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Synthesis, spectral, thermal and anti-fungal studies of organotin(IV) thiohydrazone complexes

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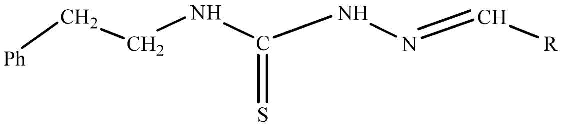
ABSTRACT

The reaction of tribenzyltin(IV) chloride and di(*para*-chlorobenzyl)tin(IV) dichloride with thiohydrazones derived by condensation of 2-phenylethyl *N*-thiohydrazide with benzaldehyde, salicaldehyde, *p*-methylacetophenone and cinnamaldehyde have been investigated in 1:1 molar ratio. These ligands act as neutral, bidentate species and coordinate to the central tin (IV) atom through the thiosulphur and azomethine nitrogen. The newly synthesized complexes have been characterized by elemental analysis and molecular weight determination. The mode of bonding of the complexes has been suggested on the basis of infrared, electronic and ^{1}H NMR spectroscopy, and probable structures have been assigned to these complexes. Phenomenological and kinetic parameters have been calculated using thermogravimetric (TG) and differential thermal analytical (DTA) curves and their variations have been correlated with some structural parameters of the complexes. The ligands and their tin(IV) complexes have been screened in vitro for their fungicidal activity against *Rhizoctonia solanii* and *Sclerotium rolfsii* and found to be quite active in this respect.

1. Introduction

Triorganotin derivatives of bidentate ligands have been extensively studied and are reported to have tetrahedral [1,2] or trigonal bipyramidal [3–6] (TBP) geometry depending upon the nature of organo group as well as the electronegativity of the atoms attached with central tin atom [2]. Thiohydrazones possess considerable biological [7] and antitumor [8] activity, which is significantly affected by substitution at the moiety's N(4) position [9,10]. Thiohydrazides and thiohydrazones can exist as thione-thiol tautomers and coordinate as a bidentate N–S ligand forming five membered chelate rings. But the coordination is pH dependent. In continuation with our previous work on various thiohydrazides [11], now we report complexes formed by the reaction of organotin(IV) chloride with thiohydrazones derived by condensation of 2-phenylethyl *N*-thiohydrazide with benzaldehyde, salicaldehyde, *p*-methylacetophenone and cinnamaldehyde. The structures of the ligands are shown in Fig. 1.



where R = Ph, *o*-OHC_6H_5, –CH=CH-Ph, –$C(CH_3)$-C_6H_4-*p*-CH_3

2. Experimental

All reagents used were AR grade and the solvents were purified and dried by standard methods and moisture was excluded from glass apparatus using $CaCl_2$ drying tubes.

2.1. Physical measurements

The elemental analysis was carried out on an Elementar Analysensysteme GmbH Varion EL *III*, Germany. The electronic spectra were recorded on a Varian Cary 100 UV–vis spectrophotometer. IR and far IR spectra were recorded on KBr and polyethylene discs, respectively, using a PerkinElmer Spectrum 2000 FTIR spectrometer and ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker spectrospin advance 300 spectrometer. Tetramethylsilane was used as an internal reference for ^{1}H NMR. Tin was determined gravimetrically as SnO_2 and chlorine was estimated volumetrically by Volhard's method. The kinetics of thermal decomposition of these complexes has been measured under dynamic temperature conditions by both thermogravimetric (TG) and differential

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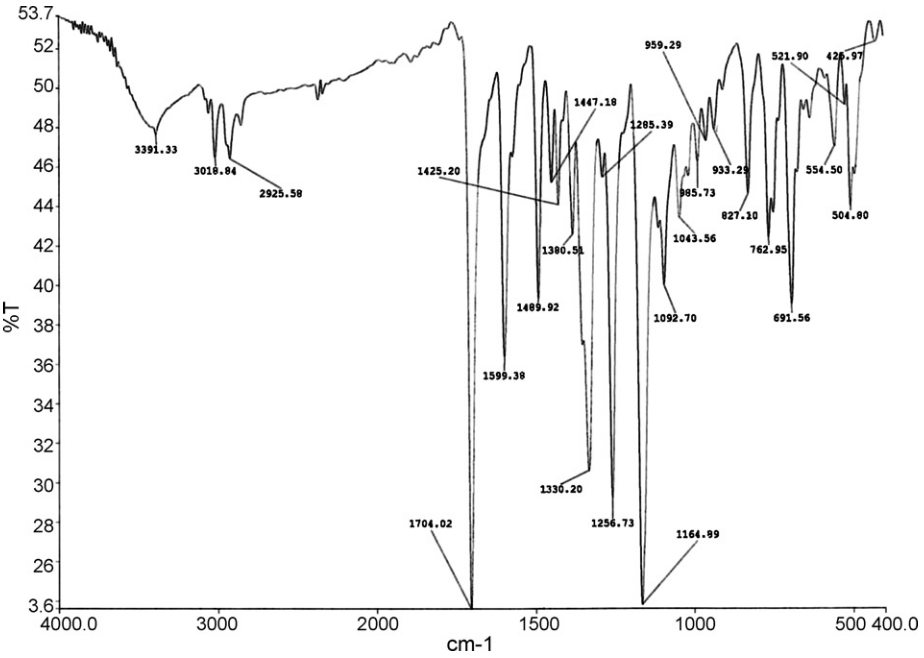
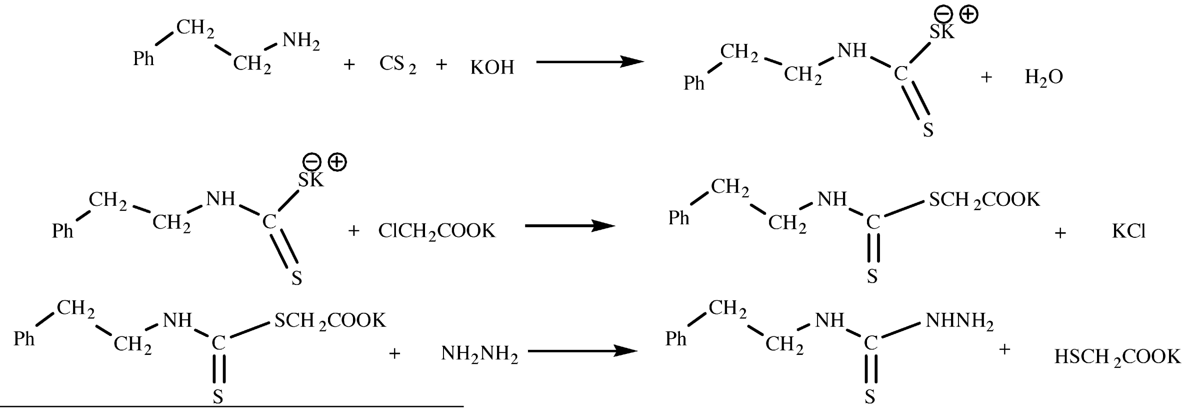


Fig. 1. IR spectra of $(p\text{-ClC}_6\text{H}_4\text{CH}_2)_2\text{Sn}(\text{L}^1)\text{Cl}_2$ complex.

thermal analysis (DTA) techniques recorded on a Thermoflex PTC-10A Rigaku Corporation, Japan in static air atmosphere. A sample size of 5–10 mg and a heating rate of $5^\circ\,\text{min}^{-1}$ were used. The Pt crucible was used with alumina as the reference material. Evaluation of kinetic parameters has been performed by means of the Horowitz–Metzger method [12].

2.2. Synthesis of organotin and ligands

Tribenzyltin(IV) chloride, $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{SnCl}$ and di(*para*-chlorobenzyl)tin(IV) dichloride, $(p\text{-ClC}_6\text{H}_4\text{CH}_2)_2\text{SnCl}_2$, were synthesized by the method given by Sisido et al. [13].



2.2.1. Synthesis of 2-phenylethyl N-thiohydrazide

All the ligands were synthesized by a modified [14] literature method [15]. Phenylethylamine (25.37 ml, 0.2 mol) (density 0.960) was dissolved in ethanol and to it KOH (11.2 g, 0.2 mol) in minimum ethanol was added. Carbon disulphide (12.06 ml, 0.2 mol) (density 1.26) was then added to the mixture, the temperature being kept below 10 °C. An off-white crystalline precipitate of the potassium salt of 2-phenylethyl dithiocarbamate separated. Its aqueous solution was treated with freshly prepared potassium chloroacetate (0.2 mol). The temperature of the reaction mixture was increased to and maintained below 40 °C for 1 h. The mixture was then left for 24 h at room temperature. Then a methanolic solution of hydrazine hydrate (9.72 ml, 0.2 mol) was added and the reaction mixture heated on a water bath for an hour, at which the desired product separated. It was cooled in ice for 24 h, and then filtered. The thiohydrazide so obtained was recrystallized and dried.

2.2.2. Thiohydrazones

Thiohydrazones were prepared by boiling under reflux the 2-phenylethyl *N*-thiohydrazide with various aldehydes and ketones in methanol.

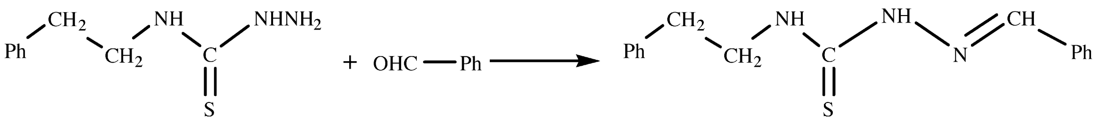


Table 1
Analytical data for thiohydrazone ligands.

Compound	Empirical formula	Color and state	mp (°C)	Analysis found (calc.) (%)		
				C	H	N
Benzaldehyde 2-phenylethyl *N*-thiohydrazone (L^1)	$C_{16}H_{17}N_3S$	Yellow	118	67.38 (67.81)	5.96 (6.05)	14.82 (14.82)
Salicaldehyde 2-phenylethyl *N*-thiohydrazone (L^2)	$C_{16}H_{17}N_3OS$	Dark brown	109	63.09 (64.19)	4.83 (5.72)	14.11 (14.04)
p-Methylacetophenone 2-phenylethyl *N*-thiohydrazone (L^3)	$C_{18}H_{21}N_3S$	Dark yellow	122	69.99 (69.42)	5.28 (6.80)	12.63 (13.49)
Cinnamaldehyde 2-phenylethyl *N*-thiohydrazone (L^4)	$C_{18}H_{19}N_3S$	Brown–red	123	68.84 (69.87)	6.20 (6.19)	13.56 (13.58)

Table 2
Analytical data for the metal complexes.

Compound	Ligand	Product, color and state	Empirical formula	mp (°C)	Analysis found (calc.) (%)				
					Sn	C	H	N	Cl
$(C_6H_5CH_2)_3SnCl$	L^1	$(C_6H_5CH_2)_3Sn(L^1)Cl$, brown and solid	$C_{37}H_{38}SnN_3SCl$	104	17.83 (16.70)	62.20 (62.51)	5.55 (5.39)	6.01 (5.91)	4.06 (4.99)
$(p\text{-}ClC_6H_4CH_2)_2SnCl_2$	L^1	$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl_2$, dirty yellow and solid	$C_{30}H_{29}SnN_3SCl_4$	84	16.17 (16.39)	50.51 (49.76)	4.24 (4.04)	6.23 (5.80)	17.29 (19.58)
$(C_6H_5CH_2)_3SnCl$	L^2	$(C_6H_5CH_2)_3Sn(L^2)Cl$, yellow and solid	$C_{37}H_{38}SnN_3SOCl$	130	15.06 (16.33)	62.30 (61.13)	5.99 (5.27)	4.89 (5.78)	5.05 (4.88)
$(C_6H_5CH_2)_3SnCl$	L^3	$(C_6H_5CH_2)_3Sn(L^3)Cl$, yellow and solid	$C_{39}H_{42}SnN_3SCl$	128	15.15 (16.46)	63.33 (63.39)	4.29 (5.73)	5.89 (5.69)	4.34 (4.80)
$(C_6H_5CH_2)_3SnCl$	L^4	$(C_6H_5CH_2)_3Sn(L^4)Cl$, brown and solid	$C_{39}H_{40}SnN_3SCl$	130	17.87 (16.11)	64.55 (63.56)	5.45 (5.47)	6.11 (5.70)	5.99 (4.81)
$(p\text{-}ClC_6H_4CH_2)_2SnCl_2$	L^4	$(p\text{-}ClC_6H_4CH_2)_2Sn(L^4)Cl_2$, brown and solid	$C_{32}H_{31}SnN_3SCl_4$	138	14.10 (15.82)	52.73 (51.23)	3.41 (4.17)	5.50 (5.60)	19.19 (18.90)

2.3. Organotin(IV) complexes

A solution of ligand in 25 ml of dioxane was added slowly to organotin(IV) chloride in 25 ml of dioxane. The mixture so obtained was refluxed for an hour and stirred for additional ~4 h and then the solution was reduced in concentration to one-fourth of its original volume under vacuum. The complex so obtained was recrystallized and finally washed with petroleum ether and dried in a dessicator over $CaCl_2$.

3. Results and discussions

The complexes synthesized were found to be pure and soluble in acetone, chloroform and dimethylsulphoxide solvents. The elemental analysis is given for thiohydrazone ligands (Table 1) and there corresponding complexes (Table 2). All the complexes were colored show sharp melting point and are crystalline and powdery.

3.1. Electronic spectra

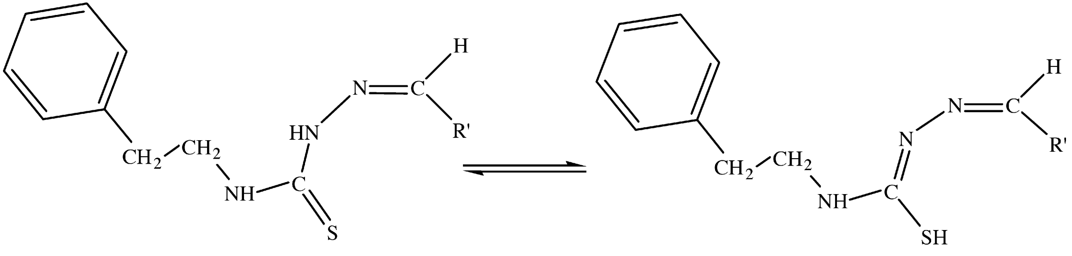
Table 3
Electronic spectra for the complexes.

Complexes	λ_{max} (nm)	log ε
$(C_6H_5CH_2)_3Sn(L^1)Cl$	275, 329, 382	1.12, 0.98, 0.26
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl_2$	276, 330, 381	1.52, 1.07, 0.54
$(C_6H_5CH_2)_3Sn(L^2)Cl$	278, 403, 564	1.73, 1.10, 0.48
$(C_6H_5CH_2)_3Sn(L^3)Cl$	243, 337, 410	1.65, 1.45, 0.56
$(C_6H_5CH_2)_3Sn(L^4)Cl$	243, 370, 411	1.59, 1.38, 0.54
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^4)Cl_2$	251, 371, 410	1.39, 0.37, 0.25

The thiohydrazones feature a strong band at ~318 nm because of n–π^* azomethine function with shoulders at higher and lower energy. This shows a very little shift in complexes but there is enhancement of intensity. One absorption band ~275 nm is observed which is assigned to π–π^* intraligand electron transition of N$\underline{\cdots}$C$\underline{\cdots}$S group. This band shifts to lower side on complexation showing the involvement of C=S group. One additional band appears in complexes because of *metal → ligand* charge transfer transitions. Electronic spectral data of thiohydrazone complexes is given in Table 3.

3.2. Infrared spectra

The thiohydrazone ligand has the capability of existing in solution either as the thioketo form (1A) or as the enethiol form (1B). The IR spectra, however, do not display the ν(SH) band at ~2521 cm^{-1}, instead, an intense band for ν(C=S) located at ~986 cm^{-1}, is observed, suggesting that in the solid state the ligands remain in thioketo form [16].



(1A) (1B)

In thiohydrazones ν(C=N) bands observed at ~1600 cm^{-1} is shifted in the spectra of metal chelates, suggesting positive involvement of the azomethine nitrogen in bonding to the metal ion. Coordination of azomethine nitrogen to the metal ions is further supported by the displacement of ν(N–N) stretching bands towards lower frequency. Significant changes in ligand bands upon

Table 4
Infrared absorption frequencies (cm^{-1}) for the organotin(IV) complexes.

Complexes	ν(C=N)	ν(N–H)	ν(C=S)	ν(N–N)	ν(M–S)	ν(M–N)	ν(M–Cl)
$(C_6H_5CH_2)_3Sn(L^1)Cl$	1598	3062	904	1042	353	697	372
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl_2$	1599	3018	827	1043	350	685	371
$(C_6H_5CH_2)_3Sn(L^2)Cl$	1598	3063	916	1042	341	700	375
$(C_6H_5CH_2)_3Sn(L^3)Cl$	1596	3059	920	1029	360	701	374
$(C_6H_5CH_2)_3Sn(L^4)Cl$	1597	3061	921	1040	342	653	384
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^4)Cl_2$	1599	3059	899	1041	348	699	372

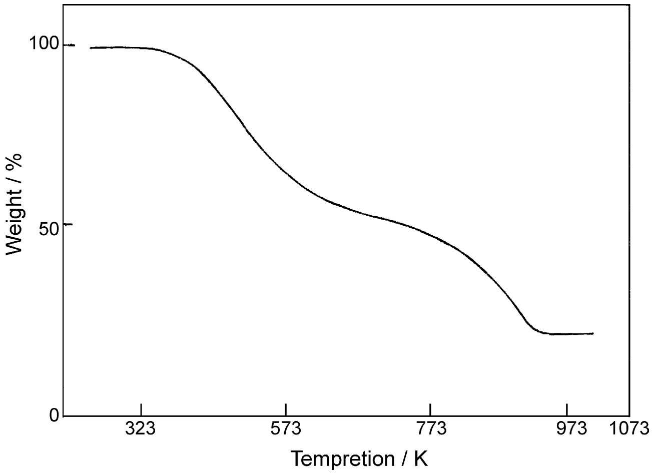


Fig. 2. TG curve for $(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl_2$ complex.

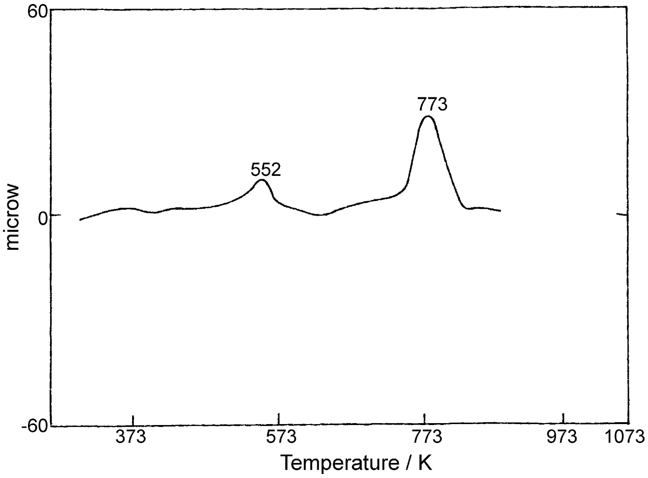


Fig. 3. DTA curve for $(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl_2$ complex.

complexation include increase in ν(C=N). These data indicate coordination through the azomethine nitrogen to the metal ion. The bands at ~986 cm^{-1} are assigned to ν(C=S) which shift to lower frequency of 827–932 cm^{-1}. These observations and appearance of medium bands having (CS) character at 770–725 cm^{-1} in the spectra of the metal chelates suggest coordination of thiocarbonyl sulphur to the metal ion [17]. L^2 has salicaldehyde OH group that can also take part in coordination. But ν(C–O) does not shift from its position ~1260 cm^{-1} in the ligands, i.e. phenolic O is not participating in coordination. Moreover in far IR region no band corresponding to M–O was observed in the region 400–430 cm^{-1}. In far i.r. region several new bands of metal complexes were observed at ν(Sn–Cl) [18] at ~371 cm^{-1}, ν(Sn–N) [19] at ~653 cm^{-1} and ν(Sn–S) [19] at 342 cm^{-1} thus lending support to the proposed coordination in the complexes. IR spectra of the complexes are given in Table 4 (Fig. 1).

3.3. ^1H NMR spectra

The proton magnetic resonance spectra of the ligands and their corresponding complexes are shown in Table 5. A number of signals have been observed which on complexation shift from their original position. (1) The chemical shift at δ (ppm) 6.83–6.77 is due to aromatic ring, which shifts to δ (ppm) 6.89–6.75 on complexation. (2) The –C=N of thiohydrazone ligands at δ (ppm) 8.21 shifts to δ (ppm) 8.28. (3) Some additional peaks have been observed due to benzyl group at δ (ppm) 3.10 due to $-CH_2$ and δ (ppm) 7.39–7.21 due to Ar–H. A downfield shift in the position of resonance signals of the complexes in comparison to the free ligands may be attributed as a result of co-ordination of the ligand to metal ion.

On the basis of spectral evidence, the following hypothesized structure representing coordination have been prepared for the complexes synthesized:

Table 5
^1H NMR spectral data for the compounds.

Compounds	CH=N	$-Sn-CH_2$	NH
L^1	8.21 (s, 1H)	–	8.93 (brs, 2H)
$(C_6H_5CH_2)_3Sn(L^1)Cl$	8.24 (s, 1H)	3.10 (s, 6H)	8.94 (brs, 2H)
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl_2$	8.28 (s, 1H)	3.01 (s, 4H)	8.96 (brs, 2H)
L^2	8.15 (s, 1H)	–	9.10 (brs, 2H)
$(C_6H_5CH_2)_3Sn(L^2)Cl$	8.19 (s, 1H)	3.10 (s, 6H)	9.11 (brs, 2H)
L^3		–	8.92 (brs, 2H)
$(C_6H_5CH_2)_3Sn(L^3)Cl$		2.89 (s, 6H)	8.95 (brs, 2H)
L^4	8.29 (d, 1H)	–	8.97 (brs, 2H)
$(C_6H_5CH_2)_3Sn(L^4)Cl$	8.30 (d, 1H)	3.03 (s, 6H)	8.99 (brs, 2H)
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^4)Cl_2$	8.34 (d, 1H)	3.10 (s, 4H)	9.02 (brs, 2H)

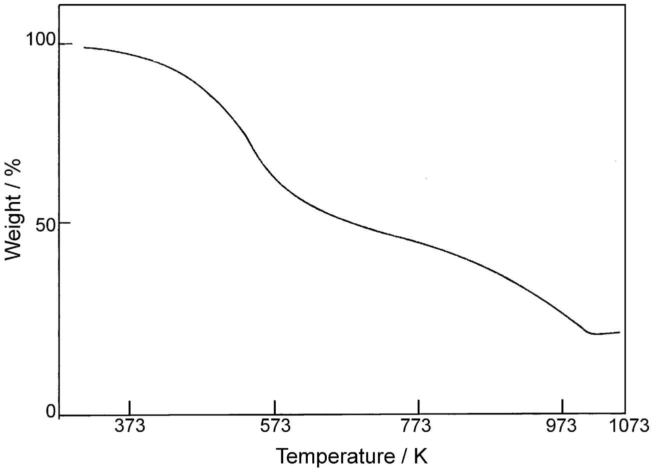
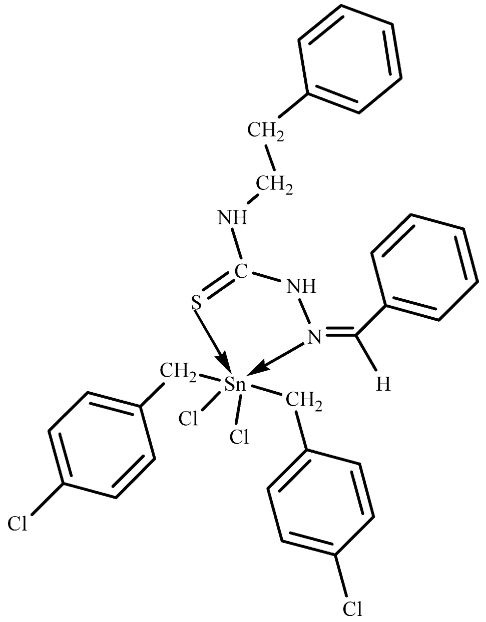


Fig. 4. TG curve for $(C_6H_5CH_2)_3Sn(L^3)Cl$ complex.



3.4. Thermal data

The order of reaction for the thermal decomposition of the above complexes was found to be one. The complexes decompose in two steps. The first step corresponds to the loss of R groups; the second step corresponds to the decomposition of the organic part (L) and ultimately, formation of SnO_2 (Figs. 2–5).

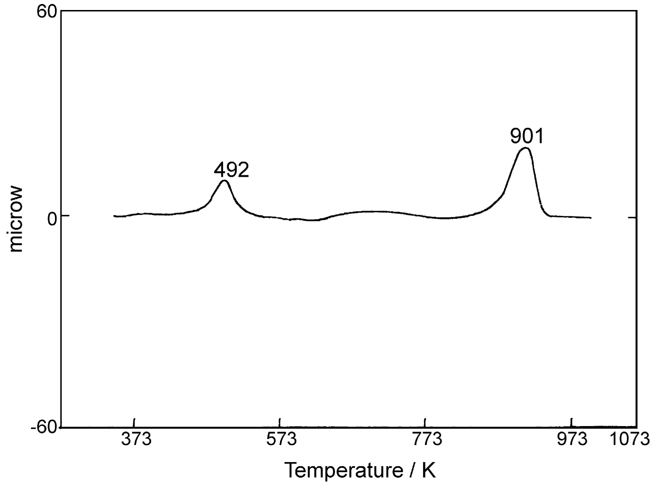


Fig. 5. TG curve for $(C_6H_5CH_2)_3Sn(L^3)Cl$ complex.

On the basis of above data, following conclusions have been drawn:

1. The Sn–R/Sn–Cl bond is weaker than Sn–L bond and hence the Sn–R bond breaks first.
2. The activation energy (E_a) value for step 1 is lower for complexes of the type $R_3Sn(L)Cl$ ($R{=}C_6H_5CH_2$) as compared to that of the complexes of type $R_2Sn(L)Cl_2$ ($R{=}p\text{-}ClC_6H_4CH_2$), because of greater steric hindrance in the $R_3Sn(L)Cl$ complexes. The energy

Table 6
Phenomenological and kinetic parameters for the thermal decomposition of the complexes.

Complexes	TG temperature range (K)	Step no.	n	TG		DTA		
				E_a (kJ mol^{-1})	S (J K^{-1} mol^{-1})	Thermal effect	T_{max} (K)	ΔH (kJ g^{-1})
$(C_6H_5CH_2)_3Sn(L^1)Cl$	323–623	1	1	23.05	0.25	Exothermic	610	13.48
	623–1026	2	1	52.04	2.33	Exothermic	840	44.35
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl_2$	392–643	1	1	31.16	2.09	Exothermic	552	8.96
	643–923	2	1	68.74	5.66	Exothermic	773	96.94
$(C_6H_5CH_2)_3Sn(L^2)Cl$	293–582	1	1	20.69	0.36	Exothermic	501	9.89
	582–903	2	1	52.36	2.56	Exothermic	820	83.63
$(C_6H_5CH_2)_3Sn(L^3)Cl$	318–593	1	1	19.84	0.257	Exothermic	492	14.62
	593–1011	2	1	50.22	1.506	Exothermic	901	103.52
$(C_6H_5CH_2)_3Sn(L^4)Cl$	313–656	1	1	22.29	0.380	Exothermic	524	4.78
	656–993	2	1	53.67	2.009	Exothermic	897	93.63
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^4)Cl_2$	369–523	1	1	42.38	6.77	Exothermic	452	7.82
	523–892	2	1	40.79	1.15	Exothermic	789	78.15

Table 7
Anti-fungal screening data of the ligands and their corresponding metal complexes.

Compound	*Rhizoctonia solanii*				*Sclerotium rolfsii*			
	25	50	100	ED_{50}	25	50	100	ED_{50}
L^1	38.33	45.62	57.39	63.84	49.9	57.86	74.90	28.86
$(C_6H_5CH_2)_3Sn(L^1)Cl$	43.21	57.29	71.61	35.21				
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl_2$	29.36	48.77	68.19	53.16	33.12	56.68	74.99	42.98
L^2	29.44	41.66	47.53	114.31	39.23	43.29	58.62	63.77
$(C_6H_5CH_2)_3Sn(L^2)Cl$	37.29	68.34	82.78	33.86	43.29	55.45	61.66	39.67
L^3	28.10	32.14	53.61	99.18	19.36	34.68	46.68	114.30
$(C_6H_5CH_2)_3Sn(L^3)Cl$	59.10	68.57	77.43	13.70	27.43	43.71	57.93	71.59
L^4	28.63	53.21	61.66	56.55	31.32	46.14	53.89	78.44
$(C_6H_5CH_2)_3Sn(L^4)Cl$	37.56	63.29	77.45	36.34	39.67	49.08	58.98	55.13
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^4)Cl_2$	29.77	67.35	71.27	41.61				

Inhibition (%) (conc. 25, 50 and 100 ppm).

of activation, in turn, reflected the kinetic liability of the complexes Table 6.

3.5. Fungitoxicity testing

The *in vitro* antifungal activities of the ligands and their corresponding complexes were tested by poisoned food technique using poison-dextrose-agar (PDA) medium at 25, 50 and 100 ppm. *Rhizoctonia solanii* Kuhn and *Sclerotium rolfsii* Saccardo were used as test organisms. A 5 mm thick disk of fungus (spores and mycelium) cut from earlier subcultured petridish was put in the centre of the solidified medium in the test petriplates and lids replaced. Both treated and control petriplates were kept in BOD incubator at $25 \pm 1\,^{\circ}$C for 4–6 days. The mycellial growth of fungus (cm) in both treated (T) and control (C) petriplates were measured diametrically in three different directions. Two replicates were taken for each treatment. From the mean growth of above reading percentage inhibition of growth (I) was calculated by using formula: $I\,(\%) = \{(C - T)/C \times 100\}$. ED_{50} values (effective dose required for 50% inhibition of fungus growth were calculated from percent inhibition (I) as follows:

$$I_{\mathrm{c}} = \frac{\%I - \mathrm{CF}}{100 - \mathrm{CF}} \times 100, \quad \text{where CF (correction factor)} = \frac{9 - C}{C} \times 100$$

where 9 is the diameter of the petriplate (cm) and C is the growth of fungus in control. From the concentration (ppm) and corresponding corrected *%I* data of each compound, the ED_{50} (ppm) was calculated with the help of Basic LD_{50} programme version 1.1 [20]. In general, when the compounds were found to posses very high activity. The results revealed that all the metal complexes are more active than their corresponding ligands against the same microorganisms. With increase in concentration of the compounds there occurs increase in percentage of inhibition. Higher concentration proves inhibitory for fungal growth Table 7.

Acknowledgements

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