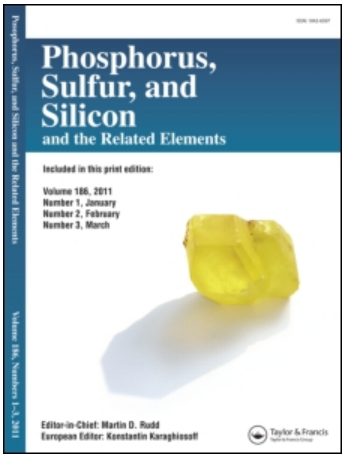

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Synthesis, Spectroscopic Studies, and In Vitro Antifungal Activity of Organosilicon(IV) and Organotin(IV) Complexes of 4-Amino-5-mercapto-3-methyl-*S*-triazole Schiff Bases

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Synthesis, Spectroscopic Studies, and In Vitro Antifungal Activity of Organosilicon(IV) and Organotin(IV) Complexes of 4-Amino-5-mercapto-3-methyl-*S*-triazole Schiff Bases

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The Schiff bases derived from condensation of s-triazole with heterocyclic aldehydes and their 1:1 and 1:2 complexes have been synthesized. These complexes have been characterized by elemental analyses, molar conductance and spectroscopic studies, including UV, IR, ^{1}H, ^{13}C, ^{29}Si, *and* ^{119}Sn *NMR spectroscopy. On the basis of these studies, the resulting complexes have been proposed to have trigonal bipyramidal and octahedral geometries. The biological activity of these complexes against various fungi has been investigated.*

Keywords Antifungal activity; metal complexes; s-Triazole; Schiff bases

INTRODUCTION

A careful survey of the literature revealed that there is a considerable scope for undertaking systematic studies including the synthesis and biochemical[1,2] applications of complexes of non-transition elements and particularly of Sn(IV) and Si(IV) with various Schiff bases. Tin(IV) and silicon(IV) complexes have been receiving more attention due to important industrial[3,4] and environmental[5,6] applications. Nitrogen, oxygen and sulfur donor ligands[7] have been used to enhance the biological activity of organotin and organosilicon derivatives.[8] These ligands are very well known for their antifungal and antibacterial[9,10] activities,

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which are probably due to their ability to chelate with traces of metals. Complexes of these ligands with non-transition metals have been extensively studied owing to their antifungal and antibacterial[11–14] activities. The coordination chemistry of tin and silicon is extensive with various geometries and coordination numbers known for both inorganic and organometallic complexes.[15] Higher coordination numbers can be generated by inter/intramolecular interaction, especially in complexes where tin or silicon is bonded to electronegative atoms such as oxygen, nitrogen and sulfur. Organotin and organosilicon complexes[16–18] are now the active components in a number of biocidal formulations, finding applications in such diverse areas as fungicides, miticides, molluscicides, surface disinfectants, and wood preservatives.[19] In the view of the diverse fields of applications of these complexes, we have synthesized and characterized some new organotin(IV) and organosilicon(IV) complexes with N and S donor ligands.

EXPERIMENTAL

All the reactions were carried out under perfectly dry conditions. Adequate care was taken to keep chemicals, glass apparatus, and organosilicon(IV) and organotin(IV) complexes free from moisture. Moisture was excluded from the glass apparatus using $CaCl_2$ guard tubes throughout the experimental work. All the chemicals and solvents used were dried and purified by standard methods.

Synthesis of Ligands

4-Amino-5-mercapto-3-methyl-*s*-triazole (AMMT) was synthesized by a reported method.[20] Schiff bases were prepared by heating under reflux a mixture of equimolar quantities of the triazole (AMMT) and the corresponding aldehydes, namely, pyridine-2-aldehyde, and furfuraldehyde (see Figure 1). Ethanol was used as solvent. After refluxing, the reaction mixture was kept overnight at room temperature and the product

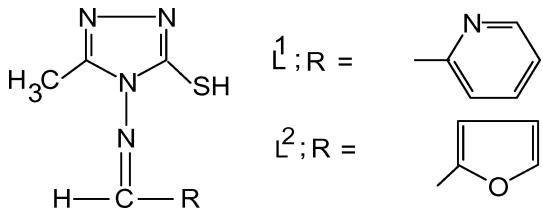


FIGURE 1 Structure of the Schiff bases used.

was filtered, washed, and recrystallized from the same solvent. The analyses and physical properties of the ligands are reported in Table I.

Synthesis of Metal Complexes

To a weighed amount of Me_2SnCl_2 and Me_2SiCl_2 in ~30 mL of dry methanol was added the calculated amount of the sodium salt of the ligand in 1:1 and 1:2 molar ratio. The excess of solvent was removed under vacuum pump and the resulting solid was repeatedly washed with 5–10 mL dry cyclohexane and again dried in vacuo. The elemental analyses and physical properties of the complexes are reported in Table I.

Analytical Methods and Physical Measurements

The complexes were analyzed by molar conductance measurements, elemental analyses, IR, ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectroscopy and electronic spectral studies. The content of silicon and tin was determined gravimetrically as SiO_2 and SnO_2. The molar conductance was measured with a conductivity bridge type 305 Systronic model. The IR spectra were recorded with a BUCK scientific M500 grating spectrophotometer in nujol mulls in the range 4000–250 cm^{-1}. NMR spectra were recorded with a BRUKER 300 ACF spectrometer in DMSO-d_6 using TMS as internal standard (^{1}H, ^{13}C, ^{29}Si) and tetramethyltin as external standard (^{119}Sn). Electronic spectra of the metal complexes were recorded in the region 1100–200 nm with a HITACHI U-2000 spectrometer.

Biological Technique

Potato dextrose medium was prepared in the flasks and sterilized. To this medium requisite quantity of the samples of ashawgandha were added so as to get desirable final concentrations, i.e., 100, 500, and 1000 ppm. The samples were thoroughly mixed by stirring. The medium was then poured into sterilized Petri dishes. The mycelial discs, which were taken from the cultures of the test fungi grown on PDA medium for seven days, were used for the purpose of inoculation in the centre of Petri dishes aseptically. Suitable controls were inoculated at 28 ± 1°C. The efficacy in each was determined by measuring radial mycelial growth. The radial growth of the colony was measured in two directions at right angles to each other, and the average of three replicates was recorded in each case. Data were expressed as percent inhibition over control from the size of the colonies, and subjected to two-way analysis

TABLE I Physical Characteristics and Analytical Data of the Ligands and Their Metal Complexes

	Empirical formula/formula wt.		Color	M.p. (°C)	Found (calcd.) %					
					C	N	H	S	Sn	Si
L^1	$C_9H_9N_5S$	219	Dark yellow	182	49.73 (49.31)	32.0 (31.96)	4.16 (14.61)	14.63 (14.61)	—	—
$Me_2SnCl(L^1)$	$C_{11}H_{15}N_5SClSn$	401	Light brown	170	33.10 (32.91)	17.56 (17.45)	3.79 (3.74)	8.0 (7.98)	29.34 (29.42)	—
$Me_2Sn(L^1)_2$	$C_{20}H_{24}N_{10}S_2Sn$	584	Brown	191	41.17 (41.07)	24.03 (23.97)	4.18 (4.10)	10.99 (10.95)	20.19 (20.12)	—
$Me_2SiCl(L^1)$	$C_{11}H_{15}N_5SClSi$	311	Light green	210	42.53 (42.44)	22.58 (22.50)	4.84 (4.82)	10.37 (10.28)	—	8.95 (9.00)
$Me_2Si(L^1)_2$	$C_{20}H_{24}N_{10}S_2Si$	494	Green	222	48.69 (48.58)	28.38 (28.34)	4.88 (4.85)	12.98 (12.95)	—	5.61 (5.66)
L^2	$C_8H_8N_4OS$	208	Dark brown	218	46.27 (46.15)	26.94 (26.92)	3.89 (3.84)	15.41 (15.38)	—	—
$Me_2SnCl(L^2)$	$C_{10}H_{14}N_4OSClSn$	390	Light yellow	145	30.79 (30.76)	14.41 (14.35)	3.61 (3.58)	8.25 (8.20)	30.18 (30.25)	—
$Me_2Sn(L^2)_2$	$C_{18}H_{22}N_8O_2S_2Sn$	562	Yellow	162	38.49 (38.43)	19.97 (19.92)	3.95 (3.91)	11.44 (11.38)	20.87 (20.99)	—
$Me_2SiCl(L^2)$	$C_{10}H_{14}N_4OSClSi$	300	Light orange	116	40.07 (40.0)	18.73 (18.66)	4.67 (4.66)	10.69 (10.66)	—	9.24 (9.33)
$Me_2Si(L^2)_2$	$C_{18}H_{22}N_8O_2S_2Si$	472	Orange	128	45.81 (48.76)	23.77 (23.72)	4.69 (4.66)	13.62 (13.55)	—	5.91 (5.93)

of variance (ANOVA). The percentage inhibition given in Table V was calculated using the formula:

$$\% \text{ inhibition} = (C - T) \times 100/C, \quad (1)$$

where C = diameter of the fungus colony in the control plate after 96 h; and T = diameter of the fungus colony in tested plates after the same period.

RESULTS AND DISCUSSION

The elemental analyses agree well with the proposed formula of the complexes. All the reported complexes were synthesized by the reaction of dimethyltindichloride and dimethylsilicondichloride with the N and S donor ligands L^1 and L^2 in 1:1 and 1:2 molar ratios in the medium of dry methanol. The resulting complexes were obtained as colored solids having sharp melting points, soluble in DMSO, DMF, and MeOH. The molar conductance values of 10^{-3}M solutions lie in the range of 10–15 $\Omega^{-1}cm^2\ mol^{-1}$ in dry DMF indicating their non-electrolytic nature. The physical characteristics and analytical data of the complexes are given in Table I.

Electronic Spectra

Electronic spectra of the ligands L^1 and L^2, and their metal complexes of Sn(IV) and Si(IV), were measured. The test solutions were prepared by dissolving the complexes in dry methanol. The electronic spectra of the ligands $L^1$and L^2 exhibit maxima at 401 nm and 369 nm, which can be assigned to the n-π^* transition of the azomethine group. These bands show a blue shift in the Sn and Si complexes and appear at 394 nm (Me_2SnL^1Cl), 370 nm ($Me_2Sn\{L^1\}_2$), 380 nm (Me_2SnL^2Cl), 364 nm ($Me_2SnL^2{}_2$), and 340 nm (Me_2SiL^1Cl), 331 nm ($Me_2Si\{L^1\}_2$), 320 nm (Me_2SiL^2Cl), 301 nm ($Me_2Si\{L^2\}_2$), respectively. This clearly indicates the coordination of the azomethine nitrogen atom to the metal atom. Further, two medium intensity bands at 300 nm and 234 nm due to $\pi - \pi^*$ transitions in the ligands remain unchanged in the spectrum of the metal complexes.

IR Spectra

The IR spectra of the ligands show a characteristic band due to ν(S—H) at ~2700 cm^{-1}. Another band at ~1100 cm^{-1} is assigned to ν(C=S).[21]The deprotonation of the thiol group is indicated by the absence of a band in the metal complexes at ~2700 cm^{-1}, which appears

due to ν(S-H) in the spectra of the ligands indicating thereby complexation through sulfur atom. A new band appears at ~750 cm^{-1}, which is assigned to ν (C—S), and which further confirms the coordination of the ligands through the sulfur atom. Metal sulfur bond formation is further supported by a band at ~ 410 cm^{-1} and ~ 455 cm^{-1} for ν (Sn—S) and ν (Si—S),[22,23] respectively. A strong band in the region of 1623–1605 cm^{-1} for the free ligands L^1 and L^2 assigned to ν (N=C—H) exhibits a shift of 10–15 cm^{-1} in the spectra of the metal complexes, indicating coordination through the azomethine nitrogen[24,25]atom of the Schiff bases. This can be explained by a reduction of the carbon-nitrogen double bond character in the azomethine group. Formation of a metal nitrogen bond is further supported by the presence of a band at 535 cm^{-1} and 575 cm^{-1} for ν (Sn—N) and ν (Si—N),[26,27] respectively, indicating the coordination of the ligand to the central metal atom through the azomethine nitrogen atom.

A strong band in the region of 480−441 cm^{-1}has been assigned to ν(M—Cl)[28] in the 1:1 metal complexes. The infrared spectral data of the ligands and their metal complexes are listed in Table II.

^{1}H NMR Spectra

The ^{1}H NMR spectroscopic data of the ligands and their tin and silicon complexes have been recorded in DMSO-d_6. In the NMR spectra of the metal complexes they indicate a shift of electron density from the ligand to the metal atom. The broad signal at δ 10.6 and 13.3 ppm is due to the –SH protons in ligands $L^1$and L^2, respectively. Disappearance of the signal for the –SH protons in the spectra of the metal

TABLE II IR Spectroscopic Data (cm^{-1}) of the Ligands and Their Metal Complexes

	ν(S—H)	ν (—C=N)	ν (—C=S)	ν (—C —S)	νM—S	νM—N
L^1	2750	1623	1096	—	—	—
$Me_2SnCl(L^1)$	—	1628	—	747	402	523
$Me_2Sn(L^1)_2$	—	1633	—	747	410	535
$Me_2SiCl(L^1)$	—	1626	—	746	450	575
$Me_2Si(L^1)_2$	—	1637	—	746	455	580
L^2	2730	1605	1096	—	—	—
$Me_2SnCl(L^2)$	—	1612	—	758	410	533
$Me_2Sn(L^2)_2$	—	1619	—	758	415	536
$Me_2SiCl(L^2)$	—	1610	—	761	443	565
$Me_2Si(L^2)_2$	—	1619	—	761	449	579

TABLE III ^{1}H NMR Chemical Shifts of the Ligands and Their Metal Complexes

	Aromatic-**H**	—S**H**	Azomethine-**H**	—C**H**$_3$
L^1	7.46–8.15	10.6	8.7	2.46
$Me_2SnCl(L^1)$	7.1–7.8	—	8.48	2.52,0.84
$Me_2Sn(L^1)_2$	6.85–7.5	—	8.1	2.6,0.5
$Me_2SiCl(L^1)$	6.75–7.8	—	8.6	2.64,0.82
$Me_2Si(L^1)_2$	7.3–8.5	—	8.02	2.57,0.96
L^2	6.6–7.72	13.3	10.2	2.4
$Me_2SnCl(L^2)$	6.25–7.35	—	9.7	2.64,0.98
$Me_2Sn(L^2)_2$	6.45–7.43	—	9.75	2.9,1.0
$Me_2SiCl(L^2)$	6.2–6.85	—	9.15	2.75,1.1
$Me_2Si(L^2)_2$	6.0–6.7	—	8.9	2.95,1.5

complexes supported the deprotonation of the thiol group. The signal of the azomethine protons is shifted to high field in the spectra of the metal complexes of tin and silicon. It appears at 8.60−8.02 ppm and at 9.75−8.90 ppm, respectively, as compared to 8.70 ppm and 10.20 ppm in the Schiff bases L^1 and L^2. This indicates complexation to the metal atom through the azomethine nitrogen atom. Additional signals in the spectra of the metal complexes of tin and silicon were found in the range of 1.0−0.50 ppm and 1.5−0.82 ppm, respectively, and are due to the methyl protons. The ^{1}H NMR spectroscopic data of the complexes are given in Table III.

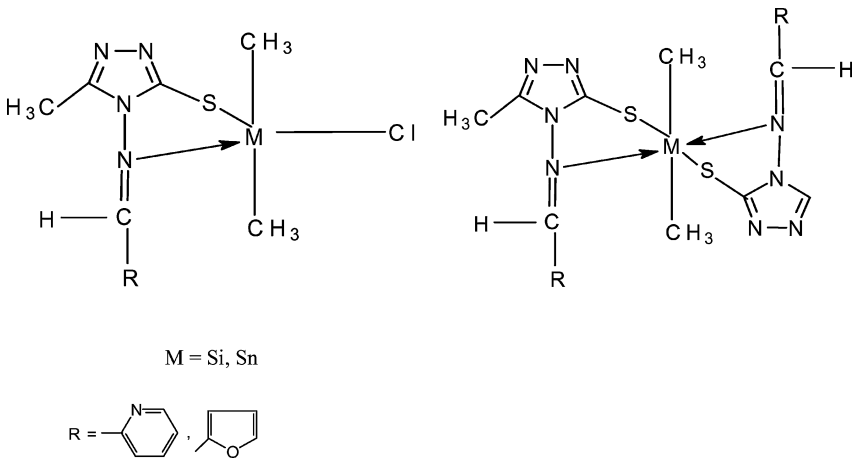
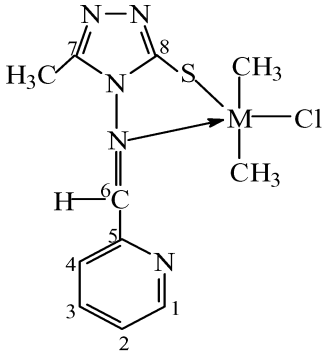
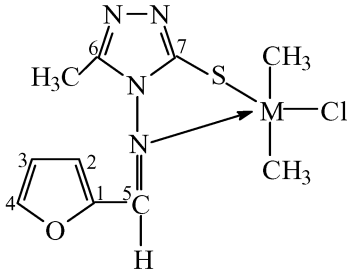


FIGURE 2 Proposed structures of the 1:1 and 1:2 complexes.

TABLE IV ^{13}C NMR Chemical Shifts of the Ligands and Their Metal Complexes





M = Si, Sn

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C—CH_3	M—CH_3
L^1	130.7	126.4	141.8	153.7	154.7	163.9	156.9	166.7	15.9	
$Me_2SnCl(L^1)$	129.3	125.7	141.4	152.0	153.5	162.5	153.3	166.6	15.6	35.7
$Me_2Sn(L^1)_2$	126.2	125.3	140.8	147.9	150.3	158.3	155.6	165.9	13.0	50.5
$Me_2SiCl(L^1)$	130.0	127.1	140.2	151.9	154.5	161.7	156.0	166.6	15.6	35.8
$Me_2Si(L^1)_2$	126.4	125.7	138.0	147.7	149.8	155.1	148.9	159.8	10.7	30.6
L^2	147.2	151.3	120.0	112.9	148.3	161.1	147.9	—	10.7	—
$Me_2SnCl(L^2)$	146.8	151.1	119.6	112.4	148.2	160.9	147.3	—	10.2	30.1
$Me_2Sn(L^2)_2$	149.5	151.4	120.3	115.6	150.5	163.8	151.5	—	10.4	14.1
$Me_2SiCl(L^2)$	146.9	151.0	120.1	112.9	151.4	161.8	147.5	—	10.9	28.5
$Me_2Si\ (L^2)_2$	149.4	154.4	120.3	117.3	153.0	163.2	150.6	—	12.7	16.2

^{13}C NMR Spectra

The ^{13}C NMR spectra also support the structures proposed for the tin and silicon complexes. The shifts of the ^{13}C resonances in the spectra of the metal complexes compared to those of the free ligands L^1 and L^2 indicate the coordination of the azomethine nitrogen atom[29,30] and of the sulfur atom to the metal. The δ values of all carbon atoms of the ligands and their metal complexes are listed in Table IV.

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

The value of δ^{29}Si and δ^{119}Sn[31] reflects the coordination number of the nucleus in the corresponding compound. In general,^{29}Si and ^{119}Sn chemical shifts move to lower frequency with increasing coordination

TABLE V Antifungal Screening Data of the Ligands and Their Metal Complexes

	Phytoextract concentrations (ppm)	*A. terrus**	*A. alternata*	*P. citrinum*
L^1	Control	0 ± 0	0 ± 0.23	0 ± 0.23
	100	0 ± 0.40	42.4 ± 0.77	48.8 ± 0.62
	500	0 ± 0.23	53.4 ± 0.07	30.2 ± 0.93
	1000	50 ± 0.27	82.1 ± 0.12	72.0 ± 0.20
$Me_2SiCl(L^1)$	Control	0 ± 0.21	0 ± 0.23	0 ± 0.23
	100	17.2 ± 0.41	18.4 ± 0.25	1.31 ± 0.21
	500	24.1 ± 0.23	28.9 ± 0.18	21.0 ± 0.35
	1000	51.7 ± 0.09	82.8 ± 0.10	27.6 ± 0.25
$Me_2Si(L^1)_2$	Control	0 ± 0.21	0 ± 0.23	0 ± 0.23
	100	12.6 ± 0.23	46.0 ± 0.10	28.9 ± 0.60
	500	62.0 ± 0.10	80.2 ± 0.03	40.7 ± 0.17
	1000	85.0 ± 0.10	86.8 ± 0.05	50.0 ± 0.47
$Me_2SnCl(L^1)$	Control	0 ± 0.04	0 ± 0.12	0 ± 0.21
	100	10 ± 0.27	23.8 ± 0.20	54.2 ± 0.05
	500	6.25 ± 0.18	25.3 ± 0.13	50.0 ± 0.18
	1000	17.5 ± 0.32	55.2 ± 0.04	57.1 ± 0.17
$Me_2Sn(L^1)_2$	Control	0 ± 0.04	0 ± 0.12	0 ± 0.12
	100	0 ± 0.09	22.3 ± 0.13	15.9 ± 0.09
	500	12.5 ± 0.07	26.8 ± 0.12	17.3 ± 0.09
	1000	15.1 ± 0.09	38.8 ± 0.54	40.5 ± 0.05
L^2	Control	0 ± 0.25	0 ± 0.35	0 ± 0.20
	100	4.0 ± 0.09	10.0 ± 0.08	57.6 ± 0.08
	500	22.6 ± 0.14	7.5 ± 0.14	70.5 ± 0.05
	1000	37.3 ± 0.27	25.0 ± 0.17	70.5 ± 0.03
$Me_2SnCl(L^2)$	Control	0 ± 0.25	0 ± 0.35	0 ± 0.20
	100	12.0 ± 0.40	0 ± 0.05	32.0 ± 0.32
	500	13.3 ± 0.17	0 ± 0.27	25.6 ± 0.28
	1000	13.3 ± 0.17	11.2 ± 0.20	52.5 ± 0.16
$Me_2Sn(L^2)_2$	Control	0 ± 0.25	0 ± 0.35	0 ± 0.20
	100	17.3 ± 0.21	21.2 ± 0.09	57.6 ± 0.08
	500	30.6 ± 0.09	13.7 ± 0.13	70.5 ± 0.05
	1000	44.0 ± 0.27	28.7 ± 0.23	70.5 ± 0.03

A. terrus*- Aspergillus terrus, A. alternata-Alternaria alternata, P. citrinum-Pencillium citrinum

number of the nuclei. In order to confirm the geometry of the complexes, ^{29}Si and ^{119}Sn NMR spectra were recorded. The spectra show in each case only a sharp singlet indicating the formation of a single species. The sharp ^{29}Si NMR signal at δ −107.7 ppm is assigned to the complex $Me_2Si(C_9H_8N_5S)_2$with a hexacoordinated environment around the silicon atom. Similarly, in the case of the corresponding tin complex, a

sharp signal at δ –467.4 ppm indicates the presence of a hexacoordinated tin atom.

On the basis of the above evidences, it is suggested that the geometries around the tin and silicon atoms in the complexes investigated are trigonal bipyramidal and octahedral as shown in Figure 2.

Antifungal Activity[32]

The antifungal activity of the ligands L^1 and L^2 and of their metal complexes with tin and silicon $[Me_2SnCl(L^1)]$, $[Me_2Sn(L^1)_2]$, $[Me_2SnCl(L^2)]$, $[Me_2Sn(L^2)_2]$, $[Me_2SiCl(L^1)]$, and $[Me_2SiCl(L^1)_2]$ have been screened against Aspergillus terrus, Alternaria alternate, and Penicillium citrinum by reported method. All of the complexes tested were found to be most active against Alternaria alternate and Penicillium citrinum at all the three concentrations (1000, 500, and 100 ppm) showing maximum inhibition, but less active against Aspergillus terrus at all the three concentrations. The fungi toxicity of the ligands and their metal complexes slightly decreased on lowering the concentration. It is clear from the fungicidal screening data that the metal complexes are found to be more fungitoxic than the ligand itself. The fungicidal screening data are compiled in Table V.

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