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Organosilicon(IV) and organotin(IV) complexes as biocides and nematicides: synthetic, spectroscopic and biological studies of $N^{\cap}N$ donor sulfonamide imine and its chelates

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A brief account is given of the synthesis and stereochemistry and the antibacterial, antifungal, nematicidal and insecticidal behaviour of organosilicon(IV) and organotin(IV) complexes of a biologically potent ligand, 2-acetylfuransulfaguanidine. The unimolar and bimolar substitution products have been characterized by elemental analyses, conductance measurements, molecular weight determinations, and spectral studies, viz. IR, ^{1}H NMR, ^{13}C NMR, UV, ^{29}Si NMR and ^{119}Sn NMR spectra. The data support the binding of the nitrogen atom to the metal atom in [$R_3M(N^{\cap}N)$], [$R_2M(N^{\cap}N)_2$] and [$R_2M(N^{\cap}N)Cl$] [(R = Me/Ph and M = Si(IV) and Sn(IV)] types of complex. Based on these studies, with coordination number five and six a trigonal bipyramidal and an octahedral geometry have been proposed for the resulting derivatives. The free ligand ($N^{\cap}NH$) and its respective metal complexes were tested *in vitro* against a number of microorganisms to assess their antimicrobial properties. The results are indeed positive. In addition to these studies, the complexes also show good nematicidal and insecticidal properties. The results of these findings have been discussed in detail.

KEYWORDS: insecticides; nematicides; fungicides; bactericides; sulfonamide-imine; organosilicon(IV) complexes; organotin(IV) complexes.

INTRODUCTION

Tin(IV) and organotin(IV) compounds, a deceptively simple area of inorganic and metal–organic chemistry, have been receiving increasing attention due to the important industrial[1] (including pesticides, anti-fouling paints and fire retardants[2]), pharmacological[3] (as antitumour drugs)[4,5] and environmental applications. Organotin(IV) chelates with nitrogen, oxygen and sulfur donor ligands have received much attention during the last few years.[6] The considerable developments over recent decades in the use of organotin compounds as reagents or intermediates in organic synthesis prompted the preparation of many new organotin compounds.[7]

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Lukevics *et al.*[8] reported anticancer properties for several quinoline derivatives bearing a trialkylsilyl group towards a panel of animal tumour systems. A silatrane derivative containing an unusual five-coordinate geometry at the silicon atom exhibits 50% inhibition of Walker 256 carcinosarcoma.[9] Generally, organosilicon compounds seem to owe their antitumour properties to the stimulation of the immunodefensive system of the organism.[10] Many five- and six-coordinated silicon complexes have been characterized and are recent examples illustrating the trigonal bipyramidal[11,12] and octahedral[13] geometries respectively typically adopted by such compounds.

This work stemmed from our interest in the development of a systematic synthetic methodology for the preparation of new series of di- and tri-organotin and di- and tri-organosilicon complexes. Organotin and organosilicon compounds exhibit a broad spectrum of biological activity

that includes bactericidal,[14] fungicidal,[15] antitumour[16] and acaricidal effects. Our ongoing work with chelated tin(IV) derivatives[17] involving such systems led us to describe the synthetic and stereochemical features of some organotin halide complexes. The interest in organosilicon compounds is generated by the wide applicability of organosiloxane elastomers, resins and liquid polymers.[18,19] The biochemistry of synthetic organometallics has generated active research relating to their biochemical significance.

An objective of the present work is to highlight a systematic study of the stereochemical and biochemical aspects of the complexes of sulfonamide imine of silicon and tin. All the complexes, along with the ligand, have been tested *in vitro* against various pathogenic fungi, viz. *Aspergillus niger*, *Fusarium oxysporum*, *Macrophomina phaseolina* and *Alternaria alternata*, and bacteria, viz. *Escherichia coli*, *Klebsiella aerogenous*, *Pseudomonas cepacicola* and *Staphylococcus aureus*. The results of these investigations seem to be promising. In addition, the results of insecticidal and nematicidal activities have also been found encouraging. The monobasic bidentate ligand used during these investigations is shown in Fig. 1.

EXPERIMENTAL

Adequate care was taken to keep the organosilicon(IV) and organotin(IV) complexes, all chemicals and the glass apparatus free from moisture. The clean and well-dried glass apparatus fitted with quickfit interchangeable standard ground joints was used throughout the experimental work. All the chemicals and solvents used were dried and purified by standard methods.

Preparation of the ligand

The sulfonamide imine was prepared by the condensation of sulfaguanidine (5.120 g) with 2-acetylfuran (9.923 g) in equimolar ratio in absolute alcohol (50 ml). The contents were refluxed for 4–5 h on a water bath, the product was recrystallized from the same solvent and then dried under reduced pressure. The physical properties of this sulfonamide imine are given in Table 1.

Synthesis of the complexes

To a calculated amount of the sodium salt of the sulfonamide imine (2-Ac-F-SgH; prepared by adding the corresponding weight of the sodium metal to the sulfonamide imine) in dry methanol, was added the methanolic solution of di- and tri-organometal chlorides (Me_2SnCl_2, Ph_2SnCl_2, Ph_3SnCl, Me_2SiCl_2, Ph_2SiCl_2 and Ph_3SiCl) in 1 : 1 or 1 : 2 stoichiometric proportions. The contents were refluxed over a ratio head for 16–18 h and the white precipitate of sodium chloride obtained was removed under suction. The excess of the solvent was then removed over the ratio head and the compounds were dried under reduced pressure for 3–4 h. These were purified by repeated washing with a (1 : 1) mixture of dry methanol and cyclohexane. All the compounds were isolated as powdered solids. The details of these reactions and the analyses of the resulting products are recorded in Table 1.

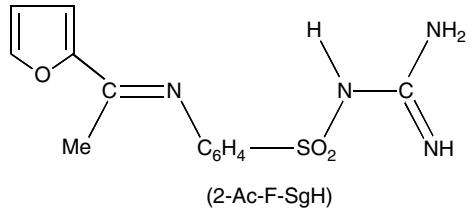


Figure 1. Structure of the ligand.

Analytical methods and physical measurements

Nitrogen and sulfur were estimated by the Kjeldahl and Messenger methods respectively. Silicon and tin were determined gravimetrically, as SiO_2 and SnO_2 respectively. Molecular weights were determined by the Rast camphor method (freezing point depression method) using resublimed camphor (m.p. 178 °C).

Conductance measurements

The conductance measurements were carried out in dry dimethylformamide (DMF) at room temperature using a Systronics conductivity bridge (Model 304) in conjunction with a cell having a cell constant of 1.0.

Electronic spectra

The electronic spectra were recorded on a Perkin Elmer UV–visible spectrophotometer in the range 200–600 nm, using dry methanol as the solvent.

Nuclear magnetic resonance measurements

Multinuclear magnetic resonance spectra (^{1}H, ^{13}C, ^{29}Si and ^{119}Sn) were recorded on an FX 90 Q JEOL spectrometer operating at 90 MHz.

^{1}H NMR spectra were recorded in deuterated methanol at 89.55 MHz using tetramethylsilane (TMS) as an internal standard.

^{13}C NMR spectra were recorded in dry methanol using TMS as the internal standard at 22.49 MHz.

^{29}Si NMR spectra were recorded at 17.75 MHz using deuterated dimethylsulfoxide (DMSO-d_6) as the solvent.

^{119}Sn NMR spectra were recorded at 33.35 MHz using DMSO-d_6 as the solvent. The chemical shifts were determined relative to the external reference tetramethyl tin and are supposed to be accurate to ±1 ppm.

RESULTS AND DISCUSSION

The unimolar and bimolar reactions of Me_2SnCl_2, Ph_2SnCl_2, Ph_3SnCl and Me_2SiCl_2, Ph_2SiCl_2, Ph_3SiCl with sulfonamide imine led to the formation of the $R_2MCl(N^{\cap}N)$, $R_3M(N^{\cap}N)$ and $R_2M(N^{\cap}N)_2$(R = Me, Ph and M = Si, Sn) types of

Table 1. Physical properties and analytical data of the ligand and its metal complexes

Reactants (g)			Complex	Formula and colour	Molar ratio	Yield (%)	M.P. (°C)	Elemental analysis (%) Found (Calc.)						Mol. wt Found (Calc.)
Starting material	Ligand	Na						C	H	N	S	M	Cl	
—	—	—	2-Ac-F-SgH	$C_{13}H_{14}N_4O_3S$	—	76	132–134	50.72	4.39	18.03	10.18	—	—	283
				Cream				(50.97)	(4.60)	(18.28)	(10.46)			(306.29)
Me_2SiCl_2	2-Ac-F-SgH	0.06	Me_2SiCl(2-Ac-F-Sg)	$C_{15}H_{19}N_4O_3SSiCl$	1 : 1	74	110–112	44.86	4.61	13.79	7.84	6.69	8.49	374
0.36	0.86			Brick red				(45.16)	(4.80)	(14.04)	(8.03)	(7.04)	(8.88)	(398.89)
Me_2SiCl_2	2-Ac-F-SgH	0.07	Me_2Si(2-Ac-F-Sg)$_2$	$C_{28}H_{32}N_8O_6S_2Si$	1 : 2	72	196–198	50.01	4.53	16.50	9.31	3.90	—	641
0.20	0.95			Yellowish brown				(50.27)	(4.82)	(16.75)	(9.58)	(4.19)		(668.96)
Ph_2SiCl_2	2-Ac-F-SgH	0.05	Ph_2SiCl(2-Ac-F-Sg)	$C_{25}H_{23}N_4O_3SSiCl$	1 : 1	77	103–105	57.08	4.26	10.59	5.79	4.99	6.48	508
0.59	0.72			Fine brown				(57.39)	(4.43)	(10.70)	(6.12)	(5.36)	(6.77)	(523.13)
Ph_2SiCl_2	2-Ac-F-SgH	0.05	Ph_2Si(2-Ac-F-Sg)$_2$	$C_{38}H_{36}N_8O_6S_2Si$	1 : 2	72	178–180	57.20	4.17	13.90	7.76	3.25	—	776
0.27	0.64			Sandy brown				(57.56)	(4.57)	(14.13)	(8.08)	(3.54)		(792.86)
Ph_3SiCl	2-Ac-F-SgH	0.04	Ph_3Si(2-Ac-F-Sg)	$C_{31}H_{29}N_4O_3SSi$	1 : 1	79	177–179	65.64	4.74	9.81	5.23	4.70	—	542
0.54	0.56			Light brown				(65.93)	(4.99)	(9.92)	(5.67)	(4.97)		(564.68)
Me_2SnCl_2	2-Ac-F-SgH	0.05	Me_2SnCl(2-Ac-F-Sg)	$C_{15}H_{19}N_4O_3SSnCl$	1 : 1	73	219–221	36.61	3.68	11.12	6.40	24.01	7.08	468
0.47	0.65			Peach				(36.80)	(3.91)	(11.44)	(6.55)	(24.24)	(7.24)	(489.50)
Me_2SnCl_2	2-Ac-F-SgH	0.05	Me_2Sn(2-Ac-F-Sg)$_2$	$C_{28}H_{32}N_8O_6S_2Sn$	1 : 2	79	134–136	44.00	4.02	14.50	8.19	15.40	—	740
0.25	0.71			Brown				(44.28)	(4.24)	(14.75)	(8.44)	(15.63)		759.53
Ph_2SnCl_2	2-Ac-F-SgH	0.04	Ph_2SnCl(2-Ac-F-Sg)	$C_{25}H_{23}N_4O_3SSnCl$	1 : 1	71	108–110	48.59	3.48	9.01	5.06	19.04	5.54	592
0.60	0.53			Brick red				(48.93)	(3.77)	(9.13)	(5.22)	(19.34)	(5.77)	(613.64)
Ph_2SnCl_2	2-Ac-F-SgH	0.06	Ph_2Sn(2-Ac-F-Sg)$_2$	$C_{38}H_{36}N_8O_6S_2Sn$	1 : 2	75	197–199	51.39	4.01	12.38	7.11	13.20	—	871
0.43	0.77			Yellowish brown				(51.66)	(4.10)	(12.68)	(7.25)	(13.43)		(883.47)
Ph_3SnCl	2-Ac-F-SgH	0.04	Ph_3Sn(2-Ac-F-Sg)	$C_{31}H_{28}N_4O_3SSn$	1 : 1	76	135–136	56.61	4.11	8.34	4.57	18.01	—	638
0.69	0.55			Cream				(56.82)	(4.30)	(8.54)	(4.89)	(18.11)		(625.29)

complex. The reactions were carried out in perfectly dry methanolic medium and proceed smoothly with the precipitation of NaCl. These reactions can be represented by the following general equations:

$$R_2MCl_2 + N^{\cap}N.Na \xrightarrow{1:1} R_2MCl(N^{\cap}N) + NaCl$$

$$R_3MCl + N^{\cap}N.Na \xrightarrow{1:1} R_3M(N^{\cap}N) + NaCl$$

$$R_2MCl_2 + N^{\cap}N.Na \xrightarrow{1:2} R_2M(N^{\cap}N)_2 + 2NaCl$$

where $N^{\cap}N$ is the donor system of the sulfonamide imine and R = Me, Ph and M = Si, Sn)

The resulting coloured solids are soluble in most of the common organic solvents. These were found to be monomeric, as evidenced by their molecular weight determinations. The low values of molar conductivity (8–15 Ω^{-1} cm^2 mol^{-1}) of the resulting metal complexes in anhydrous DMF show them to be non-electrolytes.

UV spectra

The electronic spectra of the ligand and its 1 : 1 and 1 : 2 metal complexes were recorded. The spectrum of the ligand shows a broad band at 365 nm, which can be assigned to the n–π^* transitions of the azomethine group. This band shows a blue shift in the metal complexes, appearing at around 340 nm and 346 nm for the 1 : 1 and 1 : 2 derivatives respectively, due to the polarization within the >C═N chromophore caused by the metal–ligand electron interaction.[11,12] The bands at 270 and 300 nm due to π–π^* transitions appear almost in the same region in the spectra of organometallic derivatives.

IR spectra

The IR spectra of these derivatives do not show any band in the region 3400–3150 cm^{-1} that could be assigned to ν(NH). This clearly indicates the deprotonation of the ligand as a result of complexation with the metalloid and metal atoms. A sharp band at 1625 cm^{-1} is due to the ν(>C═N) frequency of the free azomethine group in the ligand. This band got split into two sharp bands at 1610 ± 5 cm^{-1} and around 1600 cm^{-1} in the metal complexes. This splitting of the bands suggests that the azomethine groups are in a different chemical environment. The shifting of the band at 1610 ± 5 cm^{-1} in silicon complexes unequivocally suggests the coordination of the azomethine nitrogen to the silicon atom,[11,12] whereas the band at around 1600 cm^{-1} is assigned to the uncoordinated azomethine group.[20] However, in the spectra of tin complexes, this band shifted to the higher frequency (*ca* 10 cm^{-1}), thereby indicating the coordination of the azomethine nitrogen to the metal atom.[14]

In the dimethylsilicon(IV) complexes, a band at *ca* 1420 cm^{-1} has been ascribed to the asymmetric deformation vibrations of the CH_3–Si group, whereas, the band at *ca* 1270 cm^{-1} is ascribed to the symmetric deformation mode of the CH_3–Si group.[11,12]

Several new bands are observed in the spectra of the complexes at 2824–3042 cm^{-1} and 1404–1432 cm^{-1} due to C–H stretching and bending vibrations respectively. Aromatic ring stretch (C–C) appeared at 1645, 1530 and 1457 cm^{-1}. The chelation through azomethine nitrogen gets supports by the appearance of new bands at around 575 ± 5 cm^{-1} due to ν (Si←N) vibrations. A band due to ν(Si–Cl) at 441 and 427 cm^{-1} is observed in 1 : 1 diorganosilicon(IV) derivatives[11] (Table 2).

Two medium- to sharp-intensity bands observed in the far IR region of the tin complexes at 412–422 cm^{-1} and 313–325 cm^{-1} are assigned to ν (Sn←N) and ν(Sn–Cl) modes respectively, which are not observed in the spectrum of the ligand. One strong- to medium-intensity band appeared in the spectra of the complexes in the region 1230–1180 cm^{-1} can be assigned to Sn–CH_3 stretching vibrations. The presence of only one Sn–C stretching frequency at 556 cm^{-1} suggests that 1 : 2 complexes of tin exist in the trans form. Medium- to sharp-intensity bands are observed at 595 and 525 cm^{-1} and may be assigned to the asymmetric and symmetric modes of Sn–C stretching vibrations. A new band observed at 275 cm^{-1} may be assigned to ν(Sn–Ph).[14]

It has been reported that the cis form of such complexes gives rise to two ν(M–N) bands, whereas, in the trans form only one IR-active ν(M–N) band is observed. The presence of only one ν (M←N) band, in the present case, suggests that the complexes exist in the trans form.[12]

^{1}H NMR spectra

The proton magntic resonance spectral data of the ligand and its corresponding metal complexes were recorded in DMSO-d_6. The chemical shift values relative to the TMS peak are listed in Table 3.

The broad signal due to the —NH proton in the ligand at δ 10.61 ppm disappears in the case of metal complexes, showing the coordination of the metal atom to the nitrogen atom after the deprotonation of the functional group. However, another

Table 2. Spectral data (cm^{-1}) of the ligand and its metal complexes

Compound	ν (NH)	ν (C═N)	ν (M←N)	ν (M–Cl)
2-Ac-F-SgH	3400–3150	1625	—	—
Me_2SiCl(2-Ac-F-Sg)	—	1618	579	427
Me_2Si(2-Ac-F-Sg)$_2$	—	1621	584	—
Ph_2SiCl(2-Ac-F-Sg)	—	1615	577	441
Ph_2Si(2-Ac-F-Sg)$_2$	—	1609	579	—
Ph_3Si(2-Ac-F-Sg)	—	1612	573	—
Me_2SnCl(2-Ac-F-Sg)	—	1631	419	313
Me_2Sn(2-Ac-F-Sg)$_2$	—	1628	422	—
Ph_2SnCl(2-Ac-F-Sg)	—	1632	418	325
Ph_2Sn(2-Ac-F-Sg)$_2$	—	1634	415	—
Ph_3Sn(2-Ac-F-Sg)	—	1630	412	—

Table 3. ^{1}H, ^{29}Si and ^{119}Sn NMR spectral data (δ, ppm) of the ligand and its metal complexes[a]

Compound	Aromatic (m)	NH (br)	NH_2 (br)	CH_3	$M-CH_3$(s)	Multinuclear magnetic resonance	^{2}J(Sn–H) (Hz)	C–Sn–C angle (°)
2-Ac-F-SgH	8.95–7.53	10.61 (br, 1H)	2.80 (2H)	2.22 (s, 3H)	—	—	—	—
Me_2SiCl(2-Ac-F-Sg)	9.00–7.69	—	3.03 (2H)	2.36 (s, 3H)	1.05 (br, 64)	−96	—	—
Me_2Si(2-Ac-F-Sg)$_2$	9.42–7.28	—	2.94 (4H)	2.30 (s, 6H)	1.15 (br, 6H)	−127	—	—
Ph_2SiCl(2-Ac-F-Sg)	9.21–8.12	—	2.92 (2H)	2.34 (s, 3H)	—	−92	—	—
Ph_2Si(2-Ac-F-Sg)$_2$	9.30–8.22	—	2.70 (4H)	2.28 (s, 6H)	—	−107	—	—
Ph_3Si(2-Ac-F-Sg)	9.25–8.13	—	2.78 (2H)	2.32 (s, 3H)	—	−90	—	—
Me_2SnCl(2-Ac-F-Sg)	9.04–7.91	—	2.76 (2H)	2.39 (s, 3H)	1.20 (br, 6H)	−117	77	127.21
Me_2Sn(2-Ac-F-Sg)$_2$	9.44–7.35	—	2.71 (4H)	2.33 (s, 6H)	1.22 (br, 6H)	−364	82	133.41
Ph_2SnCl(2-Ac-F-Sg)	9.12–7.57	—	2.72 (2H)	2.35 (s, 3H)	—	−123	—	—
Ph_2Sn(2-Ac-F-Sg)$_2$	9.13–7.62	—	2.74 (4H)	2.30 (s, 6H)	—	−338	—	—
Ph_3Sn(2-Ac-F-Sg)	9.24–7.33	—	2.70 (2H)	2.36 (s, 3H)	—	−128	—	—

[a] m := multiplet; br: broad; s: singlet.

band at δ 11.12 ppm remains at the same position in the complexes, which suggests non-participation of this band in bond formation. The azomethine proton signal due to the methyl protons of the $CH_3-C{=}N$ group was observed at δ 2.22 ppm. The downfield shift of this band in the spectra of the complexes substantiates the coordination of azomethine nitrogen to the metal atom. The ligand shows a complex pattern in the region δ 8.95–7.53 ppm for the aromatic protons and this is observed in the region δ 9.44–7.28 ppm in the spectra of the organometal(IV) complexes. This shifting also supports the coordination through the nitrogen atom. The appearance of a signal due to the NH_2 group at about the same position in the ligand and its metal complexes shows the non-involvement of this group in the coordination. Further, a new signal at δ 1.20–1.22 ppm in the dimethyltin(IV) is assigned to methyl-group protons attached to the metal, and the signals at δ 1.05 ppm and δ 1.15 ppm in the 1 : 1 and 1 : 2 complexes respectively are due to the methyl protons of the Me_2Si group.

^{13}C NMR spectra

The conclusions drawn from the UV, IR and ^{1}H NMR spectra are concurrent with the ^{13}C NMR spectral data regarding the authenticity of the proposed structures. The ^{13}C NMR spectra of the ligand and its 1 : 1 and 1 : 2 organometallic derivatives are recorded in Table 4. The chemical shift values of the carbon atoms attached to the azomethine nitrogen lend further support to the proposed coordination in these complexes.[11,12] The new carbon signals due to M–Me/Ph are also reported.

^{29}Si and ^{119}Sn NMR spectra

The ^{29}Si NMR spectra of $Me_2SiCl(N^{\cap}N)$, $Ph_2SiCl(N^{\cap}N)$, and $Ph_3Si(N^{\cap}N)$ give sharp signals at $\delta -90$ to -96 ppm and the spectra of $Me_2Si(N^{\cap}N)_2$ and $Ph_2Si(N^{\cap}N)_2$ give sharp signals at $\delta -107$ to -127 ppm, which clearly indicates the penta- and hexa-coordinated environment respectively around the silicon atom.[12]

However, in the case of ^{119}Sn NMR spectra of the complexes $Ph_2SnCl(N^{\cap}N)Me_2SnCl(N^{\cap}N)$ and $Ph_3Sn(N^{\cap}N)$ and complexes $Ph_2Sn(N^{\cap}N)_2$ and $Me_2Sn(N^{\cap}N)_2$, the signals at $\delta -117$ to -128 and $\delta -338$ to -364 ppm are in good agreement with the pentacoordinated and hexacoordinated states around the tin atom[21] for 1 : 1 and 1 : 2 molar reactions respectively.

On the basis of the results discussed so far, including the analytical and the spectral data, suitable pentacoordinated trigonal bipyramidal and hexacoordinated octahedral geometries have been suggested for the 1 : 1 and 1 : 2 organometal(IV) derivatives respectively (Fig. 2).

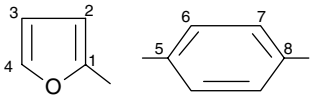
BIOCIDAL ACTIVITY

The fungicidal and bactericidal activities of sulfonamide imine and its respective organometal(IV) complexes against pathogenic fungi and bacteria are recorded in Tables 5 and 6 by the following methods.

Antifungal activity: agar plate technique

Potato-dextrose agar (PDA) medium (glucose: 20 g; starch: 20 g; agar–agar: 20 g; 1000 ml of H_2O) was prepared in a flask and sterilized. To this medium was added the requisite amount of compound after being dissolved in methanol so as to obtain the desired final concentration. A series of concentrations was prepared. The medium was then poured into the Petri plates and a small disc (0.7 cm) of the fungus culture was cut with a sterile cork borer and transferred aseptically in the centre of a Petri dish containing the medium with the desired amount of the compound. Suitable controls were kept, where the culture discs were grown under the same conditions on PDA without the compound. These Petri

Table 4. ^{13}C NMR spectral data (δ, ppm) of the ligand and its metal complexes



Compound	Azomethine C-atom	M–Me	Aromatic carbon C_1 C_5	C_2 C_6	C_3 C_7	C_4 C_8	$^1J(^{119}Sn, ^{13}C)$ (Hz)	$^2J(^{119}Sn, ^{13}C)$ (Hz)	$^3J(^{119}Sn, ^{13}C)$ (Hz)	Estimated C–Sn–C angle (°)
2-Ac-F-SgH	157.21	—	145.82	140.22	121.17	144.19	—	—	—	—
			127.48	123.64	125.86	126.16				
Me_2SiCl(2-Ac-F-Sg)	146.29	14.86	147.82	141.42	121.20	143.20	—	—	—	—
			125.84	120.84	124.32	121.32				
Me_2Si(2-Ac-F-Sg)$_2$	149.82	15.42	147.78	142.18	121.35	143.75	—	—	—	—
			126.01	120.98	123.99	121.00				
Ph_2SiCl(2-Ac-F-Sg)	155.34	—	145.98	138.21	121.00	142.10	—	—	—	—
			127.62	121.49	122.94	124.76				
Ph_2Si(2-Ac-F-Sg)$_2$	148.48	—	146.00	138.94	128.29	143.80	—	—	—	—
			130.66	121.08	122.76	125.84				
Ph_3Si(2-Ac-F-Sg)	156.11	—	144.72	132.61	121.14	143.90	—	—	—	—
			129.72	122.98	123.21	126.42				
Me_2SnCl(2-Ac-F-Sg)	152.62	16.65	149.26	141.68	120.98	142.88	580	—	—	127.6
			134.41	124.54	126.87	130.42				
Me_2Sn(2-Ac-F-Sg)$_2$	150.01	18.84	145.68	132.60	121.44	143.36	662	—	—	134.8
			130.29	126.84	128.24	129.46				
Ph_2SnCl(2-Ac-F-Sg)	154.12	—	138.80	129.82	121.46	143.77	538	42.3	133.0	123.9
			127.75	123.81	124.29	125.76				
Ph_2Sn(2-Ac-F-Sg)$_2$	154.86	—	140.72	136.87	121.56	143.31	635	93.4	146.9	132.4
			132.49	125.42	127.42	128.56				
Ph_3Sn(2-Ac-F-Sg)	156.57	—	143.74	131.29	121.78	143.90	520	40.1	130.7	122.3
			128.42	122.36	123.92	125.74				

dishes were wrapped in polythene bags containing a few drops of alcohol and were placed in an incubator at $25 \pm 2\,^{\circ}C$. Three replicates were used in each case. The colony diameter, after 96 h, compared with the control, was taken as a measure of fungitoxicity.[14] The amount of growth inhibition was then calculated as

$$\text{Inhibition}(\%) = \frac{\left(\begin{array}{c}\text{Diameter of}\\ \text{fungal colony}\\ \text{in control plate}\end{array}\right) - \left(\begin{array}{c}\text{Diameter of}\\ \text{fungal colony}\\ \text{in test plate}\end{array}\right)}{\text{Diameter of fungal colony in control plate}} \times 100$$

The compounds were dissolved in 25, 50 and 100 ppm concentrations in DMF. Controls were also run and three replicates were used in each case.

Antibacterial activity: inhibition zone technique[22]

Flat-bottomed 90 mm Pyrex Petri dishes were used. 15 ml of agar medium (peptone: 5 g; beef extract: 5 g; NaCl: 5 g; agar–agar: 20 g; 1000 ml of distilled water) was applied. The seeded agar was prepared by cooling the molten agar to 40 °C and then adding the required amount of bacterial suspension. The plate was tilted to ensure even coverage before the agar solidified. These dishes, with tops in place, were stacked in a refrigerator upside down to prevent condensation of moisture. The compounds were dissolved in methanol in 500 and 1000 ppm concentrations. Whatman No. 1 paper discs with a diameter of 5 mm were soaked in these solutions of varied concentrations. The discs were dried and placed

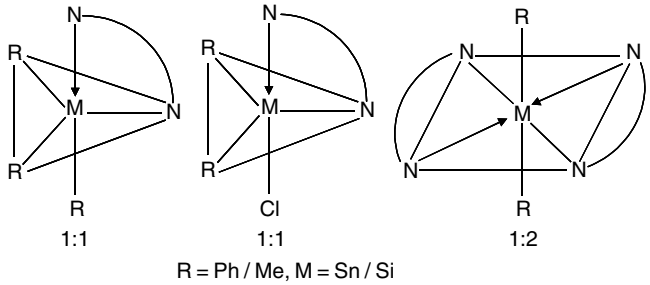


Figure 2. Structures of the complexes.

Table 5. Antifungal activity (average percentage inhibition after 96 h) of the ligand and its metal complexes (concentrations used: 25, 50 and 100 ppm)

	Average inhibition (%)											
	Aspergillus niger			*Macrophomina phaseolina*			*Fusarium oxysporum*			*Alternaria alternata*		
Compound	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm
2-Ac-F-SgH	32	50	60	34	48	67	38	55	66	42	58	65
Me_2SiCl(2-Ac-F-Sg)	36	55	71	37	51	70	40	58	70	43	60	66
Me_2Si(2-Ac-F-Sg)$_2$	40	61	77	41	56	75	44	62	71	45	64	69
Ph_2SiCl(2-Ac-F-Sg)	37	56	74	39	53	72	41	59	72	44	63	67
Ph_2Si(2-Ac-F-Sg)$_2$	42	64	79	46	59	78	45	65	75	48	66	71
Ph_3Si(2-Ac-F-Sg)	39	59	75	42	55	73	42	61	72	45	64	69
Me_2SnCl(2-Ac-F-Sg)	38	58	73	40	54	72	42	62	71	45	61	68
Me_2Sn(2-Ac-F-Sg)$_2$	44	66	79	46	57	76	46	67	76	48	65	72
Ph_2SnCl(2-Ac-F-Sg)	40	59	76	42	56	74	44	65	73	46	63	70
Ph_2Sn(2-Ac-F-Sg)$_2$	45	68	81	48	60	80	47	69	79	50	68	76
Ph_3Sn(2-Ac-F-Sg)	41	62	80	43	58	76	45	66	75	48	64	71
Bavistin	61	86	98	72	82	96	70	91	100	71	86	100

Table 6. Antibacterial activity (diameter of inhibition zone after 24 h) of the ligand and its metal complexes (concentrations used: 500 and 1000 ppm)

	Inhibition zone diameter (mm)							
	Escherichia coli (−)		*Klebsiella aerogenous* (−)		*Pseudomonas cepacicola* (−)		*Staphylococcus aureus* (+)	
Compound	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm
2-Ac-F-SgH	5	6	5	9	8	10	10	12
Me_2SiCl(2-Ac-F-Sg)	7	13	7	11	11	13	11	14
Me_2Si(2-Ac-F-Sg)$_2$	9	16	10	13	14	16	15	15
Ph_2SiCl(2-Ac-F-Sg)	8	14	9	11	12	14	13	13
Ph_2Si(2-Ac-F-Sg)$_2$	11	17	13	15	14	17	16	17
Ph_3Si(2-Ac-F-Sg)	10	15	10	12	13	15	15	15
Me_2SnCl(2-Ac-F-Sg)	8	13	8	11	10	12	11	13
Me_2Sn(2-Ac-F-Sg)$_2$	11	16	10	14	11	15	13	15
Ph_2SnCl(2-Ac-F-Sg)	9	15	9	12	12	13	13	13
Ph_2Sn(2-Ac-F-Sg)$_2$	13	18	12	15	16	18	17	18
Ph_3Sn(2-Ac-F-Sg)	11	17	10	13	13	15	15	16
Streptomycin	1	2	3	5	2	5	15	17

on the medium previously seeded with organisms in Petri dishes at suitable distances. The Petri plates were stored in an incubator at $28 \pm 2\,^{\circ}C$ for 24 h. The zone of inhibition thus formed around each disc containing the test compound was measured accurately in millimeters (Table 6).

Mode of action[21]

The degradative enzymes produced by the microorganisms are important in host infection, food deterioration and breakdown of organic matter. The enzyme production is here intended to mean both synthesis of the enzyme by the microorganisms and activity of the enzyme in the medium after it is produced. Since the organometal(IV) complexes inhibit the growth of microorganisms, it is assumed that the production of the enzymes is being affected; hence, the organisms are unable to utilize the food and, consequently, the growth ceases. The enzymes that require free sulfydryl groups (–SH) for activity appear to be especially susceptible to deactivation by ions of the complexes.

Owing to greater lipid solubility, complexes facilitate their diffusion through the spore membrane to the site of action within the spores, ultimately killing them by combining with –SH groups of certain cell enzymes. The variation in the effectiveness of different biocidal agents against different organisms, as suggested by Saxena and Singh[23] depends on the impermeability of the cell. The effect of resonating rings on the toxicity may be appraised in the light of modern electronic theory. The resonant energy is the energy in excess of the sum

of the energy of the separate bonds making up the molecule. The Arrhenius activation theory states that an excess of molecular energy seems to activate molecules and produce a more rapid rate of chemical reaction. Resonating structures, such as benzene rings (in the present case), may serve as a powerhouse to activate potentially reactive groupings. If toxicity is dependent on one or more chemical reactions, then any molecule that would increase the rate of chemical reactions must, perforce, enhance toxicity.

From the bactericidal activity, it is apparent that the complexes were more toxic towards the Gram(+) stain than the Gram(−) stain. 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. The lipopolysaccharide forms an outer-lipid membrane and contributes to the complex antigenic specificity of Gram(−) cells.

Further, the results of the biological activity were compared with a conventional fungicide, *Bavistin*, and a conventional bactericide, *Streptomycin*, taken as standards in either case. The results in Tables 5 and 6 also reveal that there is a direct relation between the activity and the coordination environment of the metal. The six-coordinated metal displayed better results than the five-coordinated metal. The compounds containing a halogen atom attached directly to the metal atom also showed moderate activity. Almost all the compounds were found to be more active against all the organisms used than the ligand itself. The mode of action of these compounds may involve the formation of a hydrogen bond with the active centres of the cell constituents, resulting in an interference with the normal cell processes.

Nematicidal activity

With 'environment' being the watchword in the days ahead, the development of environmental friendly technologies to improve and sustain agricultural production is the need of the hour to ameliorate the adverse effects of nematodes on crops.

Therefore, nematicide management in our agro-ecosystems forms a mission-oriented high-technology area involving judicious integration of nematicides of synthetic, natural and microbial origin to sustain the management of key nematode pests of crops. In this direction, field application of nematicides must be economically justifiable to suppress the nematode populations below the economic damage threshold level to obtain the optimum yield. This has to be done judiciously and intelligently. Efforts have to be directed towards methods of reducing the cost of nematicidal treatment. Therefore, field applications have to be selective and restricted to row and spot treatment at the right time and at a judicious rate using systemic nematicides that have low mobility in the soil or by using slow-release formulations.[24]

In the scenario of Indian agriculture, The reduction/complete waiver of customs duty, the manufacture of some chemicals within the country and providing subsidies to farmers are the means through which we can encourage farmers in the use of nematicides. There is also a need to develop simple, cheap and efficient nematicidal applications, and also to educate the growers in rational and judicious use of such chemicals.[24]

Treatment

A step-by-step procedure[25] was followed for obtaining quantities of clean *Meloidogyne incognita* eggs. Brinjal roots heavily infected by *M. incognita*, were washed thoroughly under running water and cut into small pieces. The pieces were placed in a beaker in 100 ml of tap water. The suspension was shaken vigorously for 5 min after adding 500 ml of 1% NaOCl and then the suspension was poured quickly through nested 150- and 400-mesh sieves. Eggs that passed through the 400-mesh sieves were recovered by repeated sieving and rinsing. The eggs that were retained on the 400-mesh sieves were washed with sufficient quantities of distilled water. From the sieves, eggs were eluted and transferred to 40 ml of water.

A centrifuge tube was two-thirds filled with 20% sucrose solution and the egg–water suspension was centrifuged at 500 *g* for 5 min. At the junction of sugar solution, a silver layer containing the suspended eggs and egg suspension was removed with the help of a pipette and quickly poured on to a 400-mesh sieve. The eggs retained on the sieve were washed three times thoroughly with distilled water and collected in a beaker.

A total of 230 eggs of nematode *M. incognita* were used per replicate sample and each treatment was replicated three times. The experiment was conducted at room temperature $30 \pm 2\,^{\circ}C$. The eggs were treated with complexes dissolved in 25, 50 and 100 ppm for 24 hours and observations in relation to hatching of *Meloidogyne* eggs were noted. We concluded that the maximum hatching was recorded in the control (H_2O), but in the eggs treated with chemicals very poor hatching was recorded. The results in Table 7 reveal that the activity increases on complexation and chelation, i.e. the

Table 7. Nematicidal activity of the ligand and its metal complexes (concentrations used: 25, 50 and 100 ppm)

	Hatching in *Meloidogyne incognita* (%)		
Compound	25 ppm	50 ppm	100 ppm
2-Ac-F-SgH	25.8	21.4	17
Me_2SiCl(2-Ac-F-Sg)	23.0	19.6	—
Me_2Si(2-Ac-F-Sg)$_2$	20.2	17.2	—
Ph_2SiCl(2-Ac-F-Sg)	22.1	18.5	—
Ph_2Si(2-Ac-F-Sg)$_2$	17.9	14.2	—
Ph_3Si(2-Ac-F-Sg)	21.0	15.9	—
Me_2SnCl(2-Ac-F-Sg)	21.8	18.7	15
Me_2Sn(2-Ac-F-Sg)$_2$	17.5	15.0	—
Ph_2SnCl(2-Ac-F-Sg)	19.6	17.3	—
Ph_2Sn(2-Ac-F-Sg)$_2$	15.1	12.5	—
Ph_3Sn(2-Ac-F-Sg)	18.7	15.1	—

Table 8. Pupicidal action of the ligand and its metal complexes

Compound	Dose level (ppm)	Average no. of adults Emerged	Average no. of pupal mortality	Adult emergence (%)	Pupal mortality (%)	Corrected mortality (%)
2-Ac-F-SgH	100	16	4	80	20	15.78
	200	14	6	70	30	26.31
Me_2SiCl(2-Ac-F-Sg)	100	14	6	70	30	26.31
	200	12	8	60	40	36.84
Me_2Si(2-Ac-F-Sg)$_2$	100	11	9	55	45	42.10
	200	8	12	40	60	57.89
Ph_2SiCl(2-Ac-F-Sg)	100	12	8	60	40	36.84
	200	9	11	45	55	52.63
Ph_2Si(2-Ac-F-Sg)$_2$	100	9	11	45	55	52.63
	200	5	15	25	75	73.68
Ph_3Si(2-Ac-F-Sg)	100	11	9	55	45	42.10
	200	7	13	35	65	63.15
Me_2SnCl(2-Ac-F-Sg)	100	13	7	65	35	31.57
	200	9	11	45	55	52.63
Me_2Sn(2-Ac-F-Sg)$_2$	100	10	10	50	50	47.36
	200	8	14	60	40	36.84
Ph_2SnCl(2-Ac-F-Sg)	100	11	9	55	45	42.10
	200	7	13	35	65	63.15
Ph_2Sn(2-Ac-F-Sg)$_2$	100	8	12	40	60	57.89
	200	4	16	20	80	78.94
Ph_3Sn(2-Ac-F-Sg)	100	10	10	50	50	47.36
	200	6	14	30	70	68.42

newly synthesized complexes have been found to be more active in inhibiting the hatching of eggs than the parent ligand itself. The nematicidal properties were calculated using the following formula:

$$\mathrm{NP}(\%) = \frac{\mathrm{HT}}{\mathrm{HC}} \times 100$$

where NP is the nematicidal property, HC is the amount of hatching in the control and HT is the amount of hatching in the test plate.

Mode of action

The indirect nematostatic effects of non-fumigant nematicides resulting from impairment of neuromuscular activity interfere with movement, feeding, invasion, development, reproduction, fecundity and hatching of nematodes are considered more important than their direct killing action. Hence, much smaller amounts of non-fumigant than fumigant nematicides are needed in plant protection against nematodes.

Insecticidal activity

To contain insect pests, man has long since been employing various strategies, including mechanical, physical, chemical and biological methods. Among the chemical control measures, tobacco was one of the first materials to be used as an insecticide in around 1763. That was the first era of pesticides, and they gained popularity due to their quick effectiveness against insects.[25]

The start of the second pesticides era was the discovery of DDT in 1938, followed by the synthesis of other organochlorine, organophosphorus and carbamate insecticides, as well as the synthetic population, and they are well tolerated by majority of crops and yield metabolites of insignificant toxicity.[26]

Treatment

A culture of *Trogoderma granarium* was maintained at 35 ± 2 °C and 70 ± 10% relative humidity. Newly transformed pupae were separated from sub-culture especially maintained for the purpose. Ten pupae were treated by the contact method in different concentrations of chemicals and then after evaporation of solvent pupae were transformed into Petri plates for observations. The experiment was replicated three times for each dose level. One control was also run using solvent. After 96 h, total emergence and mortality were counted and the percentage mortality and corrected mortality were calculated using Abott's formula.[26]

$$\text{Mortality}(\%) = \frac{\text{Mortality}}{\text{No. of insects}} \times 100 \qquad (1)$$

$$\text{Corrected mortality}(\%) = \frac{\%\mathrm{MT} - \%\mathrm{MC}}{100 - \%\mathrm{MC}} \times 100 \qquad (2)$$

where MC is the mortality in the control and MT is the mortality in the treated.

The pupicidal action of the chemicals which enter into the puparium of *T. granarium* disrupt the normal metabolic activities of the developing insect.[27] Results are given in Table 8. The results reveal that the complex $Ph_2Sn(2\text{-Ac-F-Sg})_2$ is more toxic than other metal complexes and the $Me_2SiCl(2\text{-Ac-F-Sg})_2$ is less active than all the other metal complexes. Metal complexes are more active than the parent ligand. The toxicity of tin complexes, in general, is higher than the respective silicon complexes. Further, it has been observed that dimethyltin and dimethylsilicon complexes are less active than their diphenyltin and diphenylsilicon complexes.

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