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Synthesis, structural studies and some biological aspects, including nematicidal and insecticidal properties, of organotin(IV) complexes formed with biologically active sulfonamide imine ligand

Mukta Jain[1], Sunita Maanju[2] and R. V. Singh[2]*

[1]Department of Chemistry, Seth G.B. Podar College, Nawalgarh, Jhunjhunu, Rajasthan, India
[2]Department of Chemistry, University of Rajasthan, Jaipur 302004, India

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The synthetic, spectroscopic and biological studies of some organotin(IV) complexes derived from sulfonamide imine having a nitrogen–nitrogen donor system have been undertaken. The sulfonamide imine, on interaction with organotin(IV) chlorides, yields complexes having an Sn←N bond. The structures of these compounds have been elucidated by microestimations and spectral (UV, IR, ^{1}H, ^{13}C and ^{119}Sn NMR) studies, which unerringly point to the trigonal bipyramidal and octahedral geometries for the unimolar and bimolar reactions respectively around tin(IV), as the active lone pair of nitrogen is also included in the coordination sphere. Studies were conducted to assess the comparative growth-inhibiting potential of the synthesized complexes against the sulfonamide imine for a variety of fungal and bacterial strains. The studies demonstrate that the concentrations reached levels sufficient to inhibit and kill the pathogens. The results of the biological studies have also been compared with the conventional standards, Bavistin and Streptomycin, taken for antifungal and antibacterial activities respectively. The complexes also show higher nematicidal and insecticidal properties. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: organotin(IV); sulfonamide imine; fungicide; bactericide; nematicide; insecticide

INTRODUCTION

Many organometallic compounds exhibit interesting antitumour activity against several human cancer cell lines, and organotin(IV) compounds are a widely studied class of metal-based antitumour drugs. Their intensive investigation has led to the discovery of compounds with excellent *in vitro* antitumour activity, but in many cases there is disappointingly low *in vivo* toxicity.[1,2] Organotin(IV) compounds have a range of pharmacological applications. The use of organotin(IV) halides as anti-inflammatory agents against different types of oedema in mice has been reported.[3] Organotin(IV) complexes are also used in agriculture. They are efficient fungicides and bactericides.[4,5] An objective of this account is to highlight a systematic study of the stereochemical and biochemical aspects of the organotin(IV) complexes of sulfonamide imine. The metal chelates, along with their chelating agent, have been tested *in vitro* against pathogenic fungi, viz. *Fusarium oxysporum*, *Aspergillus niger*, *Macrophomina phaseolina* and *Alternaria alternata*, and bacterial, viz. *Klebsiella aerogenous*, *Pseudomonas cepacicola*, *Staphylococcus aureus* and *Escherichia coli*. The resulting complexes are also tested against nematode *Meloidogyne incognita* and insect *Trogoderma granarium*. The results of these investigations are quite encouraging. Based on the coordination sites available in the ligand system, this may be classified as a monobasic bidentate ligand (Fig. 1).

*Correspondence to: R. V. Singh, Department of Chemistry, University of Rajasthan, Jaipur 302004, India.
E-mail: kudiwal@datainfosys.net
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EXPERIMENTAL

Adequate care was taken to keep the organotin(IV) complexes, chemicals and glass apparatus free from moisture. Clean and well-dried glass apparatus fitted with quickfit

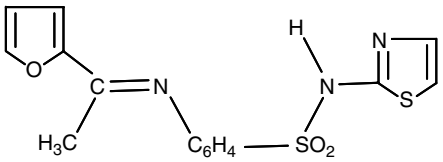

Figure 1. Structure of sulfonamide imine.

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 ligand was prepared by the condensation of 2-acetyl furan with sulfathiazole in equimolar ratio in alcohol. The contents were refluxed for 5–6 h, when the amount of solution remaining is almost half. The refluxing temperature was 40–50 °C. This was allowed to precipitate by overnight cooling, after which the precipitate was filtered, dried and then recrystallized from the same solvent and again dried under reduced pressure. The physical properties of this ligand are recorded in Table 1.

Synthesis of the organotin(IV) complexes

To the calculated amount of the sodium salt of the sulfonamide imine (prepared by adding corresponding weight of sodium to the sulfonamide imine) in dry methanol was added the methanolic solution of organotin chloride (Me_2SnCl_2, Ph_2SnCl_2, or Ph_3SnCl) in 1 : 1 or 1 : 2 stoichiometric proportions. The contents were refluxed over a ratio-head for 16–18 h; the white precipitate of NaCl obtained was removed under suction. The excess of the solvent was then removed 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.

Analytical methods and physical measurements

Nitrogen and sulfur were estimated by the Kjeldahl and Messenger methods respectively. Tin was determined gravimetrically as SnO_2. The conductance was measured with a type 305 Systronics model conductivity bridge and the molecular weights were determined by the Rast camphor method. IR spectra were recorded on a Perkin–Elmer 577 Grating spectrophotometer in the range 4000–200 cm^{-1} as Nujol mulls using KBr optics. Carbon and hydrogen analyses were performed at the RSIC, Chennai. Multinuclear magnetic resonance spectra were recorded on an FX 90Q JEOL spectrometer operating at 90 MHz. ^1H NMR spectra were recorded in deuterated dimethylsulfoxide (DMSO-d_6) at 89.55 MHz using tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were recorded in dry DMSO using TMS as the internal standard at 22.49 MHz. ^{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 tetramethyltin and are supposed to be accurate to ±1 ppm. The electronic spectra were recorded on a Perkin Elmer UV–visible spectrophotometer in the range 200–600 nm, using dry DMSO as the solvent.

RESULTS AND DISCUSSION

The 1 : 1 and 1 : 2 molar reactions of organotin chloride (Me_2SnCl_2, Ph_2SnCl_2, or Ph_3SnCl) with the sodium salt of the nitrogen–nitrogen donor system containing sulfonamide imine in dry methanol proceed smoothly with the precipitation of NaCl, which was removed by filtration. The resulting new derivatives have been obtained as coloured solids and are completely soluble in most of the common organic solvents. All these derivatives were purified by crystallization. Their purity was further checked by thin-layer chromatography using silica gel-G. It was observed that the spot moves as such for a particular type of compound, which clearly indicates the purity of the compounds. The molecular weight determinations show these compounds to be monomers. The molar conductivity in dry dimethylformamide was found in the range (10–22 Ω^{-1} cm^2 mol^{-1}) and thereby indicating their non-electrolytic behaviour.

UV spectra

Regarding the $\pi-\pi^*$ transitions, in the sulfonamide imine the bands observed at 255 nm (C_6H_5) and 285 nm (>C═N) shift to a higher and lower wavelength regions respectively in the case of metal complexes. A band at 370 nm due to the >C═N ($n-\pi^*$) chromophore shifts towards the shorter wavelength side in the metal complexes and appears in the range 345–359 nm, indicating the coordination of the azomethine nitrogen to the tin metal atom. This is probably due to the donation of the lone pair of electrons by the nitrogen of the sulfonamide imine to the central tin atom.

IR spectra

The sulfonamide imine shows a broad absorption in the 3150–3400 cm^{-1} region due to the presence of hydrogen-bonded ν(NH). This band disappears in the tin derivatives, indicating the chelation of the tin atom to the nitrogen atom. A strong band at 1628 cm^{-1} in the sulfonamide imine is characteristic of the azomethine group (>C═N). This band is shifted to lower frequency in the tin derivatives, indicating the coordination of the tin metal to the nitrogen atom. Further, two new bands in the regions 400–410 cm^{-1} and 350–360 cm^{-1} in the tin complexes may be assigned to the ν(Sn←N) and ν(Sn–Cl) modes respectively. A 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 560 cm^{-1} suggests that 1 : 2

Table 1. Physical properties of sulfonamide imine and its tin(IV) complexes[a]

Sulfonamide imine/complex	Reactant (g)	Colour and state	Yield (%)	M.p. (°C)	Elemental analysis (%) C Found (Calc.)	H Found (Calc.)	N Found (Calc.)	S Found (Calc.)	Sn Found (Calc.)	Cl Found (Calc.)	Mol. wt Found (calc.)
SIH $C_{15}H_{13}N_3S_2O_2$	SIH + Sn + Na (0.76+0.48+0.05)	Light yellow solid	73	124–130	51.63 (51.86)	3.51 (3.77)	11.84 (12.09)	18.19 (18.45)	— 	— 	325 (347.39)
$Me_2SnCl(SI)$ $C_{17}H_{18}N_3O_3S_2SnCl$		Brown solid	72	138–140	38.19 (38.48)	3.24 (3.41)	7.77 (7.91)	11.94 (12.08)	22.01 (22.36)	6.48 (6.68)	512 (530.60)
$Me_2Sn(SI)_2$ $C_{32}H_{30}N_6O_6S_4Sn$	(0.92 + 0.29 + 0.06)	Dark brown solid	76	189–191	45.45 (45.67)	3.33 (3.59)	9.80 (9.98)	15.04 (15.24)	13.92 (14.10)	— 	828 (841.53)
$Ph_2SnCl(SI)$ $C_{27}H_{22}N_3O_3S_2SnCl$	(0.63 + 0.63 + 0.04)	Cream solid	72	131–132	49.40 (49.53)	3.11 (3.38)	6.09 (6.41)	9.52 (9.79)	17.90 (18.12)	5.26 (5.41)	630 (654.74)
$Ph_2Sn(SI)_2$ $C_{42}H_{34}N_6O_6S_4Sn$	(0.69 + 0.34 + 0.04)	Brown solid	76	154–156	52.00 (52.23)	3.33 (3.54)	8.52 (8.70)	12.91 (13.28)	12.01 (12.29)	— 	948 (965.67)
$Ph_3Sn(SI)$ $C_{33}H_{27}N_3O_3S_2Sn$	(0.64 + 0.71 + 0.04)	Peach solid	73	81–83	56.78 (56.91)	3.77 (3.90)	5.90 (6.03)	9.02 (9.20)	16.84 (17.04)	— 	674 (693.39)

[a] SIH: 2-acetylfuran sulfathiazole.

complexes of tin exist in the trans form. Medium-to-sharp-intensity bands are observed at 590 and 520 cm^{-1} and may be assigned to the asymmetric and symmetric modes of Sn–C stretching vibrations. A new band observed at 280 cm^{-1} may be assigned to ν (Sn–Ph).[6]

^{1}H NMR spectra

The ^{1}H NMR spectra of the sulfonamide imine and its tin derivatives were recorded in DMSO-d_6 and the chemical shift values δ for the different protons are given in Table 2. The following points, which confirm the suggested structures for the tin derivatives, are worth mentioning.

The NH proton signal of the sulfonamide imine appears at δ 10.54 ppm and disappears in the tin complexes, thereby showing the loss of the NH proton on complexation and the coordination of nitrogen with the tin metal. A sharp singlet due to $H_3C–C{=}N–$ protons at 2.10 ppm in the sulfonamide imine undergoes a downfield shift, appearing at δ 2.13–2.21 ppm, indicating the coordination of the azomethine nitrogen to the tin atom. In the spectra of the tin complexes, a downfield shift in the position of the aromatic protons also indicates the coordination of the azomethine nitrogen to the metal atom, resulting in the formation of coordinate linkage (Sn←N). A new signal at δ 1.03–1.10 ppm in dimethyltin(IV) is assigned to the protons of methyl groups attached to the tin atom. The C–Sn–C angles 124.96° and 133.40° have been calculated[7] using

$$(C–Sn–O) = 0.0161[^{2}J(Sn–H)]^{2} - 1.32[^{2}J(Sn–H)] + 133.4$$

^{13}C NMR spectra

The ^{13}C NMR spectra of the sulfonamide imine and its triphenyl-, diphenyl- and dimethyl-tin derivatives show marked shifts in the positions of carbon atoms attached to different participating groups in the spectra of the complexes, compared with the sulfonamide imine. This clearly indicates the deprotonation of the –NH group and the consequent bond formation with the metal atom and bonding of the azomethine nitrogen. The values of θ(C–Sn–C) angle of these complexes were estimated using

$$^{1}J(^{119}Sn, ^{13}C) = 11.4\theta(C–Sn–C) - 875$$

The values 126.49° and 134.47° are very near to 124.96° and 133.40° which calculated from ^{2}J(Sn–H) coupling constant for organomethyltin(IV) complexes.

^{119}Sn NMR spectra

The ^{119}Sn NMR spectra of organotin(IV) complexes display sharp signals at δ −125 to −365 ppm, clearly showing the penta- and hexa-coordinated environments respectively around the tin atom.

Thus, on the basis of the above spectral factors, as well as on the analytical data, penta- and hexa-coordinated trigonal bipyramidal and octahedral geometries have been established for organotin(IV) complexes (Fig. 2).

Table 2. ^{1}H and ^{13}C NMR spectral studies of sulfonamide imine and its tin complexes

Sulfonamide imine/complex	$^{1}J(^{119}Sn, ^{13}C)$ (Hz)	$^{2}J(^{119}Sn, ^{13}C)$ (Hz)	$^{3}J(^{119}Sn, ^{13}C)$ (Hz)	Estimated C–Sn–C angle (°)	^{2}J(Sn–H) (Hz)	C–Sn–C angle (°)	^{119}Sn
SIH	—	—	—	—	—	—	—
$Me_2SnCl(SI)$	567	—	—	126.49	75	124.96	−149
$Me_2Sn(SI)_2$	658	—	—	134.47	82	133.40	−365
$Ph_2SnCl(SI)$	541	40.8	130.2	124.21	—	—	−125
$Ph_2Sn(SI)_2$	627	91.2	146.3	131.75	—	—	−336
$Ph_3Sn(SI)$	532	38.9	128.0	123.42	—	142	

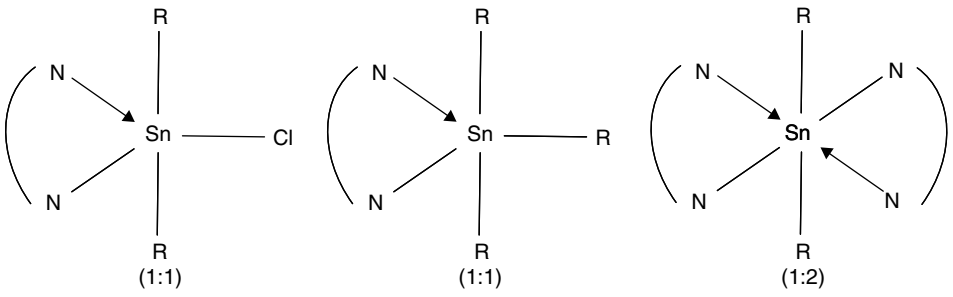

Figure 2. Structures of the complexes.

BIOLOGICAL ASPECTS

Many infections of plants are caused by fungi. The lesions produced include various types of blights, mildews, leaf spots, and galls, and such systemic diseases like rusts and smuts. In contrast to plants, far fewer infectious diseases of animals and humans are caused by fungi than are initiated by bacteria and viruses. Cultures of test organisms were grown on PDA media (starch, glucose, agar-agar and water) for fungi and on agar media (peptone, beef extract, agar-agar, NaCl and water) for bacteria for 7 days at the optimum temperature for growth. All the glassware used was sterilized in an autoclave before use. The radial growth method[8] and the paper-disc plate method[9] were employed to evaluate the fungicidal and bactericidal activities respectively.

Radial growth method

To the medium was added the requisite amount of the compound after being dissolved in methanol so as to obtain the desired final concentration. A series of concentrations was prepared. The medium was than 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 a certain amount of the compound. Suitable controls were also prepared, where the culture discs were grown under the same conditions on PDA without the compound. These Petri 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 the fungi toxicity and the growth inhibition was calculated.

Paper-disc plate method

Agar medium (15 ml) was pipetted into the Petri dish. After the agar solidified, 5 ml of warm seeded agar was applied. The seeded agar was prepared by cooling the molten agar to $40\,^{\circ}C$ and then adding the amount of bacterial suspension. The plate was tilted to ensure even coverage before the agar solidified. These discs, 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 at various concentrations. The discs were dried and placed 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 millimetres).

The action of the sulfonamide imine and its organotin(IV) complexes as fungicides against pathogenic fungi (*A. niger*, *M. phaseolina*, *F. oxysporum* and *A. alternata*) and as bactericides

Table 3. Sulfonamide imine and its tin complexes as fungicides, inhibition percentage after 96 h (conc. 25, 50 and 100 ppm)

	Aspergillus niger			*Macrophomina phaseolina*			*Fusarium oxysporum*			*Alternaria alternata*		
Sulfonamide imine/complex	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm
SIH	34	53	61	35	50	68	39	56	65	43	60	66
$Me_2SnCl(SI)$	39	59	74	41	55	72	44	60	71	46	60	68
$Me_2Sn(SI)_2$	45	67	82	46	58	77	48	63	78	49	65	73
$Ph_2SnCl(SI)$	41	61	77	43	56	75	46	62	74	47	62	69
$Ph_2Sn(SI)_2$	47	70	8	49	61	82	49	65	83	52	69	78
$Ph_3Sn(SI)$	43	64	81	44	57	77	47	62	77	48	65	72
Bavistin	69	86	98	72	82	96	70	91	100	71	86	100

Table 4. Sulfonamide imine and its tin complexes as bactericides, diameter inhibition zone (mm) after 24 h (conc. 500 and 1000 ppm)

	Escherchia coli (−)		*Klebsiella aerogenous* (−)		*Pseudomonas cepacicola* (−)		*Staphylococcus aureus* (+)	
Sulfonamide imine/complex	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm
SIH	6	6	6	11	10	12	9	13
$Me_2SnCl(SI)$	10	14	11	15	13	13	11	13
$Me_2Sn(SI)_2$	12	18	14	18	16	16	15	16
$Ph_2SnCl(SI)$	11	15	12	16	15	15	14	14
$Ph_2Sn(SI)_2$	14	19	15	19	18	19	19	18
$Ph_3Sn(SI)$	12	17	13	17	16	17	16	17
Streptomycin	1	2	3	5	2	5	15	17

against bacteria (*E. coli*(−), *K. aerogenous*(−), *P. cepacicola*(−) and *S. aureus*(+), are recorded in Tables 3 and 4.

The metal chelates are more active than the chelating agent itself. One reason might be that complexation reduces hydrogen bonding, but bioactivity increases. The activity of the complexes is thought to be enhanced due to the introduction of the metal ions in the ligand, i.e. sulfonamide imine. The microbial activity was also compared with a conventional fungicide, Bavistin, and a conventional bactericide, Streptomycin, taken as standards.

The toxicity of all the organatin(IV) complexes can be well understood by considering chelation theory. Chelation reduces the polarity of the central ion, mainly because of the 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 favours its permeation through the lipid layer of the membrane.

Nematicidal study

Plant parasitic nematodes infect almost every plant on Earth, causing heavy economic losses. The yields of okra, tomato and brinjal typically suffer 90.9%, 46.2% and 2.3% losses respectively due to *Meloidogyne incognita*.[10] The root-knot nematode (*Meloidogyne* spp.) produces galls on the roots of many vegetable crops, pulses, some fruit crops, tobacco, ornamental crops and causes severe losses. The avoidable yield losses due to *M. incognita* were estimated to be 28.08%, 33.68%, 43.48% and 28.60% in okra, brinjal, french bean and cowpea respectively.[11] By obtaining quantities of clean *M. incognita* eggs, the method followed as step by step.[12]

200 eggs were taken and subjected to treatment in each nematode hatching dish. After 24, 48 and 72 h, the numbers of juveniles were counted. After 72 h, sieves containing the unhatched eggs were removed from the test solution, washed thoroughly with distilled water and left in distilled water for 24 h to record any further hatching. Water and methanol solutions were used for this experiment. Each treatment was replicated four times and the mean taken of four such readings.

The indirect nematostatic effects of non-fumigant nematicides resulting from impairment of neuromuscular activity,[13] interference 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 study

Trogoderma granarium (Khapra beetle) is a serious pest of stored grains. It is distributed extensively and more common in warmer regions of the world. It consumes spices, gums, seeds, dry fruits and other dried plant and animal materials. Khapra beetle crawls into cracks and crevices in the walls of grain storage. It can survive for long periods without food by entering into diapause under adverse conditions. The stock culture was established in the laboratory in large glass jars on wheat grains. 100 pairs of fresh insects were released on disinfested wheat grains inside the jars. Healthy conditions of the stock culture were maintained by frequent replacement of the stale grains with fresh ones. The jars were kept at $35 \pm 2\,^{\circ}C$ and at $60 \pm 10\%$ relative humidity. After the stock culture bloomed to its youth, subsequent cultures were also established by releasing a few pairs of freshly emerged adult beetles on disinfested wheat grains in smaller glass jars. Beetles were removed after allowing 7–8 days for *oviposition*. By repeating the process every week, a continuous supply for experimentation was thus maintained. To prevent the food effects, fresh wheat was used for subculture. Before use, all the jars and grains were sterilized to rule out the possibilities of infection, and the insects were transferred with the help of forceps and hair brushes.

Ovicidal treatment

To determine the efficacy of the chemicals as an ovicide, eggs were treated by the contact method. A thin film of the desired concentration was prepared by spreading 1 ml of chemical solutions on Petri dishes (5.0 cm diameter). The solvent was allowed to evaporate. 20 eggs, aged 0–24 h, were kept in contact with the insecticidal film throughout their incubation period. A control was also run with each set of experiments, in which the eggs were kept in 1 ml of solvent. Using Abott's formula,[14] the percentage egg mortality and percentage corrected egg mortality were calculated.

Larvicidal treatment

The Larvicidal efficacy of the chemicals was assessed by the feeding method first instar larvae were separated from the subculture in vials containing 5 g of topically treated wheat grains with 1 ml of chemicals. Larvae were allowed to continue their development until pupae formation on this diet. Each dose was replicated three times. The food was treated with only solvent as a control. Abbot's formula was used to calculate the percentage larvae mortality and percentage corrected mortality.[15]

Final larval instars were removed from the subculture and kept in a separate container on the same rearing medium; pupae of known age (0–12 h) were taken out and were dipped in the desired concentration of chemicals. Along with a control for each dose, three replicates were carried out, and total emergence and pupal mortality was recorded after 96 h. Abott's formula was used to calculate the percentage pupal mortality and pupal corrected mortality.

Adulticidal treatment

The contact method was used to assess the adulticidal action using 1 ml of the respective doses for which 5 g of wheat grains were treated. The solvent was allowed to evaporate completely. Along with a control, the experiment was replicated three times. Newly emerged adults were taken

Table 5. Sulfonamide imine and its tin complexes as ovicides

Sulfonamide imine/complex	Dose level (ppm)	Average no. of eggs hatching	Average no. of eggs unhatched	Eggs hatching (%)	Eggs unhatched (%)	Corrected mortality (%)
SIH	100	15	5	75	25	21.05
	200	11	9	55	45	42.10
$Me_2SnCl(SI)$	100	12	8	60	40	38.84
	200	7	13	35	65	63.15
$Me_2Sn(SI)_2$	100	8	12	40	60	57.89
	200	5	15	25	75	73.68
$Ph_2SnCl(SI)$	100	10	10	50	50	47.36
	200	6	14	30	70	68.42
$Ph_2Sn(SI)_2$	100	7	13	35	65	63.15
	200	3	17	15	85	84.21
$Ph_3Sn(SI)$	100	8	12	40	60	57.89
	200	5	5	25	75	73.68
Control	—	19	1	95	5	—

Table 6. Sulfonamide imine and its tin complexes as larvicides

Sulfonamide imine/complex	Dose level (ppm)	Average no. of pupae formed	Average no. of dead larvae	Pupae formation (%)	Larval mortality (%)	Corrected mortality (%)
SIH	100	16	4	80	20	15.78
	200	13	7	65	35	31.57
$Me_2SnCl(SI)$	100	12	8	60	40	38.84
	200	8	12	40	60	57.89
$Me_2Sn(SI)_2$	100	9	11	45	55	52.63
	200	6	14	30	70	68.42
$Ph_2SnCl(SI)$	100	11	9	55	45	42.10
	200	7	13	35	65	63.15
$Ph_2Sn(SI)_2$	100	8	12	40	60	57.89
	200	4	16	20	80	78.94
$Ph_3Sn(SI)$	100	10	10	50	50	47.36
	200	6	14	30	70	68.42
Control	—	19	1	95	5	—

Table 7. Sulfonamide imine and its tin complexes as pupicides

Sulfonamide imine/complex	Dose level (ppm)	Average no. of adults emerged	Average no. of pupal mortality	Emerged adults (%)	Pupal mortality	Corrected mortality (%)
SIH	100	15	5	75	25	21.05
	200	14	6	70	30	26.31
$Me_2SnCl(SI)$	100	13	7	65	35	31.57
	200	9	11	45	55	52.63
$Me_2Sn(SI)_2$	100	10	10	50	50	47.36
	200	6	14	30	70	68.42
$Ph_2SnCl(SI)$	100	11	9	55	45	42.10
	200	7	13	35	65	63.15
$Ph_2Sn(SI)_2$	100	8	12	40	60	57.89
	200	5	15	25	75	73.68
$Ph_3Sn(SI)$	100	10	10	50	50	47.36
	200	6	14	30	70	68.42
Control	—	19	1	95	5	—

Table 8. Sulfonamide imine and its tin complexes adulticides

Sulfonamide imine/complex	Dose level (ppm)	Average no. of adults each vial	Average mortality after 48 h	Adult mortality (%)	Corrected mortality (%)
SIH	100	20	4	20	15.78
	200	20	6	30	26.31
$Me_2SnCl(SI)$	100	20	8	40	38.84
	200	20	11	55	52.63
$Me_2Sn(SI)_2$	100	20	10	50	47.36
	200	20	14	70	68.42
$Ph_2SnCl(SI)$	100	20	9	45	42.10
	200	20	13	65	63.15
$Ph_2Sn(SI)_2$	100	20	12	60	57.89
	200	20	16	80	78.94
$Ph_3Sn(SI)$	100	20	11	55	52.63
	200	20	14	70	68.42
Control	—				

from the subculture and placed into plastic vials containing treated food. After 48 h, observations were made and Abott's formula was used to calculate the percentage corrected mortality.

The different ways in which an insecticide acts on a target organism depend on their physical and chemical make up. Some insecticides are physical poisons, causing asphyxiation; some are protoplastic poisons; a few are respiratory poisons; but majority are nerve poisons. The action of insecticides upsets the normal behaviour and actions of the target organisms, and the surest and quickest way to achieve this is to poison the nervous system.[16,17]

Those chemicals that are applied by contact and as stomach poisons seem to be the most hazardous for the beetles. These chemicals, when mixed with their food, penetrate rapidly through the body wall of the insects and thereby obstruct the normal respiratory activities of the adults by adversely affecting the spiracles. The pupicidal action may be due to the chemical entering into the puparium and disrupting the normal metabolic activities of the developing insect. High larvicidal activities were obtained with the present chemicals. It was observed that earlier larval instars were more sensitive than the later instars. This suggests that chemicals penetrate into the insect cuticle. These chemical-treated grains were slowly or very less fed by the larvae of *T. granarium* which leads to the starvation in the developing larvae. It was observed that a few egg shells split and undeveloped larvae failed to come out of the eggs; it was also observed that some other treated eggs were disfigured and stuck to the surface as a dried yellow mass without showing shell splitting. This may suggest that the toxic substances in the chemicals interfere with normal embryonic development, which in turn may result in certain disturbances during the process of cell division and blastokinesis, thus exhibiting impressive ovicidal properties against *T. granarium*.

The data for the ovicidal, larvicidal, pupicidal and adulticidal actions are shown in Tables 5–8. The following results are indicated.

1. All metal complexes are more active than sulfonamide imine.
2. Bimolar complexes are more toxic than unimolar complexes.
3. Organo-aryl compounds are more toxic than the organo-alkyl derivatives.
4. Triphenyl organotin(IV) complex is more active in all the unimolar complexes.

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REFERENCES

1. Gielen M. *Appl. Organometal. Chem.* 2002; **16**: 481.
2. Bregadze VI, Glazun SA, Petrovskii PV, Starikova ZA, Buyanovskaya AG, Takazova RU, Gielen M, de Vos D, Kemmer M, Biesemans M, Willem R. *Appl. Organometal. Chem.* 2003; **17**: 191.
3. Arakava Y, Wada O. *Biochem. Biophys. Commun.* 1989; **125**: 59.
4. Belwal S, Saini RK, Singh RV. *Indian J. Chem. A* 1998; **37**: 245.
5. Belwal S, Joshi SC, Singh RV. *Main Group Met. Chem.* 1997; **20**: 313.
6. Belwal S, Singh RV. *Appl. Organometal. Chem.* 1998; **12**: 39.
7. Lockhart TP, Manders WF. *Inorg. Chem.* 1986; **25**: 892.
8. Fahmi N, Singh RV. *Trans. Met. Chem.* 1994; **19**: 453.
9. Singh VP, Singh RV, Tandon JP. *J. Inorg. Biochem.* 1990; **39**: 237.
10. Bhatti DS, Jain RK. *Indian J. Nematode* 1997; **7**: 37.
11. Reddy PP, Singh DB. Assessment of avoidable losses in okra, brinjal, french bean and cowpea due to root-knot nematodes. In

IIIrd International Symposium on Plant Pathology, New Delhi, 1981; 93.
12. Jain M, Kumar D, Singh RV. *Main Group Met. Chem.* 2003; **26**: 99.
13. Jain M, Singh RV. *Int. J. Chem. Sci.* 2003; **1**(1): 17.
14. Abott WS. *J. Econ. Entomol.* 1925; **18**: 265.
15. Jain M, Gaur S, Singh VP, Singh RV. *Appl. Organometal. Chem.* 2004; **18**: 73.
16. Dwivedi SC, Mathur B. *J. Ecotoxicol. Environ. Monit.* 1991; **9**: 19.
17. Rajapakse, Rohan HS, Maculatus C. *Entomon* 1996; **21**: 211.

