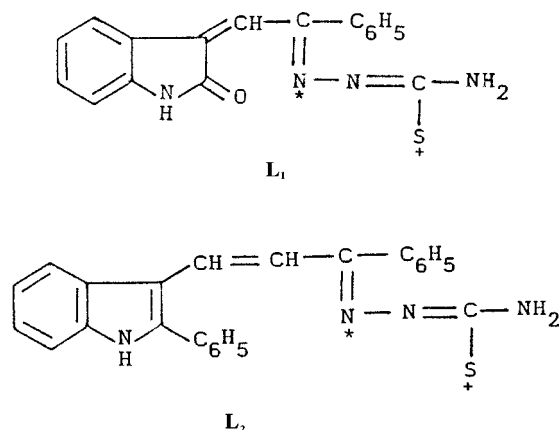
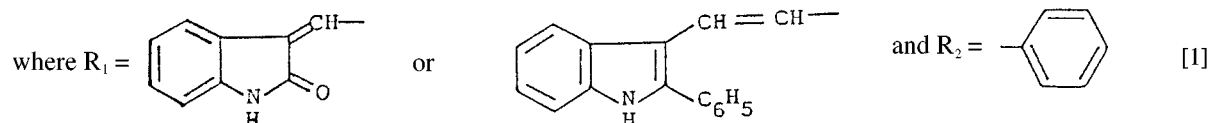


Table 1 Physical properties and analytical data of ligands and their complexes

Compound	Colour	M.p. (°C)	Analysis (%)		
			N Found (calcd)	S Found (calcd)	Sn/Si Found (calcd)
L ₁ H	Red	173–175	17.09 (17.37)	9.36 (9.34)	—
Ph ₂ SnCl(L ₁)	Orange	178–180	8.05 (8.89)	5.01 (5.09)	18.50 (18.73)
Ph ₂ Sn(L ₁) ₂	Wine red	178–182	12.03 (12.23)	6.75 (7.00)	12.23 (12.96)
Me ₂ SnCl(L ₁)	Orange	180–183	10.93 (11.08)	6.15 (6.34)	23.17 (23.47)
Me ₂ Sn(L ₁) ₂	Red	185–187	14.01 (14.15)	8.05 (8.10)	14.52 (14.99)
Ph ₂ SiCl(L ₁)	Wine red	175–178	10.05 (10.39)	5.50 (5.95)	5.07 (5.21)
Ph ₂ Si(L ₁) ₂	Brown	179–180	13.08 (13.58)	7.07 (7.77)	3.18 (3.40)
Me ₂ SiCl(L ₁)	Peach	160–163	13.01 (13.50)	7.50 (7.72)	6.22 (6.76)
Me ₂ Si(L ₁) ₂	Brown	159–161	15.11 (15.98)	9.05 (9.14)	3.90 (4.00)
L ₂ H	Peach	178–180	14.03 (14.13)	8.00 (8.08)	—
Ph ₂ SnCl(L ₂)	Yellow	180–182	7.02 (7.96)	4.16 (4.55)	16.23 (16.86)
Ph ₂ Sn(L ₂) ₂	Orange	185–187	10.05 (10.53)	5.93 (6.03)	11.06 (11.16)
Me ₂ SnCl(L ₂)	Red	186–189	9.23 (9.66)	5.17 (5.53)	20.15 (20.47)
Me ₂ Sn(L ₂) ₂	Wine red	190–192	11.50 (11.92)	6.50 (6.82)	12.30 (12.63)
Ph ₂ SiCl(L ₂)	Brown	160–168	9.03 (9.14)	5.09 (5.23)	4.14 (4.58)
Ph ₂ Si(L ₂) ₂	Brown	168–170	11.23 (11.51)	6.13 (6.59)	2.50 (2.89)
Me ₂ SiCl(L ₂)	Orange	172–175	11.15 (11.45)	6.20 (6.55)	5.45 (5.74)
Me ₂ Si(L ₂) ₂	Peach	179–180	13.05 (13.20)	7.17 (7.55)	3.16 (3.31)

$$\text{Percentage inhibition} = \frac{(C - T) \times 100}{C}$$



diameter of 5 mm were soaked in these solutions. These discs were placed on the appropriate medium previously seeded with organisms in Petri dishes and stored in an incubator at $30 \pm 1^\circ\text{C}$. The inhibition zone thus formed around each disc was measured (in mm) after 24 h.

In vivo tests were conducted under field conditions, on Guar (guar blight) and Bajra (rust). Disease severity was measured using the Horsfall and Barratt scale for guar blight and the Peterson scale for the rust. The parameter measured, percentage disease incidence (PDI), is

given by Eqn [2]:

$$\text{PDI} = \frac{\text{number of plant units infected} \times 100}{\text{total number of plants observed} \times \text{maximum rating (10)}} \quad [2]$$

The effectiveness of the complexes was calculated using Eqn [3]:

$$\text{Disease control (\%)} = \frac{\text{PID in treated plants} - \text{PDI in untreated plants}}{\text{PDI in untreated plants}} \times 100 \quad [3]$$

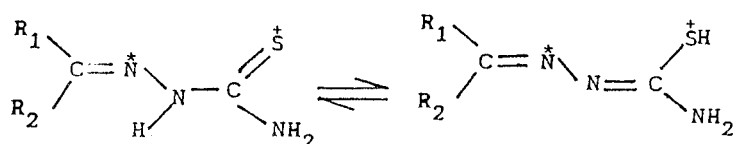


Table 2 ^1H NMR data (δ , ppm) of ligands and their complexes

Compound	NH(I) ring (bs) ^a	NH(II) free (bs)	NH ₂ (bs)	Aromatic protons (m) ^a	>C=N (s)	M-CH ₃ /C ₆ H ₅
L ₁ H	12.80	10.32	3.46	7.94–7.54	8.64	—
Ph ₂ SnCl(L ₁)	12.64	—	3.72	7.68–6.65	8.33	6.84
Ph ₂ Sn(L ₁) ₂	12.88	—	3.14	7.88–6.74	8.72	6.92
Me ₂ SnCl(L ₁)	12.72	—	3.12	7.96–6.90	8.68	1.14
Me ₂ Sn(L ₁) ₂	12.68	—	3.16	7.78–6.70	8.72	1.05
Ph ₂ SiCl(L ₁)	12.77	—	3.36	7.92–6.76	8.70	6.24
Ph ₂ Si(L ₁) ₂	12.78	—	3.08	7.94–6.54	8.65	6.44
Me ₂ SiCl(L ₁)	12.36	—	3.04	7.24–6.96	8.35	0.74
Me ₂ Si(L ₁) ₂	12.32	—	3.00	8.64–7.16	8.32	0.98
L ₂ H	10.04	9.72	2.04	8.16–6.96	8.24	—
Ph ₂ SnCl(L ₂)	10.72	—	2.74	8.40–6.96	8.64	7.00
Ph ₂ Sn(L ₂) ₂	10.68	—	2.65	8.48–7.12	9.08	7.08
Me ₂ SnCl(L ₂)	10.70	—	2.32	8.24–7.72	8.16	1.22
Me ₂ Sn(L ₂) ₂	10.64	—	2.28	8.64–7.16	8.08	1.24
Ph ₂ SiCl(L ₂)	10.68	—	2.35	8.28–7.10	8.56	6.36
Ph ₂ Si(L ₂) ₂	10.36	—	2.36	8.48–7.08	8.80	6.32
Me ₂ SiCl(L ₂)	10.16	—	2.28	8.04–6.84	8.24	0.84
Me ₂ Si(L ₂) ₂	10.12	—	2.26	8.08–6.92	8.12	0.66

^a bs, broad singlet; s, singlet; m, multiplet. DMSO-d₆, δ 2.54 ppm (s).

Table 3 ^{13}C NMR data (δ , ppm) of ligands and their complexes

Compound	Thiolo C atom	Azomethine C atom	NH-C=O NH-C-Ph	Aromatic carbons	M-Me/Ph ^a
L_1H	167.65	158.92	165.86	141.29, 126.72, 129.10 129.64, 123.52, 123.41	—
$\text{Ph}_2\text{SnCl}(\text{L}_1)$	165.88	156.08	165.04	150.10, 131.20, 129.80 141.40, 130.60, 131.50	129.13, 130.12 132.64, 136.86
$\text{Ph}_2\text{Sn}(\text{L}_1)_2$	166.08	156.51	165.48	146.50, 135.07, 126.30 129.56, 127.60, 125.18	132.04, 132.96 134.16, 136.92
$\text{Me}_2\text{SiCl}(\text{L}_1)$	162.42	146.82	165.32	143.82, 127.96, 126.68 123.32, 122.36, 120.66	14.56
$\text{Me}_2\text{Si}(\text{L}_1)_2$	164.32	148.24	166.02	143.92, 127.88, 126.66 123.46, 122.48, 120.66	15.34
L_2H	168.58	157.64	168.50	143.66, 123.34, 120.23 146.04, 127.85, 126.54	—
$\text{Me}_2\text{SnCl}(\text{L}_2)$	159.73	152.56	168.08	152.32, 145.07, 130.60 129.80, 126.90, 135.07	16.37
$\text{Me}_2\text{Sn}(\text{L}_2)_2$	158.64	150.28	167.98	143.66, 129.64, 135.70 128.72, 123.52, 123.98	18.08
$\text{Ph}_2\text{SiCl}(\text{L}_2)$	157.32	156.51	167.58	141.28, 129.76, 129.43 126.87, 124.58, 123.58	138.18, 134.26 137.33, 130.15
$\text{Ph}_2\text{Si}(\text{L}_2)_2$	159.76	149.16	166.76	141.34, 129.48, 133.24 126.79, 123.24, 123.58	133.24, 136.17 137.86, 139.32

^a M = Sn or Si.

RESULTS AND DISCUSSION

The 1:1 and 1:2 molar reactins of R_2SnCl_2 and R_2SiCl_2 (where $\text{R}=\text{Ph}$ or Me) with the mono-basic bidentate ligands (TSCZH) led to the formation of $\text{R}_2\text{SnCl}(\text{TSCZ})$, $\text{R}_2\text{Sn}(\text{TSCZ})_2$, $\text{R}_2\text{SiCl}(\text{TSCZ})$ and $\text{R}_2\text{Si}(\text{TSCZ})_2$ complexes. The resulting coloured solids are soluble in most of the common organic solvents, and have been found to be monomeric as evidenced by their molecular weight determinations. The low

values of the molar conductivities ($8\text{--}15\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$) of the resulting complexes in anhydrous dimethylformamide (DMF) show them to be non-electrolytes. The complexes isolated are presented in Table 1 together with their analytical data.

IR spectra

The infrared spectra of the ligands and their tin and silicon complexes were recorded and important features may be summarized as follows.

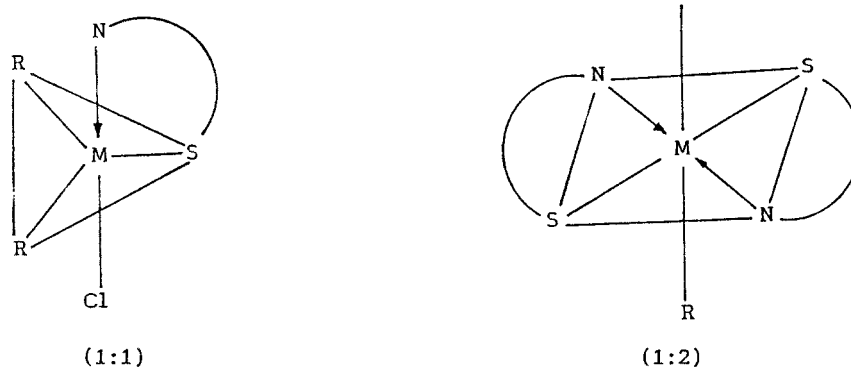


Figure 1 Suggested structures for complexes with a penta- and hexa-coordinated Sn or Si atom; $\text{R}=\text{Me}$ or Ph ; $\text{M}=\text{Sn}$ or Si ; NS=donor sites of the ligand molecule (TSCZH).

Sharp bands at 1615 and 1620 cm^{-1} in the ligands L_1H and L_2H are attributed to $\nu(>\text{C}=\text{N})$.¹⁶ These bands appear at $(1630 \pm 10 \text{ cm}^{-1})$ in the organotin¹⁷ complexes, while in case of the silicon complexes they showed a similar shift towards lower wave-

numbers, indicating coordination of the azomethine ($\text{C}=\text{N}-$) nitrogen atom in L_1 or L_2 with the metal atom.

The appearance of broad absorption bands around 3300 and $\sim 2700 \text{ cm}^{-1}$ due to $\nu(\text{NH})$ and $\nu(\text{SH})$, respectively, suggest that the ligands

Table 4 Fungicidal screening data of ligands and their complexes (percentage inhibition after 96 h)

Treatment	Concentration (ppm)	<i>Alternaria alternata</i> Replications (zone of inhibition in mm) ^a			<i>Fusarium oxysporum</i> Replications (zone of inhibition in mm) ^a		
		R_1 (angular value)	R_2	R_3	R_1 (angular value)	R_2	R_3
L_1H	25	35 (36.27)	39 (28.65)	40 (39.23)	34 (35.67)	35 (3.6.27)	39 (38.65)
	50	48 (43.85)	52 (46.15)	50 (45.00)	46 (42.71)	50 (45.00)	51 (45.57)
$\text{Me}_2\text{SnCl}(\text{L}_1)$	25	40 (39.23)	42 (40.40)	41 (3.9.82)	40 (39.23)	36 (36.87)	39 (38.65)
	50	56 (47.87)	53 (46.72)	51 (45.57)	48 (43.85)	52 (46.15)	55 (47.87)
$\text{Me}_2\text{Sn}(\text{L}_1)_2$	25	43 (40.98)	45 (42.13)	42 (40.40)	45 (42.13)	46 (42.71)	43 (40.98)
	50	56 (49.02)	55 (47.87)	52 (46.15)	44 (41.55)	55 (47.87)	59 (50.18)
$\text{Me}_2\text{SiCl}(\text{L}_1)$	25	41 (39.82)	39 (38.65)	40 (39.23)	37 (37.46)	38 (38.06)	35 (36.27)
	50	48 (42.85)	55 (47.87)	50 (45.00)	45 (42.13)	48 (43.85)	49 (44.43)
$\text{Me}_2\text{Si}(\text{L}_1)_2$	25	45 (42.13)	40 (39.23)	43 (40.98)	44 (41.55)	45 (42.13)	41 (39.82)
	50	53 (46.72)	54 (47.29)	52 (46.15)	44 (41.55)	53 (46.72)	56 (48.45)
L_2H	25	40 (39.23)	42 (40.40)	45 (42.13)	35 (36.27)	39 (38.65)	37 (37.46)
	50	50 (45.00)	53 (46.72)	54 (47.29)	50 (45.00)	51 (45.57)	52 (46.15)
$\text{Ph}_2\text{SnCl}(\text{L}_2)$	25	45 (42.13)	43 (40.98)	46 (42.71)	39 (28.65)	40 (39.23)	38 (38.06)
	50	53 (46.72)	52 (46.15)	55 (47.87)	52 (46.15)	51 (45.57)	54 (47.29)
$\text{Ph}_2\text{Sn}(\text{L}_2)_2$	25	46 (42.71)	48 (43.85)	50 (45.00)	39 (28.65)	42 (40.40)	43 (40.98)
	50	55 (47.87)	56 (49.02)	54 (47.29)	54 (47.29)	55 (47.87)	54 (47.29)
$\text{Ph}_2\text{SiCl}(\text{L}_2)$	25	40 (39.23)	41 (39.82)	39 (38.65)	37 (37.46)	35 (36.27)	35 (36.27)
	50	50 (45.00)	49 (44.43)	51 (45.57)	50 (45.00)	46 (42.71)	43 (40.98)
$\text{Ph}_2\text{SiO}(\text{L}_2)_2$	25	41 (39.82)	43 (40.98)	43 (40.98)	35 (36.27)	36 (36.87)	35 (36.27)
	50	52 (46.15)	53 (46.72)	54 (47.29)	52 (46.15)	45 (42.13)	50 (45.00)

^a After four days.

Table 5 Antibacterial activity of ligands and their complexes (percentage inhibition after 24 h)

Treatment	Concentration (ppm)	<i>Staphylococcus aureus</i> (+)			<i>Pseudomonas cepacicola</i> (–)		
		Replications (zone of inhibition in mm) ^a			Replication (zone of inhibition in mm) ^a		
		<i>R</i> ₁ (angular value)	<i>R</i> ₂ (angular value)	<i>R</i> ₃ (angular value)	<i>R</i> ₁ (angular value)	<i>R</i> ₂ (angular value)	<i>R</i> ₃ (angular value)
<i>L</i> ₁ H	500	9 (17.46)	13 (21.13)	8 (16.43)	11 (19.37)	9 (17.46)	7 (15.34)
	1000	14 (21.97)	11 (19.37)	11 (19.37)	11 (19.37)	13 (21.13)	9 (17.46)
Me ₂ SnCl(<i>L</i> ₁)	500	12 (20.27)	11 (19.37)	13 (21.13)	12 (20.27)	14 (21.97)	11 (19.37)
	1000	14 (21.97)	13 (21.13)	12 (20.27)	18 (25.10)	16 (23.58)	13 (21.13)
Me ₂ Sn(<i>L</i> ₁) ₂	500	13 (21.13)	12 (20.27)	14 (21.37)	15 (22.79)	16 (23.58)	13 (21.13)
	1000	16 (23.58)	15 (22.79)	18 (25.10)	19 (25.84)	17 (24.35)	16 (23.58)
Me ₂ SiCl(<i>L</i> ₁)	500	12 (20.27)	11 (19.37)	10 (18.43)	11 (19.37)	10 (18.43)	11 (19.37)
	1000	13 (21.13)	12 (20.27)	15 (22.79)	12 (20.27)	13 (21.13)	11 (19.37)
Me ₂ Si(<i>L</i> ₁) ₂	500	13 (21.13)	12 (20.27)	14 (21.97)	13 (21.13)	14 (21.97)	11 (19.37)
	1000	16 (23.58)	15 (22.79)	14 (21.97)	15 (22.79)	17 (24.35)	18 (25.10)
<i>L</i> ₂ H	500	8 (16.43)	9 (17.46)	13 (21.13)	12 (20.27)	14 (21.97)	19 (25.84)
	1000	12 (20.27)	11 (19.37)	10 (18.43)	17 (24.35)	15 (22.97)	16 (25.58)
Ph ₂ Sn(<i>L</i> ₂) ₂	500	14 (21.97)	16 (23.58)	12 (20.27)	13 (21.13)	15 (22.97)	18 (25.10)
	1000	15 (22.97)	16 (23.58)	13 (21.13)	18 (25.10)	16 (23.58)	17 (24.35)
Ph ₂ Sn(<i>L</i> ₂) ₂	500	14 (21.97)	15 (22.97)	13 (21.13)	17 (24.35)	15 (22.97)	18 (25.10)
	1000	18 (25.10)	16 (23.58)	14 (21.97)	19 (25.84)	18 (25.10)	20 (26.57)
Ph ₂ SiCl(<i>L</i> ₂)	500	13 (21.13)	15 (22.97)	12 (20.27)	11 (19.37)	14 (21.97)	19 (25.84)
	1000	14 (21.97)	16 (23.58)	13 (21.13)	18 (25.10)	16 (23.58)	15 (22.97)
Ph ₂ Si(<i>L</i> ₂) ₂	500	15 (22.97)	16 (23.58)	13 (21.13)	15 (22.97)	16 (23.58)	17 (24.35)
	1000	17 (24.35)	16 (23.58)	19 (25.84)	18 (25.10)	17 (24.35)	19 (25.84)

^a After 24 h.

exist as keto–enol-type tautomers (Eqn [4]). The disappearance of both $\nu(\text{NH})$ and $\nu(\text{SH})$ indicates that the S atom coordinates but not this N atom, since it is the azomethine N atom that coordinates instead.

Two sharp bands at *ca* 3440 and 3360 cm^{–1}, probably due to the asymmetric and symmetric vibrations of the NH₂ group in the ligand, remain almost unchanged in the spectra of the metal complexes, showing the non-involvement of this

Table 6 Disease control (%) obtained from field experiment using PDI technique

Treatment	PDI in treated plant	Disease control (%)
L ₁ H	11	60.7
Ph ₂ SnCl(L ₁)	6	78.5
Ph ₂ Sn(L ₁) ₂	5	82.1
Me ₂ SnCl(L ₁)	7	75.0
Me ₂ Sn(L ₁) ₂	6	78.5
Ph ₂ SiCl(L ₁)	8	71.4
Ph ₂ Si(L ₁) ₂	7	75.0
Me ₂ SiCl(L ₁)	8	71.4
Me ₂ Si(L ₁) ₂	6	78.8
L ₂ H	15	46.4
Ph ₂ SnCl(L ₂)	8	71.4
Ph ₂ Sn(L ₂) ₂	7	75.0
Me ₂ SnCl(L ₂)	9	67.8
Me ₂ Sn(L ₂) ₂	8	71.4
Ph ₂ SiCl(L ₂)	8	71.4
Ph ₂ Si(L ₂) ₂	7	75.0
Me ₂ SiCl(L ₂)	10	64.2
Me ₂ Si(L ₂) ₂	9	67.8

group in complexation.¹⁸ The band at $\sim 1035\text{ cm}^{-1}$ may be assigned to $\nu(\text{C}=\text{S})$, which disappears in metal complexes due to covalent bond formation of the ligand with the metal through the sulphur atom.¹⁹

Several new bands have appeared in the spectra of the complexes assigned to $\nu(\text{Sn}\leftarrow\text{N})$ ²⁰, $\nu(\text{Sn}-\text{S})$, $\nu(\text{Si}\leftarrow\text{N})$ and $\nu(\text{Si}-\text{S})$ vibrations in the region $400\text{--}600\text{ cm}^{-1}$, further supporting the participation of the sulphur atom and the azomethane nitrogen atom in complexation.

¹H NMR spectra

The proton magnetic resonance spectra of the ligands, as well as of their corresponding metal complexes, have been recorded in DMSO-*d*₆ using tetramethylsilane (TMS) as the internal standard. The spectra of the ligands (Table 2) exhibit signals due to $-\text{CH}$ aromatic protons, the $-\text{NH}$ of the isatin ring and the $-\text{NH}$ of thiosemicarbazone. The disappearance of that later signal in the organometallic derivatives indicate coordination of the azomethine nitrogen (*) as well as covalent-bond formation between metal and sulphur (+) due to deprotonation of the enolic form of the ligand. Further, in the spectra of the complexes, a downfield shift in the position of the aromatic protons also indicates the coordination of the azomethine nitrogen to the metal atom. The appearance of a signal due to the NH₂

group at about same position in the ligand and its metal complexes shows the non-involvement of this group in coordination. Further, a new signal at about $\delta 1.14\text{ ppm}$ in the dimethyltin(IV) is assigned to methyl-group protons attached to the metal.

¹³C NMR spectra

In the ¹³C NMR spectra of the ligands and their complexes, considerable shifts in the position of carbon atoms adjacent to atoms involved in complex formation clearly indicate the bonding of the azomethine nitrogen atom and thione/thiolic sulphur atom to the metal atom (Table 3).

¹¹⁹Sn and ²⁹Si NMR spectra

The ¹¹⁹Sn NMR spectra of the complexes Ph₂SnCl(L₁) and Ph₂Sn(L₁)₂ show the signals at $\delta -155$ and $\delta 192.06\text{ ppm}$ which are in good agreement with penta-coordinated and hexa-coordinated states around the tin atom for 1:1 and 1:2 molar reactions respectively.

However, in the cases of the silicon complexes Ph₂SiCl(L₂) and Ph₂Si(L₂)₂, signals at $\delta -92.05$ and $\delta -120.12\text{ ppm}$ are assigned for penta- and hexa-coordinated states around the silicon atom. On the basis of the above results, structures for penta- and hexa-coordinated compounds may be suggested as shown in Fig. 1.

Results of the fungicidal screening tests are given in Table 4, of antibacterial determination in Table 5, and of disease control experiments in Table 6.

The compounds inhibit the growth of fungi and bacteria to a greater extent as the concentration is increased. The mechanism of the toxicity of these complexes to microorganisms may be due to inhibition of energy or ATP production,²² for instance by inhibition of respiration or by uncoupling of oxidative phosphorylation. The energy-producing processes are located partly in the cytoplasm and partly in the mitochondria. Strong inhibition of such processes eventually has a fungicidal and bactericidal effect.

CONCLUSION

Complexes obtained by 1:1 molar reactions of ligands L₁H and L₂H with organosilicon(IV) and

organotin(IV) chlorides were found to have penta-coordinated trigonal-bipyramidal geometry. Hexa-coordinated octahedral geometry was assigned to complexes prepared by 1:2 molar reactions of the reactants. The microbial activity of the complexes and ligands showed that the former are more active than their parent ligands. The data in Tables 4 and 5 reveal that $\text{Ph}_2\text{Sn}(\text{L}_2)_2$, $\text{Ph}_2\text{Si}(\text{L}_1)_2$ and $\text{Ph}_2\text{Sn}(\text{L}_2)_2$ were found to be more toxic than the other complexes, and the hexa-coordinated complexes display better results than the penta-coordinated complexes.

Acknowledgement The authors thank the UGC, New Delhi, for financial assistance.

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