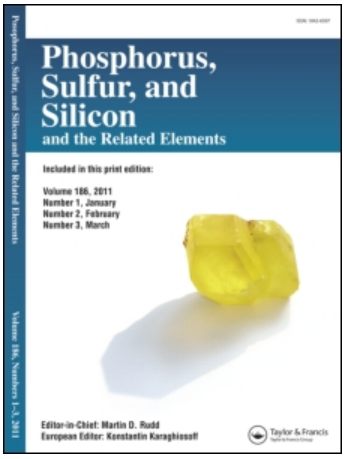

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Anita Kumari[a]; R. V. Singh[a]; J. P. Tandon[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

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SPECTRAL CHARACTERIZATION AND ANTIFUNGAL ACTIVITY OF SOME NEWLY SYNTHESIZED SULFUR CONTAINING TRIORGANOTIN(IV) DERIVATIVES

ANITA KUMARI, R. V. SINGH* and J. P. TANDON
Department of Chemistry, University of Rajasthan, Jaipur-302004 India

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Triorganotin(IV) complexes having an azomethine linkage have been prepared by the substitution reactions of trimethyl tin chloride with heterocyclic thiosemicarbazones and characterized by elemental analyses, molecular weight determinations and conductivity measurements. On the basis of infrared, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy studies, a trigonal bipyramidal geometry for the resulting complexes has been proposed. The nitrogen atom occupies the axial site, while two methyl groups rest in equatorial positions. The antifungal activity of some of the ligands and their metal complexes has also been evaluated against different pathogenic fungi.

Key words: Triorganotin(IV) derivatives; thiosemicarbazone, IR spectra; ^{1}H, ^{13}C and ^{119}Sn NMR spectra; antifungal activity.

INTRODUCTION

The study of organotin(IV) compounds continues to be of unabated interest on account of their striking structural behaviour and biological importance.[1–3] In general, the biological effects of organotin(IV) compounds depend on the nature of organo group attached to the tin(IV) atom and the triorganotin(IV) compounds have been found to be biologically more active than diorgano and monoorganotin compounds.[4,5] The activity may further be modified by ligation of tin(IV) atom to other biologically active moieties in place of the electronegative group (X) in organotin compounds of the type, $R_nSn\,X_{4-n}$. As a part of our growing interest in the field of coordination chemistry of organotin complexes with biologically active sulfur and nitrogen donor ligands,[6–8] we have synthesized and characterized triorganotin(IV) derivatives of some heterocyclic thiosemicarbazones along with the evaluation of their antifungal activity. The results of these investigations are reported in the present communication.

RESULTS AND DISCUSSION

Me_3SnCl reacts with the potassium salt of ligand in 1:1 molar ratio in the medium of benzene and methanol according to the following equation:

$$Me_3SnCl + \overset{\frown}{N\ S}K \xrightarrow{1:1} Me_3Sn(\overset{\frown}{N\ S}) + KCl$$

(where $\overset{\frown}{N\ S}$ is the donor set of heterocyclic thiosemicarbazones). All the complexes are coloured solids and soluble in common organic solvents. These are

TABLE I

Analyses and physical characteristics of triorganotin(IV) complexes

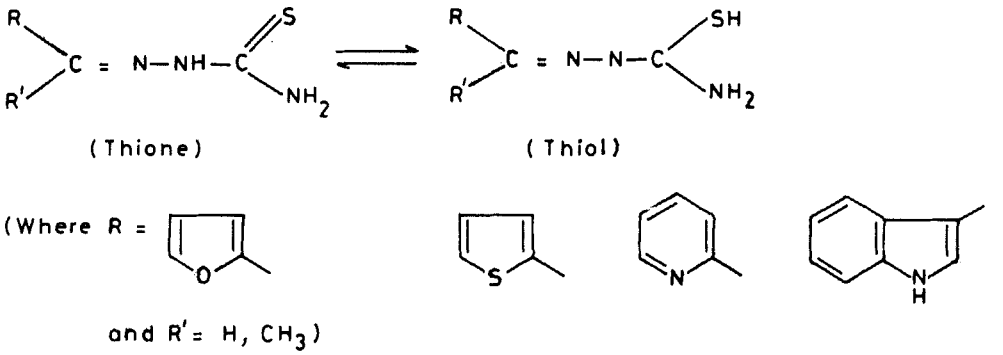
Compound and Colour	Melting Point (°C)	Yield (%)	Analyses (%)					Mol.Wt. Found (Calc.)
			C Found (Calc)	H Found (Calc)	N Found (Calc)	S Found (Calc)	Sn Found (Calc)	
$(CH_3)_3Sn$(Fur.Tscz) Orange Solid	140	64	32.98 (32.56)	4.01 (4.55)	12.39 (12.66)	9.42 (9.66)	35.63 (35.75)	314.00 (332.00)
$(CH_3)_3Sn$(Thiop.Tscz) light yellow solid	185	71	30.81 (31.06)	4.68 (4.34)	11.87 (12.07)	18.36 (18.42)	33.96 (34.10)	326.00 (348.06)
$(CH_3)_3Sn$(Pyd.Tscz) Brown solid	200	76	34.69 (35.02)	4.27 (4.70)	16.02 (16.33)	9.40 (9.35)	34.48 (34.60)	318.00 (343.02)
$(CH_3)_3Sn$(Ind.Tscz) Dark Yellow solid	192	70	40.47 (40.98)	4.19 (4.76)	14.44 (14.70)	8.26 (8.41)	30.91 (31.15)	367.00 (381.02)
$(CH_3)_3Sn$(2-Ac Fur.Tscz) Light Brown solid	164	61	34.26 (34.71)	4.47 (4.95)	12.25 (12.14)	9.18 (9.27)	32.15 (34.30)	325.00 (346.02)
$(CH_3)_3Sn$(2-Ac Thiop.Tscz) Dark brown solid	130	65	32.84 (33.17)	5.06 (4.78)	11.27 (11.60)	17.56 (17.71)	32.92 (32.78)	349.00 (362.10)
$(CH_3)_3Sn$(2-Ac Pyd.Tscz) Dark Brown solid	156	70	36.84 (37.00)	4.86 (5.08)	15.47 (15.69)	8.81 (8.98)	32.87 (33.24)	336.00 (357.05)
$(CH_3)_3Sn$(3-Ac Ind.Tscz) Brown semi solid	-	62	42.07 (42.56)	5.53 (5.10)	13.78 (14.18)	8.41 (8.11)	30.26 (30.04)	377.00 (395.11)

monomeric in nature and nonelectrolytic as shown by the low value of molar conductance (below 12 $ohm^{-1}\ cm^2\ mol^{-1}$). The analytical data of all the complexes are listed in Table I.

SPECTRAL STUDIES

IR Spectra

The infrared spectra of ligands in solid and solution forms indicate that the ligand exists in the tautomeric forms as indicated below:



A broad band at Ca. 3100–3300 cm^{-1} due to νNH disappears in the solution spectra and the appearance of a new band at Ca. 2600 cm^{-1} may be ascribed to νSH clearly indicating the tautomeric equilibrium between the two forms of the ligands.[2]

The absence of νSH/NH in the solid and solution spectra of the metal complexes shows the involvement of this group in bond formation followed by deprotonation during complexation. A strong band observed at 1610 ± 5 cm^{-1} in both the solution and solid state spectra of free ligands attributable to $\nu(\rangle C{=}N)$ gets shifted to 1625 ± 10 cm^{-1} in the spectra of complexes indicating the participation of azomethine group in coordination. The chelation of ligands through azomethine nitrogen and thiolic sulfur gets support by the appearance of new bands at Ca. 420 and 325 cm^{-1} in the spectra of complexes due to ν(Sn←N) and ν(Sn—S) vibrations, respectively.

Apart from this, the bands observed at Ca. 540 and 510 cm^{-1} assignable to $\nu(Sn{-}C)_{asym.}$ and $\nu(Sn{-}C)_{sym.}$ modes, respectively suggest the cis-geometry for triorganotin complexes containing the pyramidal $(CH_3)_3$ Sn group.[14]

^{1}H NMR Spectra

The ^{1}H NMR spectra of three ligands and their corresponding triorganotin(IV) complexes have been recorded in $CDCl_3$. The broad signals observed at δ10.74 ppm (Fur. TsczH), δ10.67 ppm (Pyd.TsczH) and δ10.91 ppm (Thiop.TsczH) due to NH protons in the spectra of the ligands disappear in the case of tin(IV) complexes indicating the bonding of thiolic sulfur with the central tin atom.

The azomethine proton signals undergo downfield shifting in the spectra of complexes as compared to their position in ligands owing to the coordination of $\rangle C{=}N$ group with the metal atom. The complexes show additional signals at δ0.9–1.21 ppm due to the protons of Sn—CH_3 group. In addition to these $^2J(^{119}Sn{-}C{-}^1H)$ have been calculated and recorded in Table II. The observed values of coupling constants clearly indicate the cis-trigonal bipyramidal structure for the resulting complexes as reported earlier also by several workers.[14]

TABLE II

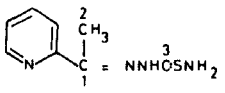
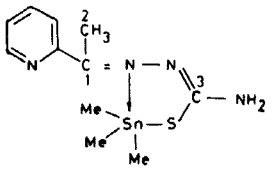
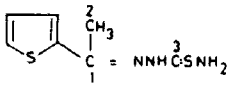
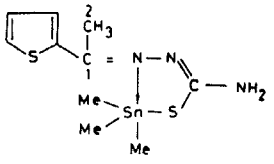
Coupling constants and ^{1}H NMR spectral data (δ, ppm) of ligands and their organotin(IV) derivatives

Compound	NH	Aromatic	$-NH_2$	Azomethine	Sn-CH_3	$^2J(^{119}Sn{-}C{-}^1H)$
Fur.TsczH	10.74	8.69-7.20	2.83	8.94	-	-
Me_3Sn(Fur.Tscz)	-	917-7.32	2.88	*	0.92	55.4
Pyd.TsczH	10.63	8.44-7.18	2.93	8.77	-	-
Me_3Sn(Pyd.Tscz)	-	8.89-7.26	3.10	8.98	1.14	57.2
Thiop.TsczH	10.91	8.73-7.29	2.86	8.87	-	-
Me_3Sn(Thiop.Tscz)	-	9.04-7.31	2.94	9.11	1.21	*

* Satellites were not clear.

TABLE III

^{13}C NMR spectral data (δ, ppm) of ligands and their corresponding triorganotin(IV) complexes

Compound	Chemical shift values							
	1	2	3	Aromatic				Sn-Me
	154.23	13.68	178.24	147.67	147.54	135.62	123.14 119.94	
	149.35	11.27	169.97	148.68	148.53	136.14	125.36 121.61	14.56
	150.25	15.87	177.98	140.29	128.91	128.87	128.46	
	144.84	14.42	170.46	142.74	130.13	129.65	129.25	16.82

^{13}C NMR Spectra

Further, the mode of bonding in these derivatives has been substantiated by the ^{13}C NMR spectral studies. The marked shift in the positions of carbons attached to sulfur and nitrogen atoms clearly indicates the involvement of thiolic sulfur and azomethine nitrogen in complexation (Table III).

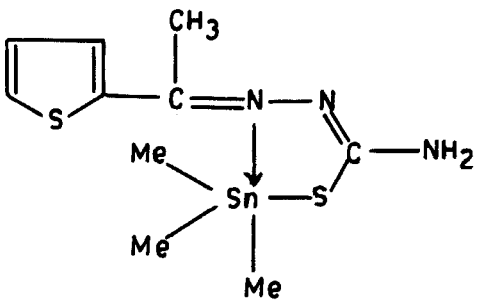
^{119}Sn NMR Spectra

The signal observed at $\delta - 142$ ppm in the ^{119}Sn NMR spectrum of Me_3Sn (Fur.Tscz) indicates the coordination number five around tin atom.[18]

On the basis of above spectral evidences and reports already available in the literature,[12–14] a trigonal bipyramidal structure (I) with the Sn←N bond occupying the axial position may be tentatively proposed for the resulting derivatives.

ANTIFUNGAL ACTIVITY

The antifungal activity of some representative ligands and their corresponding triorganotin(IV) complexes has been evaluated against various pathogenic fungi and the results are recorded in Table IV. The experimental data of antifungal



(I)

TABLE IV

Fungicidal activity of ligands and their organotin(IV) complexes

Compound	Average percentage inhibition after 7 days					
	Alternaria brassicae conc. (ppm)		Alternaria tenuis conc. (ppm)		Aspergillus niger conc. (ppm)	
	200	400	200	400	200	400
2-Ac Fur. TsczH	24	31	21	28	32	37
2-Ac Pyd.TsczH	30	36	29	34	37	44
2-Ac Thiop.TsczH	35	39	31	38	41	47
Me_3Sn(2-Ac Fur.Tscz)	72	81	65	79	73	86
Me_3Sn(2-Ac Pyd. Tscz)	84	97	77	89	84	96
Me_3Sn(2-Ac Thiop.Tscz)	96	100	91	99	94	100

screening reveal that the metal chelates are more fungitoxic as compared to the parent ligands and this can possibly be explained in the light of well known chelation theory.[15] The triorganotin(IV) complex of 2-acetyl thiophene thiosemicarbazone has been found to be the most active against all the fungi and this is proabaly due to the presence of two sulfur atoms in the metal complex.[16]

EXPERIMENTAL

All the manipulations were carried out under anhydrous conditions and the chemicals were dried and distilled by standard methods. The ligands were prepared by the earlier reported methods[17,18] and analysed before use. The abbreviations used for the ligands are given below:

Furfuraldehyde thiosemicarbazone = Fur.TsczH, Thiophene-2-carboxaldehyde thiosemicarbazone = Thiop.TsczH, Pyridine-2-carboxaldehyde thiosemicarbazone = Pyd.TsczH, Idole-3-carboxaldehyde thiosemicarbazone = Ind.TsczH, 2-Acetylfuran thiosemicarbazone = 2-Ac Fur.TsczH, 2-Acetylthiophene thiosemicarbazone = 2-Ac Thiop.TsczH, 2-Acetyl pyridine thiosemicarbazone = 2-Ac Pyd.TsczH, 3-Acetyl indole thiosemicarbazone = 3-Ac Ind.TsczH

The potassium salt of the ligands was prepared by reacting the ligand with potassium in 1:1 molar ratio in the medium of methanol.

Preparation of complexes. The methanolic solution of potassium salt of the ligand (0.005 mole) was added to the requisite amount of Me_3SnCl (0.005 mole) in dry benzene. The reaction mixture was

refluxed for 10–12 hrs and the potassium chloride so precipitated was filtered off. Benzene was added to the filtrate and the mixture was again refluxed for the completion of reaction. It was then filtered and the process of refluxing and filtration was repeated until all of the potassium chloride precipitated out. The excess of solvent was removed under vacuum and resulting products were repeatedly washed with dry *n*-hexane and pet ether and finally dried in vacuo under reduced pressure.

Analytical methods and physical measurements. Carbon and hydrogen analyses were carried out at the microanalytical laboratory of the department, whereas tin and sulfur were estimated gravimetrically.[17] Nitrogen was estimated by the Kjeldahl's method.

Molar conductivity was measured by the systronics conductivity bridge model 305 and molecular weights were determined by the Rast Camphor method.

IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Jeol FX90Q spectometer in $CDCl_3$ and Dry DMSO solutions, respectively.

The antifungal activity of the representative ligands and their corresponding tin(IV) complexes was evaluated by the reported method.[18]

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REFERENCES

1. R. C. Poller, The Chemistry of Organotin Compounds, Academic Press, New York, 1970.
2. Anil Saxena and J. P. Tandon, *Polyhedron*, **2**, 443 (1983).
3. P. Dixit, J. P. Tandon, R. B. Goyal and J. P. Agnihotri, *Main Group Met. Chem.*, **13** (1991) in press.
4. A. G. Davies and P. J. Smith, *Adv. Inorg. Chem. and Radiochem.*, **23**, 1 (1979).
5. B. M. Eliot, W. N. Aldridge and J. M. Bridges, *Biochem J.*, **177**, 461 (1979).
6. A. Saxena, J. P. Tandon and A. J. Crowe, *Polyhedron*, **4**, 1085 (1985).
7. P. Dixit and J. P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.*, **18**, 439 (1988).
8. P. Dixit and J. P. Tandon, *J. Prakt. Chem.*, **331**, 659 (1989).
9. M. A. Ali, S. E. Livingstone and D. J. Phillips, *Inorg. Chim. Acta*, **6**, 11 (1972).
10. A. K. Saxena, J. J. Zuckerman, K. C. Molloy and J. P. Tandon, *Inorg. Chim. Acta*, **63**, 71 (1982).
11. B. Y. K. Ho and J. J. Zuckerman, *Inorg. Chem.*, **12**, 1553 (1973).
12. P. G. Harrison, T. J. King and K. C. Molloy, *J. Organomet. Chem.*, **185**, 199 (1980).
13. J. D. Cashion, G. Domazetis and B. D. James, *J. Organomet. Chem.*, **185**, 433 (1980).
14. P. G. Harrison and J. A. Richards, *J. Organomet. Chem.*, **185**, 9 (1980).
15. R. S. Srivastava, *Inorg. Chim. Acta*, **56**, L65 (1981).
16. B. G. Tweedy, *Phytopathology*, **54**, 910 (1964).
17. Kiran Singh, R. V. Singh and J. P. Tandon, *Polyhedron*, **7**, 151 (1988).
18. K. Singh, P. Dixit, R. V. Singh and J. P. Tandon, *Main Group Met. Chem.*, **12**, 155 (1989).