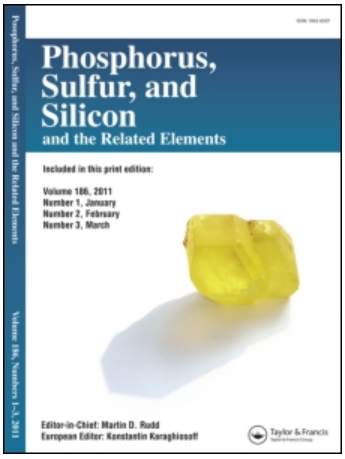

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Coordination Behavior of Unsymmetrical Ligand Complexes of Diorganotin and Diorganosilicon Derived From Schiff Bases

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Coordination Behavior of Unsymmetrical Ligand Complexes of Diorganotin and Diorganosilicon Derived From Schiff Bases

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Hexacoordinated organotin and organosilicon derivatives have been prepared and characterized by analytical and spectroscopic techniques including UV, IR, ^{1}H NMR, and ^{13}C NMR spectra. The ligands used in the present account were derived by the condensation of thiosemicarbazide and 1H-Indol-2,3-dione, 1,3-dihydro-3-[2-(4-fluorophenyl)-2-oxo-ethylidene]-2H-indol-2-one, and 1,3-dihydro-3-[2-(4-fluoro-3-methyl-phenyl)-2-oxo-ethylidene]-2H-indol-2-one under microwave irradiation as well as by conventional heating. Newly synthesized complexes with their corresponding ligands were tested for their antifungal and antibacterial activities. The aim of the present study is to synthesize some novel ecofriendly fungicides and bactericides that have important pharmacodynamic significance.

Keywords Antimicrobial assay; silicon (IV) and tin (IV) complexes; spectral studies; thio-ligands

INTRODUCTION

The chemistry of Schiff base complexes attracts many researchers[1,2] because of their wide application in the food industry, dyes industry, analytical chemistry, catalysis, and many agrochemical fields. The potential antitumor, antibacterial, antiviral, fungicidal, and antimalarial activities of thiosemicarbazones and their metal complexes have spurred the study of the coordination chemistry of these ligands.[3–10] Organotin compounds exhibit a broad spectrum of biological activity, which includes bactericidal, fungicidal,[11] antitumor,[12]and acaricidal[13] properties. The interest in organosilicon (IV) compounds is due to their

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versatile applicability in pharmaceutical and chemical industries. For example, the use of very bulky silicon-containing ligands allows the isolation of a wide range of previously inaccessible types of compounds, and silicon-substituted methyl groups are capable of making considerable adjustments, especially in the inner CSi_3 skeleton in response to the electronic demands of the adjacent element.[14] Organotin compounds are toxic to a variety of microorganisms and find widespread applications in biocidal compositions.[15] Keeping this in mind, it was considered worthwhile to synthesize organotin and organosilicon complexes of some stereochemical as well as biological interest.

EXPERIMENTAL

All glass apparatus used were fitted with quickfit interchangeable standard ground joints. The apparatuses were cleaned, rinsed, and well dried in an electric oven for 2–3 h. All chemicals and solvents were dried and purified.

Preparation of Schiff Bases

The ligands were prepared by the condensation of 2-(1,2-dihydro-2-oxo-3H-indol-3-ylidenyl) (1.0 gm, 7.76 mmol), 1,3-dihydro-3-[2-(4-fluorophenyl)-2-oxo-ethylidene]-2H-indol-2-one (1.0 gm, 4.02 mmol), and 1,3-dihydro-3-[2-(4-fluoro-3-methyl-phenyl)-2-oxo-ethylidene]-2H-indol-2-one (1.0 gm, 3.80 mmol) with thiosemicarbazide (0.71 gm, 7.79 mmol), (0.37 gm, 4.06 mmol), and (0.35 gm, 3.84 mmol), respectively in a equimolar ratio in a 50 mL alcohol. The contents were refluxed for 45 min at 40–50°C. After cooling, the precipitate was filtered, dried, and then recrystallized from the same solvent and again dried under reduced pressure. The physical properties of the ligands are recorded in Table I.

For the sake of convenience, these have been abbreviated as 2-(1,2-dihydro-2-oxo-3H-indol-3-ylidenyl)thiosemicarbazone ($HTSCZ^1$), 1,3-dihydro-3-[2-(4-fluorophenyl)-2-oxo-ethylidene]-2H-indol-2-one thiosemicarbazone ($HTSCZ^2$), and 1,3-dihydro-3-[2-(4-fluoro-3-methyl-phenyl)-2-oxo-ethylidene]-2H-indol-2-one thiosemicarbazone ($HTSCZ^3$) (Figure 1).

Preparation of the Complexes

Conventional Method

To a weighed quantity of organotin/organosilicon chloride (1.19–1.75 gm, 3.58–13.56 mmol) in methanol was added an equimolar amount of

TABLE I Analysis and Physical Characterization of the Ligands and Their Complexes

Reactants (gm, [mmol])								Analysis			
Si/Sn	HTSCZ[1]	HTSCZ[2] and HTSCZ[3]	Na	Compound	Color	M.P. (°C)	Yield (%)	N Found (Calcd.)	S Found (Calcd.)	Si/Sn Found (Calcd.)	Mol. Wt. Found (Calcd.)
—	—	—	—	HTSCZ[1]	Yellow	246	74	25.22 (25.43)	14.32 (14.55)	—	209 (220)
—	—	—	—	HTSCZ[2]	Orange	185	73	16.12 (16.48)	9.09 (9.43)	—	323 (340)
—	—	—	—	HTSCZ[3]	Orange	165	68	15.78 (15.83)	9.02 (9.06)	—	335 (354)
1.36 (10.54)	2.32 (10.54)	3.58 (10.53)	0.48 (20.88)	$Me_2Si[TSCZ^1][TSCZ^2]$	Brick red	295	65	17.71 (18.16)	9.88 (10.39)	4.16 (4.55)	609 (616)
1.75 (13.56)	2.98 (13.54)	4.79 (13.53)	0.62 (26.97)	$Me_2Si[TSCZ^1][TSCZ^3]$	Red	252	72	17.25 (17.76)	9.68 (10.17)	4.02 (4.45)	624 (630)
1.56 (6.16)	1.35 (6.14)	2.09 (6.15)	0.28 (12.18)	$Ph_2Si[TSCZ^1][TSCZ^2]$	Reddish brown	>300	82	14.65 (15.12)	8.09 (8.65)	3.25 (3.25)	734 (740)
1.45 (5.73)	1.26 (5.73)	2.03 (5.73)	0.26 (11.31)	$Ph_2Si[TSCZ^1][TSCZ^3]$	Light brown	272	73	14.33 (14.84)	7.95 (8.49)	3.52 (3.71)	746 (754)
1.19 (5.42)	1.19 (5.41)	1.84 (5.41)	0.25 (10.87)	$Me_2Sn[TSCZ^1][TSCZ^2]$	Peach	265	74	15.40 (15.84)	8.57 (9.07)	16.25 (16.78)	698 (707)
1.63 (7.42)	1.63 (7.41)	2.62 (7.40)	0.34 (14.79)	$Me_2Sn[TSCZ^1][TSCZ^3]$	Brown	258	66	15.08 (15.54)	8.36 (8.89)	15.94 (16.46)	716 (721)
1.23 (3.58)	0.79 (3.59)	1.22 (3.59)	0.16 (6.96)	$Ph_2Sn[TSCZ^1][TSCZ^2]$	Cherry	278	68	13.03 (13.48)	7.26 (7.71)	13.79 (14.27)	826 (831)
1.54 (4.48)	0.98 (4.45)	1.58 (4.46)	0.20 (8.70)	$Ph_2Sn[TSCZ^1][TSCZ^3]$	Red	269	76	12.79 (13.26)	7.26 (7.58)	13.54 (14.03)	839 (845)

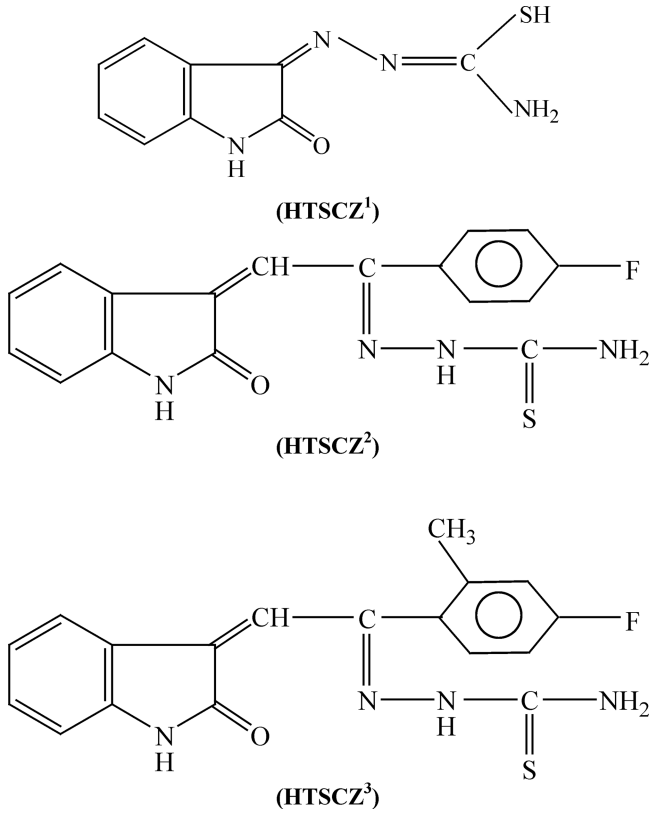

FIGURE 1

sodium salt of the ligands (prepared by adding corresponding weight of sodium [0.16–0.62 gm, 6.96–26.97 mmol] to the ligands ([0.79–4.79 gm, 3.59–13.54 mmol]). The reaction mixture was refluxed for 8–10 h. The solid products were precipitated. These were then dried in vacuum and recrystallized from the same solvent. The main characterstics of these complexes are given in Table I.

Microwave Method

A mixture of Me_2SiCl_2 (1.36 gm, 10.54 mmol), HTSCZ[1] (2.32 gm, 10.54 mmol), HTSCZ[2] (3.58 gm, 10.53 mmol), and sodium (0.48, 20.88 mmol) were taken in an open borosil beaker. The reaction medium was methanol. The mixture was irradiated inside a microwave oven until completion of the reaction. The resulting products were washed and

dried under vaccum. A drastic reduction in reaction time was thus observed due to rapid heating capability of microwaves.

Likewise, following the same procedure, all the compounds were prepared in microwaves.

Analytical Methods and Physical Measurements

The various analytical methods were adopted for the proper characterization of the compounds. Nitrogen and sulphur were estimated by Kjeldahl's and Messenger's methods, respectively. Tin and silicon were determined gravimetrically as SnO_2 and SiO_2, respectively, and molecular weights were determined by the Rast Camphor Method. UV spectra were recorded on a Hitachi-U-2000 spectrophotometer. IR spectra were recorded as KBr discs on a Perkin-Elmer 577 grating spectrophotometer. ^{1}H NMR spectra were recorded on JEOL AL 300 FT NMR in DMSO-$d_6$with TMS as the internal standard. All chemical shifts are reported in parts per million (ppm) relative to TMS.

RESULTS AND DISCUSSION

The reactions of Me_2SnCl_2 Ph_2SnCl_2, Me_2SiCl_2, and Ph_2SiCl_2 with the sodium salts of monobasic bidentate thiosemicarbazones result in the replacement of chloride and isolation of $[R_2M(TSCZ^1)(TSCZ^2)]$ and $[R_2M(TSCZ^1)(TSCZ^3)]$ types of complexes. The reactions may be represented as follows:

$$R_2MCl_2 + HTSCZ^1 + HTSCZ^2 \rightarrow R_2M(TSCZ^1)(TSCZ^2) + NaCl$$

$$R_2MCl_2 + HTSCZ^1 + HTSCZ^3 \rightarrow R_2M(TSCZ^1)(TSCZ^3) + NaCl$$

The resulting colored solids are soluble in DMF and DMSO. Their low molar conductivity values show that they are non-electrolytes.

SPECTRAL STUDIES

UV Spectra

In the electronic spectra of the ligands, a band arising from the >C=N chromophore at ~370 nm shifted to a shorter wave length for the complexes. Such a shift in the n-π^* band was probably due to the donation of the lone pair of electrons by the nitrogen of the ligand to the central metal atom. The bands of medium intensity at s~270 and 300 nm arising from $\pi - \pi^*$ transition of the ligand remained almost unchanged in the spectra of organosilicon and organotin derivatives.

IR Spectra

In the IR spectra of the ligands, a broad band in the region 3250–3100 cm^{-1} and 2700 cm^{-1} may be assigned to ν(NH) and ν(SH) vibrations, respectively. The νNH and νSH bands disappeared in the spectra of the resulting complexes, indicating possible deprotonation of the ligands on complexation and the formation of (M-S) and (M←N) bonds. In the spectra of HTSCZ[1], HTSCZ[2], andHTSCZ[3],a sharp band due to the >C=N frequency appeared in the range 1620–1630 cm^{-1}, which shifted to a lower frequency[16] in the silicon complexes and to a higher frequency[17] (ca. 15 cm^{-1}) in the tin complexes, indicating coordination of the azomethine nitrogen to the silicon and tin atoms.

Several new bands observed in the far IR region of the complexes at ~325 cm^{-1}; 415 cm^{-1}, ~540 cm^{-1} and 580 cm^{-1} were assigned to ν(Sn-S), ν(Sn←N), ν(Si-S), and ν(Si←N), respectively.

^{1}H NMR Spectra

The proton magnetic resonance spectra of the ligands and their complexes were recorded in DMSO-d_6. The chemical shift values relative to the TMS peak are listed in Table II. The broad signal due to the –NH proton in the ligand disappeared in the case of the complexes, showing the bond formation between thiolic sulphur and the metal atom. The appearance of a signal due to a $–NH_2$ group at about the same position in the ligand and its metal complexes showed the non-involvement of this group in coordination. The additional signals in the region δ

TABLE II ^{1}H NMR Spectral Data (δ ppm) of the Ligands and Their Corresponding Complexes

Compound	—NH (free)	—NH[1] (ring)	—NH[2 or 3] (ring)		—NH_2^1	M-Ph/ aromatic
HTSCZ[1]	11.28	12.56	—	3.44	—	8.04–7.84
HTSCZ[2]	10.04	—	11.08	—	3.16	7.94–7.54
HTSCZ[3]	10.24	—	11.12	—	2.64	7.72–6.34
Me_2Si[TSCZ[1]][TSCZ[2]]	—	12.52	11.14	3.45	3.18	8.40–7.56
Me_2Si[TSCZ[1]][TSCZ[3]]	—	12.54	11.18	3.52	2.68	8.12–7.53
Ph_2Si[TSCZ[1]][TSCZ[2]]	—	12.60	11.24	3.64	3.45	8.48–6.72
Ph_2Si[TSCZ[1]][TSCZ[3]]	—	12.62	11.28	3.62	2.68	8.56–7.98
Me_2Sn[TSCZ[1]][TSCZ[2]]	—	12.58	11.16	3.54	3.54	8.24–7.29
Me_2Sn[TSCZ[1]][TSCZ[3]]	—	12.56	11.28	3.48	2.72	8.08–7.72
Ph_2Sn[TSCZ[1]][TSCZ[2]]	—	12.54	11.32	3.72	3.65	8.28–6.79
Ph_2Sn[TSCZ[1]][TSCZ[3]]	—	12.58	11.44	3.68	2.85	8.32–7.36

TABLE III ^{13}C NMR Spectral Data (δ ppm) of the Ligands and Their Corresponding Complexes

Compound	Thiolo carbon	Azomethine carbon	Aromatic carbons
HTSCZ[1]	178.02	161.98	131.59, 130.78, 121.89, 120.43, 119.19
HTSCZ[2]	178.62	157.66	148.08, 144.05, 136.25, 135.71, 133.22, 132.13
HTSCZ[3]	172.52	155.12	147.24, 144.28, 136.92, 135.72, 130.22, 129.71
$Me_2Si[TSCZ^1][TSCZ^2]$	161.82	156.94	137.23, 122.38, 132.62, 128.51, 125.12, 162.61
$Me_2Si[TSCZ^1][TSCZ^3]$	168.51	150.51	136.51, 128.32, 126.58, 122.82, 124.56, 110.61
$Ph_2Si[TSCZ^1][TSCZ^2]$	165.38	152.63	132.43, 126.51, 122.80, 119.62, 121.53, 112.30
$Ph_2Si[TSCZ^1][TSCZ^3]$	170.63	154.58	131.19, 127.91, 131.58, 120.58, 119.56, 110.08
$Me_2Sn[TSCZ^1][TSCZ^2]$	173.91	153.52	131.62, 125.69, 128.52, 119.61, 120.51, 119.68
$Me_2Sn[TSCZ^1][TSCZ^3]$	167.48	150.39	129.58, 120.62, 125.81, 120.08, 120.62, 110.81
$Ph_2Sn[TSCZ^1][TSCZ^2]$	168.34	155.10	128.42, 119.51, 129.82, 120.91, 120.28, 112.62
$Ph_2Sn[TSCZ^1][TSCZ^3]$	165.42	153.02	124.41, 116.53, 125.62, 119.62, 121.83, 110.52

0.63–1.17 ppm, δ 6.34–8.56 ppm, δ 0.5–0.8 ppm, and δ 6.34–8.56 ppm are due to (CH_3Sn), (C_6H_5Sn)/aromatic, (CH_3Si), and (C_6H_5Si)/aromatic groups, respectively.

^{13}C NMR Spectra

^{13}C NMR spectra of the ligands and their complexes were recorded in DMSO. The carbons attached to the thiolic sulphur and azomethine nitrogen in the ligand underwent a marked shift, which clearly showed

TABLE IV Fungicidal Screening Data of the Ligands and Their Corresponding Complexes (Conc. in ppm)

	Fusarium oxysporum			*Aspergillus niger*		
Compound	50	100	200	50	100	200
HTSCZ[1]	66	70	72	72	80	83
HTSCZ[2]	70	75	80	74	79	80
HTSCZ[3]	75	80	85	76	80	85
$Me_2Si[TSCZ^1][TSCZ^2]$	76	82	86	77	81	86
$Me_2Si[TSCZ^1][TSCZ^3]$	75	80	84	76	82	85
$Ph_2Si[TSCZ^1][TSCZ^2]$	77	85	89	78	82	87
$Ph_2Si[TSCZ^1][TSCZ^3]$	75	82	87	79	85	90
$Me_2Sn[TSCZ^1][TSCZ^2]$	76	82	91	86	91	96
$Me_2Sn[TSCZ^1][TSCZ^3]$	79	80	89	77	85	93
$Ph_2Sn[TSCZ^1][TSCZ^2]$	76	82	88	76	82	89
$Ph_2Sn[TSCZ^1][TSCZ^3]$	77	83	89	77	80	86
Standard (Bavistin)	86	100	100	90	100	100

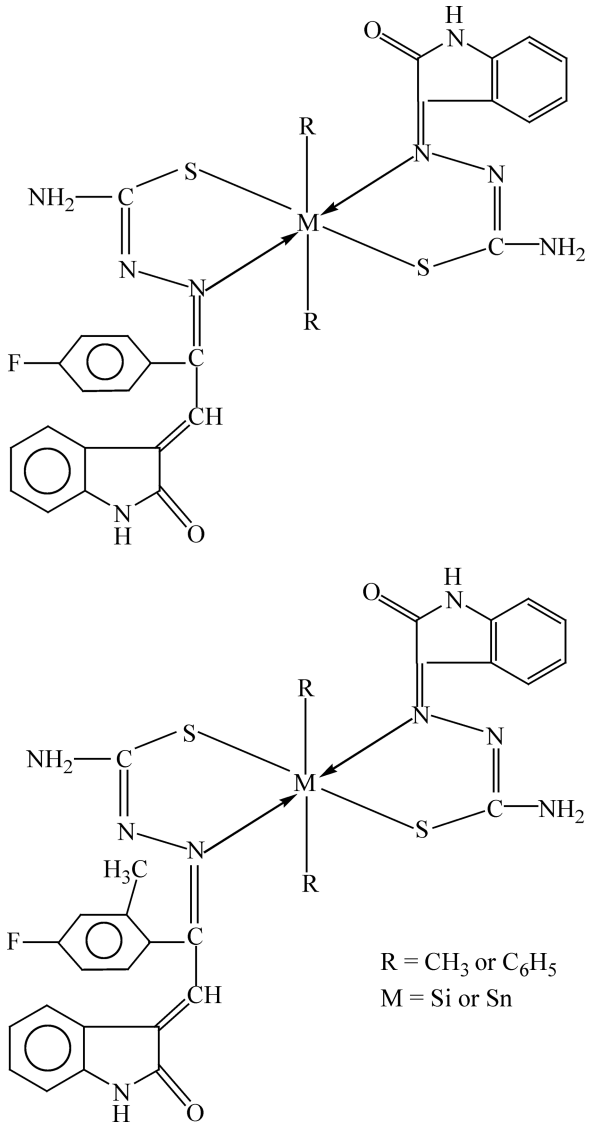

FIGURE 2

the complexation of metal through the sulphur and nitrogen atoms. The chemical shift values are listed in Table III.

On the basis of previous discussion, the geometry shown in Figure 2 has been proposed for the complexes.

TABLE V Bactericidal Screening Data of the Ligands and Their Corresponding Complexes

	Diameter of inhibition zone (mm)			
	Staphylococcus aureus		*Escherichia coli*	
Compound	500	1000	500	1000
$HTSCZ^1$	5	7	3	5
$HTSCZ^2$	4	7	4	5
$HTSCZ^3$	5	9	5	6
$Me_2Si[TSCZ^1][TSCZ^2]$	6	9	5	7
$Me_2Si[TSCZ^1][TSCZ^3]$	9	10	7	9
$Ph_2Si[TSCZ^1][TSCZ^2]$	7	10	7	9
$Ph_2Si[TSCZ^1][TSCZ^3]$	8	13	8	10
$Me_2Sn[TSCZ^1][TSCZ^2]$	12	16	9	14
$Me_2Sn[TSCZ^1][TSCZ^3]$	13	15	10	13
$Ph_2Sn[TSCZ^1][TSCZ^2]$	11	15	11	14
$Ph_2Sn[TSCZ^1][TSCZ^3]$	12	16	12	15
Standard (Streptomycin)	15	17	17	18

MICROBIAL ASSAY

Fungicidal and bactericidal activities of the ligands and their complexes against fungi and bacteria have been recorded in Tables IV and V by the methods reported earlier.[18]

CONCLUSION

The spectral studies reasonably proved that complexation of the metal and ligand took place. A hexacoordinated environment has been suggested around a silicon and tin atom. The resulting products are lipophilic in nature. The enhancement of the activity on complexation can also be explained by chelation theory.[19] According to this theory, chelation reduces the polarity of the central metal atom because of partial sharing of a positive charge with the donor groups and possible π electron delocalization within the whole chelate ring. The chelation increases the lipophilic nature of the central atom, which favors the permeation of the complexes in the lipid layer of the cell membrane. After entering the cells, these compounds inhibit cell division.[20] Changes in concentration influence the antimicrobial property. These compounds, even at lower concentration, inhibit the growth of microorganisms.

This experiment has shown good activity against pathogenic human bacteria (*Staphylococcus aureus*) and fungus (Aspergillus species)

because these compounds can be explored as fungicides and bactericides for human use and may come out as future pesticides. Nonetheless, their synthesis is a step by which making of safe biocidal drugs may be possible.

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