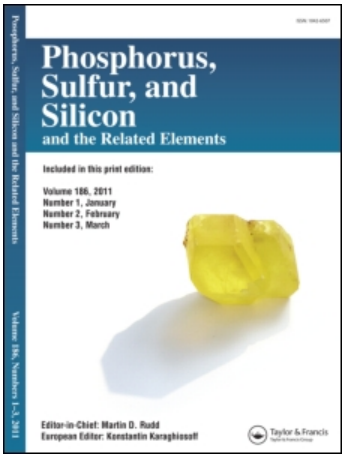

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Synthesis, Spectral, and 3D Molecular Modeling of Tin(II) and Organotin(IV) Complexes of Biologically Active Schiff Bases Having Nitrogen and Sulfur Donor Ligands

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Synthesis, Spectral, and 3D Molecular Modeling of Tin(II) and Organotin(IV) Complexes of Biologically Active Schiff Bases Having Nitrogen and Sulfur Donor Ligands

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Reaction of tin(II) chloride and dimethyltin dichloride with Schiff bases derived from S-benzyldithiocarbazate leads to the formation of a new series of tin(II) and organotin(IV) complexes of general formula $SnCl_2.L$ and $Me_2SnCl_2.L$ (where L = Schiff bases are derived from the condensation of S-benzyldithiocarbazate with heterocyclic aldehydes). An attempt has been made to prove the structures of the resulting complexes on the basis of elemental analysis, conductance measurements, molecular weight determinations, infrared, and multinuclear magnetic resonance (^1H, ^{13}C, and ^{119}Sn NMR) spectral studies. A few representative ligands and their tin complexes have also been screened for their antibacterial and antifungal activities and found to be quite active in this respect.

Keywords Antimicrobial activity; complexes; dimethyltin dichloride; dithiocarbazate; heterocyclic aldehydes; spectral studies; tin(II) chloride

INTRODUCTION

In recent years, a large number of metal complexes of thio-Schiff bases containing NS or ONS donor atoms have been studied.[1–5] The increased interest in the field may be attributed to their structural features and the reported carcinostatic and antiviral activity of NS and ONS donor ligands and their metal complexes. It has also been observed that a small structural change, such as the change of a substituent in the

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ligand may lead to an enhanced anticancer, antiviral, and antimicrobial activity of the transition metal complexes.[6–9]

Little is known about the complexing behavior of non-transition elements with these ligands. Among the non-transition elements, tin occupies an important position owing to the number of modern physicochemical and biochemical techniques that can be applied for a detailed structural study of its compounds. It is, therefore, considered of interest to synthesize organotin(IV) and tin(II) derivatives of Schiff bases derived by condensation of heterocyclic aldehydes with S-benzyldithiocabazate.

RESULTS AND DISCUSSION

The reaction of tin(II) chloride and dimethyltin dichloride with Schiff bases of dithiocarbazate may be depicted by the following equation:

$$SnCl_2 + L \rightarrow SnCl_2 \cdot L$$

$$MeSnCl_2 + L \rightarrow Me_2SnCl_2 \cdot L$$

where L represents the Schiff bases of S-benzyldithiocarbazate.

The resulting compounds are colored sticky solid and fairly soluble in organic solvents DMSO and DMF. The molecular weights of the compounds are determined by the Rast camphor method corresponding to the formula weight indicating their monomeric nature. The molar conductances of 10^{-3} M solution of the compounds in dimethylformamide are in the range of 10–15 Ω^{-1} cm^2 mol^{-1}, indicating their non-electrolytic nature.

Electronic Spectra

The electronic spectra of the ligands exhibit two bands at 342 and 410 nm which are assignable to π–π^* and n–π^* transitions, respectively. A red-shift is observed in the spectra of the complexes as these bands appear at 348 and 415 nm. This may be due to the polarization of the >C=N-bond caused by metal ligand electron transfer interaction. Further, a few sharp bands are observed in the region 245–270 nm in the spectra of complexes, which could be assigned as charge transfer bands, suggesting the formation of σ bonds and $d\pi \rightarrow p\pi$ bonds between p-orbital of nitrogen and sulfur and vacant 5d orbitals of tin.[10,11]

IR Spectra

In the IR spectra of the ligands, a strong band observed in the region 1615–1620 cm^{-1} assignable to ν(C=N)[12,13] is shifted to lower wave number in the spectra of complexes,[14] indicating the coordination of ligands through nitrogen atom of the azomethine group to the metal atom. Two medium intensity bands observed in the spectra of the ligands in the regions 1035 ± 6 cm^{-1} and 1315 ± 5 cm^{-1} are assigned to ν(C=S) and ν(C-S), respectively.[15,16] The lowering of these bands in the spectra of the corresponding tin complexes shows the coordination of sulfur to the tin atom.

Besides this, several new bands in the complexes observed at ~615 cm^{-1}, ~430 cm^{-1}, ~330 cm^{-1}, and 305 cm^{-1} may be assigned to ν(Sn-C),[17] ν(Sn←S),[18] ν(Sn←N),[19] and ν(Sn-Cl),[20] respectively, thus lending support to the proposed coordination in the complexes.

^{1}H NMR Spectra

To further confirm the bonding pattern in these complexes, ^{1}H NMR spectra of ligands and their tin complexes were recorded in $CDCl_3$ or DMSO-d_6 using TMS as internal reference. The Schiff bases of dithiocarbazate exhibit a NH proton signal at ~ δ10.82 ppm. This signal shifts downfield in the complexes (~ δ 11.10 ppm) due to the involvement of the adjacent sulfur in bonding with the tin atom, as a result of which the NH proton becomes less shielded.

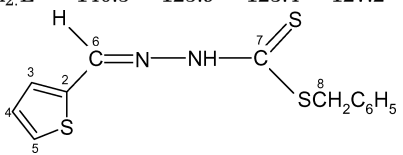
In the ^{1}H NMR spectra of the ligands, a sharp signal is observed at ~ δ 8.50 ppm due to the –CH=N-proton. It moves downfield (~ δ 8.62 ppm) in the complexes in comparison with its original position in the ligands due to the coordination of azomethine nitrogen to the metal atom. The ligands show a complex multiplet in the region δ 7.60–6.60 ppm for the aromatic protons and a siglet at δ 4.20 ppm for the methylene protons, and it remains at almost the same position in the spectra of the tin complexes. The organotin(IV) complexes, however, show additional signals at δ 0.35 ppm owing to the protons of the methyl group.

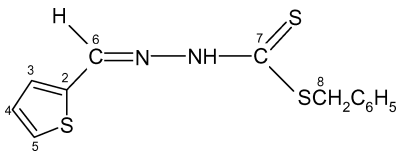
^{13}C NMR Spectra

^{13}C NMR spectra of S-benzyl-β-N(thienylmethlidene) dithiocarbazate (L^I) and S-benzyl-β-N-(furylmethlidene) dithiocarbazate (L^2), and their corresponding tin(II) and organotin(IV) complexes have also been recorded in $CDCl_3$. A considerable shift (Table I) in the position of carbons attached to the different participating groups clearly indicates

TABLE I ^{13}C NMR Spectral Data for Ligands and Their corresponding Tin Complexes

Compounds	Chemical Shift δ ppm											Sn-Me
	C-2	C-3	C-4	C-5	C-6	C-7	C-8	Aromatic Carbon				
L^1	143.3	124.8	122.1	134.4	149.0	195.7	39.4	137.2	127.1	128.2	127.6	–
$SnCl_2.L^1$	142.4	123.7	121.6	135.8	162.2	182.5	39.2	137.3	127.9	127.4	127.8	–
$Me_2SnCl_2.L^1$	142.9	124.2	121.8	134.9	156.3	185.1.	40.2	137.0	127.6	127.9	128.1	9.4
L^2	141.1	125.4	124.7	127.6	144.3	198.5	38.7	137.4	127.5	128.6	127.1	–
$SnCl_2Ch.L^2$	138.0	126.5	122.8	127.2	157.4	179.8	39.7	137.5	129.1	126.6	128.8	–
$Me_2SnCl_2.L^2$	140.5	125.9	123.4	127.2	155.7	180.1	39.4	137.5	128.4	127.1	128.6	8.6





the bonding of the azomethine nitrogen and thiolic sulfur to the tin atom.

^{119}Sn NMR Spectra

Tin(II) complexes give sharp signals at δ –575 to –582 ppm in the ^{119}Sn NMR spectra, which is below the reported valuefor tri-coordinated hydrated tin(II) chloride. Therefore, a four-coordinate square-planar geometry may be proposed for the resulting tin(II) complexes.[21,22] The organotin(IV) complexes give sharp signals at $\sim \delta$ –360 ppm, in ^{119}Sn NMR spectra, which strongly support the six coordination around tin in a distorted octahedral geometry. Values[22,23] for similar six-coordinated organotin(IV) complexes have been reported in the range of δ –355 to –503 ppm.

Thus on the basis of above discussion, it is clear that the ligand, by coordinating to tin atom through the thioketonic nitrogen, behaves as bidentate ligand. Since all the resulting tin complexes are monomeric, the structures in Figure 1 have been proposed for the tin(II) and organotin(IV) complexes.

Molecular Modeling and Analysis

In view of the hexa-coordination of the present tin complexes, [$Me_2SnCl_2.L^3$], the molecular modeling of the compound as a representation, is based on its octahedral structure and all the 121

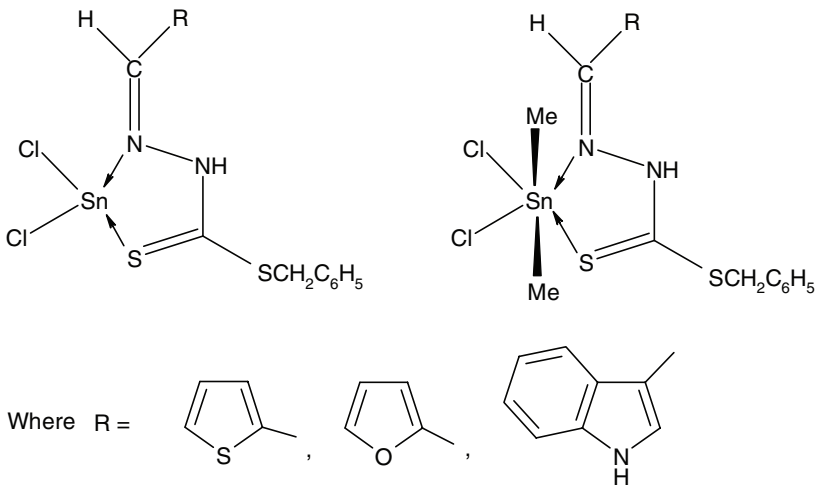


FIGURE 1 Structures of the tin(II) and organotin(IV) complexes.

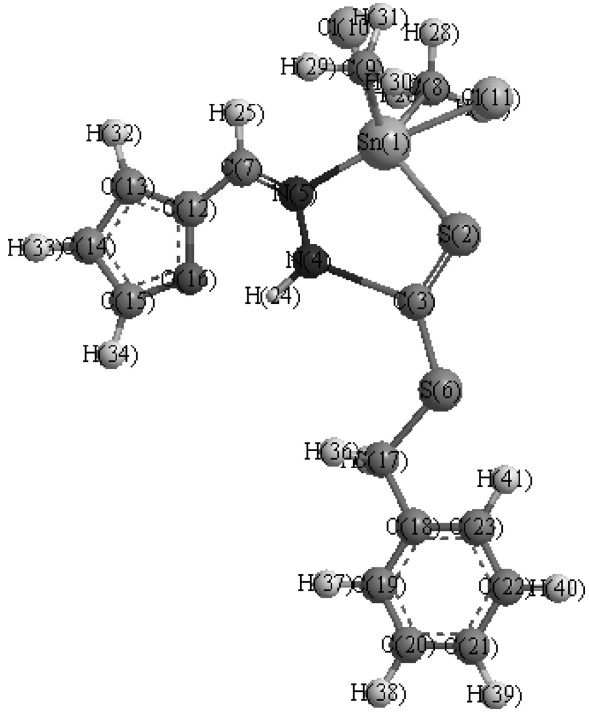


FIGURE 2 The 3D structure of $[Me_2SnCl_2.L^3]$.

measurements are obtained (bond angles, 78 in numbers and the bond lengths, 43 in numbers). In most of the cases, the actual bond angles and lengths are close to the optimal values, and thus the proposed structure of the compound is acceptable (Figure 2).

Antimicrobial Activity

In-vitro antimicrobial activity of the ligands and their corresponding tin complexes was tested by a paper disk diffusion method[24–28] at a concentration of 100 ppm in the broth agar medium. Streptomycin and Mycostatin were used as the reference compounds for antibacterial and antifungal activities, respectively. These data are presented in Table II. *Escherichia coli*, *Staphyllococcus aureus*, *P. syringae*, *P. mirabilis*, *Asergillus flavus*, *Aspergillus niger*, and *Penicillium crysogenes* were used as the test organisms. The liquid medium containing the bacterial subcultures was autoclaved for 20 min at 15 lb pressure before incubation. The bacteria were cultured for 24 h at 36°C in an

TABLE II Antimicrobial Activity of Ligands and Their Corresponding Metal Complexes

S.No	Compounds	Zone of Inhibition in mm-Organisms (mean ± SD)								
		L^1	$SnCl_2.L^1$	$Me_2SnCl_2.L^1$	L^2	$SnCl_2.L^2$	$Me_2SnCl_2.L^2$	L^3	$SnCl_2.L^3$	$Me_2SnCl_2.L^3$
1.	*E. coli*	6 ± 0.04	7 ± 0.05	10 ± 0.05	8 ± 0.03	10 ± 0.07	12 ± 0.06	7 ± 0.02	08 ± 0.02	09 ± 0.03
2.	*S. aureus*	8 ± 0.03	9 ± 0.01	13 ± 0.02	7 ± 0.06	11 ± 0.06	12 ± 0.05	8 ± 0.05	9.2 ± 0.05	175 ± 0.05
3.	*P. syringae*	4 ± 0.02	5 ± 0.01	06 ± 0.01	4 ± 0.05	06 ± 0.02	07 ± 0.04	5 ± 0.02	07 ± 0.06	08 ± 0.05
4.	P. mirabilis	3 ± 0.06	5 ± 0.05	07 ± 0.03	5 ± 0.02	07 ± 0.01	06 ± 0.02	3 ± 0.01	04 ± 0.04	06 ± 0.05
5.	*Aspergillus flavus*	5 ± 0.05	6 ± 0.05	09 ± 0.05	6 ± 0.05	08 ± 0.05	09 ± 0.05	4 ± 0.05	06 ± 0.05	08 ± 0.05
6.	*Aspergillus niger*	6 ± 0.05	8 ± 0.05	10 ± 0.05	5 ± 0.05	06 ± 0.05	09 ± 0.05	4 ± 0.05	07 ± 0.05	10 ± 0.05
7.	*Penicillium crysogenes*	8 ± 0.05	10 ± 0.05	14 ± 0.05	6 ± 0.05	10 ± 0.05	12 ± 0.05	6 ± 0.05	07 ± 0.05	08 ± 0.05

incubator. Mueller Hinton broth is used for preparing basal medium for the bioassay of the organisms. Nutrient agar was poured onto a plate and allowed to solidify. The test compounds in ethanol solution were added dropwise on a 5 mm diameter filter paper disk placed in the center of the agar plates. The plates were then kept at 5°C for 1 h and transferred to an incubator maintained at 36°C and 27°C, respectively, for bacteria and fungi. The width of the growth inhibition zone around the disk was measured after 24 h and 60 h incubation for bacteria and fungi, respectively. Three replicates were taken for each treatment.

The tin complexes were more active than the free ligands, which indicates that metallation increases antimicrobial activity. All the tin complexes tested were found to be highly active against all the microorganisms. The complexes that contain the organotin(IV) derivatives have been found to be more active as compared to the corresponding tin(II) derivatives. The preliminary results achieved have led us to conclude that these types of complexs should be studied in detail for their applications in diverse areas.

EXPERIMENTAL

Tin(II) chloride was dehydrated by dissolving it in acetic anhydride.[29] Chemicals and solvents used were dried and purified by standard method,[31] and moisture was excluded from the glass apparatus using $CaCl_2$drying tubes. All the chemicals used were commercially available products of analytical reagent grade, except the ligands L^1 [S-Benzyl-β-N-(indolymethylidene) dithiocarbazate, $C_{17}H_{15}N_3S_2$], L^2 [S-Benzyl-β-N-(thienylmethylidene) dithiocarbazate, $C_{13}H_{12}N_2S_3$], and L^3[S-Benzyl-β-N-(furylmethylidene) dithiocarbazate $C_{I3}H_{12}N_2OS_2$], the preparation of which has been described ealier.[28]

Synthesis of Tin(II) and Organotin(IV) Complexes

The requisite amounts of tin (II) chloride and dimethyltin dichloride were added to the calculated amount of the ligands in 1:1 molar ratio in dry THF as the reaction medium in an oxygen-free nitrogen atmosphere. The color of the solution changed immediately. The solution was then stirred magnetically for 5–6 h. The excess solvent was removed under reduced pressure, and the compound was dried in vacuo at 45 $\pm$ 5°C after repeated washing with dry cyclohexane. The compounds were purified by recrystallization from methanol. The purity of the compounds was checked by TLC using silica gel-G as an adsorbent.

Compound 1

$SnCl_2.L^1$: Formula; $C_{17}H_{15}N_3S_2Cl_2Sn$; Yield 85%; Mol. Wt.: Found(Calc.): 512(515); yellow sticky solid; Analysis {%F(C)}: Sn, 22.96(23.04); C,39.60(39.64); H,2.90(2.94); N, 8.07(8.16); S, 12.40(12.45); Cl, 13.72(13.77). IR (cm^{-1}): ν(C=N), 1610; ν(C=S), 1025; ν(Sn←N), 430; ν(Sn←S), 330; ν(Sn-Cl), 305; ^{1}H NMR (δ ppm): 6.85–7.60, (arom.); 8.62, (CH=N); 11.09 (NH); ^{119}Sn NMR (δ ppm); –582.

Compound 2

$SnCl_2.L^2$: Formula; $C_{13}H_{12}N_2S_3Cl_2Sn$; Yield 78%; Mol. Wt.: Found(Calc.): 476(482); golden yellow solid; Analysis {%F(C)}: Sn, 24.59(24.62); C, 32.31(32.39); H, 2.48(2.51); N, 5.78(5.81); S, 19.88(19.95); Cl, 14.68(14.71). IR (cm^{-1}): ν(C=N), 1614; ν(C=S), 1028; ν(Sn←N), 434; ν(Sn←S), 327; ν(Sn-Cl), 308; ^{1}H NMR (δ ppm): 6.60–7.38, (arom.); 8.60, (CH=N); 11.10 (NH); ^{119}Sn NMR (δ ppm);–575.

Compound 3

$SnCl_2.L^3$: Formula; $C_{13}H_{12}N_2S_2OCl_2Sn$; Yield 80%; Mol. Wt.: Found(Calc.): 461(465); light yellow solid; Analysis {%F(C)}: Sn, 25.40(25.47); C, 33.45(33.61); H, 2.59(2.60); N, 5.94(6.01); S, 13.70(13.76); Cl, 15.19(15.22). IR (cm^{-1}): ν(C=N), 1612; ν(C=S), 1025; ν(Sn←N), 432; ν(Sn←S), 332; ν(Sn-Cl), 306; ^{1}H NMR (δ ppm): 6.75–7.42, (arom.); 8.63, (CH=N); 11.08 (NH); ^{119}Sn NMR (δ ppm);–578.

Compound 4

$Me_2SnCl_2.L^1$: Formula; $C_{19}H_{21}N_3S_2Cl_2Sn$; Yield 82%; Mol. Wt.: Found(Calc.): 536(545); yellow solid; Analysis {%F(C)}: Sn, 21.71(21.77); C, 41.83(41.86); H, 3.85(3.88); N, 7.63(7.71); S, 11.69(11.76); Cl, 12.94(13.01). IR (cm^{-1}): ν(C=N), 1610; ν(C=S), 1029; ν(Sn←N), 430; ν(Sn←S), 328; ν(Sn-Cl), 307; ν(Sn-C), 615; ^{1}H NMR (δ ppm): 6.80–7.50, (arom.); 8.64, (CH=N); 11.10, (NH); 0.35, (-CH_3); ^{119}Sn NMR (δ ppm);–360.

Compound 5

$Me_2SnCl_2.L^2$: Formula; $C_{15}H_{18}N_2S_3Cl_2Sn$; Yield 76%; Mol. Wt.: Found(Calc.): 501(512); dark brown solid; Analysis {%F(C)}: Sn, 23.16(23.18); C, 35.14(35.18); H, 3.52(3.54); N, 5.40(5.47); S, 18.73(18.78); Cl, 13.78(13.85). IR (cm^{-1}): ν(C=N), 1615; ν(C=S), 1030; ν(Sn←N), 433; ν(Sn←S), 329; ν(Sn-Cl), 305; ν(Sn-C), 612; ^{1}H NMR (δ ppm): 6.70–7.35, (arom.); 8.62, (CH=N); 11.08, (NH); 0.38, (-CH_3); ^{119}Sn NMR (δ ppm);–350.

Compound 6

$Me_2SnCl_2.L^3$: Formula; $C_{15}H_{18}N_2S_2OCl_2Sn$; Yield 78%; Mol. Wt.: Found(Calc.): 492(496); brownish yellow sticky solid; Analysis {%F(C)}: Sn, 23.90(23.93); C, 36.25(36.32); H, 3.63(3.66); N, 5.60(5.65); S, 12.89(12.93); Cl, 14.20(14.29). IR (cm^{-1}): ν(C=N), 1612; ν(C=S), 1028; ν(Sn←N), 434; ν(Sn←S), 330; ν(Sn-Cl), 304; ν(Sn-C), 614; ^{1}H NMR (δ ppm): 6.68–7.28, (arom.); 8.60, (CH=N); 11.12, (NH); 0.33, (-CH_3); ^{119}Sn NMR (δ ppm);–360.

Analytical Methods

Tin was estimated gravimetrically as SnO_2, and chlorine was estimated volumetrically using Volhard's method.[30] Nitrogen and sulfur were estimated by Kjeldahl's and Messenger's methods, respectively.[32] Molar conductance measurements were made in anhydrous DMF at $40 \pm 1\,^{\circ}C$ using a Systronics conductivity bride model-305. Molecular weight determinations were carried out by the Rast camphor method.

Spectral Measurements

The electronic spectra were recorded in methanol on a Toshniwal spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 577 IR spectrophotometer in the region 4000–200 cm^{-1}. A Perkin Elmer model RB-12 spectrometer was used to obtain the ^{1}H NMR spectra, $CDCl_3$ and DMSO-$d_6$were used as the solvent (TMS as internal standard). ^{13}C NMR spectra were recorded on a 90 MHz JEOL NMR spectrometer using $CDCl_3$ and dry DMSO as the solvent (TMS as internal standard). The ^{119}Sn NMR spectra with proton noise decoupling were recorded using a 90 MHz Jeol spectrometer in dry DMSO with tetramethyltin (TMT) as an external standard at 22.7 MHz. The 3D molecular modeling of a representative compound was carried out on a CS Chem. 3D Ultra Molecular Modeling and analysis program.

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