

## Research Article

# Synthesis of Triphenyltin (IV) and Dibutyltin (IV) Complexes of 1-Aryl-2,5-dithiohydrazodicarbonamides and Their Characterization

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Organotin complexes of the types  $\text{Ph}_3\text{SnL}$  and  $\text{Bu}_2\text{SnL}$  [where Ph = phenyl and Bu = butyl; HL = 1-phenyl-2,5-dithiohydrazodicarbonamide (HPhthc), 1-benzyl-2,5-dithiohydrazodicarbonamide (Hbzthc), 1-(4-ethoxyphenyl)-2,5-dithiohydrazodicarbonamide (HEtOPhthc)] have been prepared. Molar conductance studies demonstrate the nonionic behavior of the complexes. The  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance and FAB mass spectra of the complexes are consistent with the proposed stoichiometry. Infrared spectra suggest an anionic bidentate coordinating behavior of the ligands.

## 1. Introduction

Dithiohydrazodicarbonamides have proved to be compounds of versatile behavior. This particular ligand system and its 3d metal complexes have been shown to possess high antimicrobial activity [1, 2]. Anticorrosion properties of these ligands have also been recognized for the corrosion of copper in aqueous chloride solutions [3]. Some 1-aryl-2,5-dithiohydrazodicarbonamides and their molybdenum and tungsten complexes have been found to act as excellent extreme-pressure lubrication additives [4] and corrosion inhibitors for mild steel in 1.0 N sulfuric acid [5]. Biocidal activity of organotins is well recognized [6–8]. These have been enormously used as antifouling paints [9, 10]. Organotins derived from carboxylic acid, phosphoric group, N, S donating groups have been studied as corrosion inhibitors [11–22]. Organotins are known for their friction and wear reducing properties [23–25]. Organotin derivatives of alkylphenols have been successfully used as antiwear additives for lubricating oils [26]. Since organotins and dithiohydrazodicarbonamides both are well known for their biocidal behavior, friction and wear reducing properties and anticorrosive properties, synthesis of organotin complexes

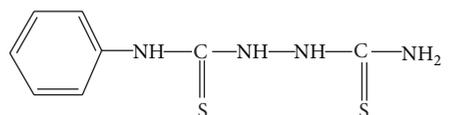
with dithiohydrazodicarbonamides was undertaken with intent to explore their applicability as corrosion inhibitors. The present communication, therefore, describes the synthesis of some triphenyltin and dibutyltin dithiohydrazodicarbonamides and their characterization by infrared, proton, and  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy and FAB mass spectrometry.

## 2. Experimental

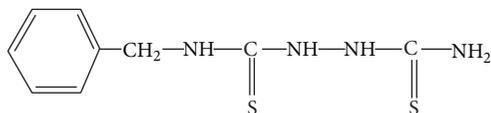
**2.1. Materials.** Analytical grade reagents were used in the present investigation. The ligands were prepared by refluxing thiosemicarbazide with appropriate aryl isothiocyanates in 50% ethanol using previously reported methods [27]. In a representative experiment 1-phenyl-2,5-dithiohydrazodicarbonamide was synthesized as given below.

Thiosemicarbazide (0.05 mol) and phenyl isothiocyanate (0.05 mol) were mixed with 50 mL of 50% ethanol and the mixture was refluxed for one hour. The solid that appeared was filtered, washed with water, and crystallized from ethanol, m.pt. 174°C.

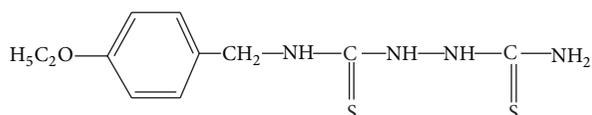
The structures of dithiohydrazodicarbonamides used for preparation of complexes are given in Figure 1.



1-Phenyl-2,5-dithiohydrazodicarbonamide (HPhthc)



1-Benzyl-2,5-dithiohydrazodicarbonamide (HBzthc)



1-(4-Ethoxyphenyl)-2,5-dithiohydrazodicarbonamide (HEtOPhthc)

FIGURE 1: Structures and acronyms of the various dithiohydrazodicarbonamides.

## 2.2. Preparation of the Complexes

**2.2.1. Triphenyltin Complexes.** To an ethanolic solution of triphenyltin chloride (3.8 g, 10 mmol), an ethanolic solution of the corresponding ligand (10 mmol) was added with constant stirring. The reaction mixture was stirred at solvent reflux for 4 hrs and excess solvent was removed by distillation at reduced pressure. On addition of excess of petroleum ether to the residual liquid, a dirty-white solid precipitated. The solvent was removed by evaporation and the residual solid was dried at reduced pressure. It was then recrystallized from acetone.

**2.2.2. Dibutyltin Complexes.** Dibutyltin complexes were synthesized by adding dropwise an ethanolic solution of dibutyltin dichloride (3.04 g, 10 mmol) to a stirred ethanolic solution of the corresponding ligand (20 mmol). The reaction mixture was stirred at solvent reflux for 3 hrs and the excess solvent was removed by distillation at reduced pressure. The residual liquid was allowed to cool to room temperature. Upon the addition of excess petroleum ether (b.p. 60–80°C), a solid product formed. The solid was collected by filtration, washed with ethanol, and dried at reduced pressure. It was then recrystallized from acetone.

## 3. Instrumentation

Electrical conductance of  $10^{-3}$  M solutions of the complexes in DMSO was measured at room temperature using an inversion-type special conductivity cell with a bright platinum electrode (WTW model LBR/B). Infrared spectra were obtained using a Perkin Elmer 983 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Jeol FX Fourier Transform Multinuclear NMR spectrometer and solutions in DMSO- $d_6$  using tetramethylsilane as internal reference.

FAB mass spectra were recorded using a Jeol SX 6000 mass spectrometer and xenon/6 KV/10 mA as the FAB gas and NBA *m*-nitrobenzyl alcohol as matrix. Powder X-ray diffraction (XRD) data of the complexes were recorded at room temperature using a Rigaku Cu-rotating anode (Japan) X-ray diffractometer operating at 40 KV and 100 mA at 1.5406 Å wavelength (Cu- $K\alpha_1$  radiation).

## 4. Result and Discussion

The complexes were analyzed for their tin, sulfur, hydrogen, carbon, and nitrogen contents. Tin and sulfur were determined gravimetrically as  $\text{SnO}_2$  and  $\text{BaSO}_4$ , respectively [28]. Carbon, hydrogen, and nitrogen were determined microanalytically. The analytical data together with molar conductance values are given in Table 1. As indicated by analytical data, the complexes of the types  $\text{Ph}_3\text{SnL}$  and  $\text{Bu}_2\text{SnL}_2$  where [LH = HPhthc, Hbzthc, HEtOPhthc] are formed. All the complexes are soluble in common organic solvents. The molar conductance values of all the complexes are in the range 9–15.5  $\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$  which shows them to be nonionic [29].

**4.1. Infrared Spectra.** Prominent IR spectral bands and the corresponding assignments are displayed in Table 2. The IR spectrum of the ligand 1-phenyl-2,5-dithiohydrazodicarbonamide (HPhthc) exhibits four bands at 3420, 3390, 3210, and 3150  $\text{cm}^{-1}$  which are assigned to  $\nu(\text{N-H})$ ,  $\nu(\text{NH}_2)$ ,  $\nu(\text{NH})$  ( $\text{ArNH}_2$ ) and  $\nu(\text{N-H})$  ( $-\text{NH}-\text{NH}-$ ), respectively [1]. These bands appear at 3400, 3380, 3220, and 3140  $\text{cm}^{-1}$ , respectively, in HEtOPhthc and at 3410, 3370, 3250, and 3180  $\text{cm}^{-1}$ , respectively, in Hbzthc. The position of the first two bands is almost unaffected by complexation indicating that the primary amino ( $-\text{NH}_2$ ) nitrogen is not involved in the coordination. Upon complexation, the third band of the ligands becomes broad and the fourth band is absent suggesting that at least one of the  $>\text{NH}$  groups is involved in coordination and formation of the complexes. The  $\beta(\text{NH}_2)$  and  $\nu(\text{N-N})$  absorption bands of strong intensity in the spectra of the ligand appearing at 1600–1640 and 980  $\text{cm}^{-1}$ , respectively, show lower and higher energy shifts of 10–20 and 20–40  $\text{cm}^{-1}$ , respectively, on complexation indicating that one of the hydrazinic nitrogen atoms is involved in coordination [1]. The thioamide band I [ $\beta(\text{NH}) + \nu(\text{CN})$ ] and thioamide band II [ $\nu(\text{CN}) + \beta(\text{NH})$ ] appearing for the ligands at approximately 1500 and 1300  $\text{cm}^{-1}$ , respectively, undergo shifts of higher energy 20–90  $\text{cm}^{-1}$  upon complexation due to the reduction of the  $>\text{C}=\text{S}$  bond order from two to one and an increase in the  $>\text{C}-\text{N}$  bond order from one to two as a result of thioenolisation.

The position of absorption for the thioamide IV bands appearing at 880–840  $\text{cm}^{-1}$  in the ligands remains almost unchanged in the spectra of the complexes and a new band around 810–770  $\text{cm}^{-1}$  due to the  $\nu(\text{C}-\text{S})$  stretching vibration is present, suggesting that one of the  $>\text{C}=\text{S}$  groups is not involved in the coordination. The appearance of a new band in the region 810–770  $\text{cm}^{-1}$  in the spectra of the complexes

TABLE 1: Analytical data and behavior of organotin (IV) dithiohydrazodicarbonamide complexes.

Complex empirical formula	Color	Anal. %			Found (calculated)		Molar conductance $10^{-3}$ M in DMSO ( $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$ )
		C	H	N	S	Sn	
$\text{Ph}_3\text{Sn}(\text{Phthc})$ $\text{C}_{26}\text{H}_{24}\text{N}_4\text{S}_2\text{Sn}$	Pale white	54.73 (54.35)	4.21 (4.18)	9.82 (9.75)	11.22 (11.14)	20.70 (20.55)	10.90
$\text{Bu}_2\text{Sn}(\text{Phthc})_2$ $\text{C}_{24}\text{H}_{36}\text{N}_8\text{S}_4\text{Sn}$	Pinkish white	42.35 (42.22)	5.29 (5.27)	16.47 (16.42)	18.82 (18.76)	17.35 (17.30)	15.50
$\text{Ph}_3\text{Sn}(\text{Bzthc})$ $\text{C}_{27}\text{H}_{26}\text{N}_4\text{S}_2\text{Sn}$	White	55.91 (55.10)	4.40 (4.42)	9.49 (9.52)	10.84 (10.88)	20.01 (20.06)	9.63
$\text{Bu}_2\text{Sn}(\text{Bzthc})_2\text{Et}$ $\text{C}_{26}\text{H}_{40}\text{N}_8\text{S}_4\text{Sn}$	Dirty white	44.08 (43.94)	5.64 (5.63)	15.81 (15.77)	18.07 (18.02)	16.66 (16.61)	14.70
$\text{Ph}_3\text{Sn}(\text{EtOPhthc})$ $\text{C}_{28}\text{H}_{28}\text{N}_4\text{OS}_2\text{Sn}$	Cream	54.45 (54.19)	4.86 (4.83)	9.07 (9.03)	10.37 (10.32)	19.12 (19.03)	6.15
$\text{Bu}_2\text{Sn}(\text{EtOPhthc})_2$ $\text{C}_{28}\text{H}_{44}\text{N}_8\text{O}_2\text{S}_4\text{Sn}$	White	43.86 (43.63)	5.74 (5.71)	14.62 (14.54)	16.71 (16.62)	15.40 (13.32)	9.61

TABLE 2: IR spectral bands ( $\text{cm}^{-1}$ ) and their assignments.

Complex	$\nu$ (N-H)	$\nu$ ( $\text{NH}_2$ )	$[\beta(\text{N-H}) + \nu$	$[\nu(\text{CN}) + \beta$	$[\nu(\text{C=S})/\text{C-S}]$	$\beta(\text{NH}_2)$	$\nu(\text{Sn-C})$	$\nu(\text{Sn-S})$	$\nu(\text{Sn-N})$	$\nu(\text{N-N})$
			(CN)]	(N-H)]						
HPhthc	3420	3210	1500	1300	840	1640	—	—	—	980
	3390	3150								
$\text{Ph}_3\text{Sn}(\text{Phthc})$	3410	3200	1555	1385	770	1650	600	384	354	1005
	3380	3150								
$\text{Bu}_2\text{Sn}((\text{Phthc}))_2$	3400	3180	1560	1390	760	1645	590	370	360	1010
	3364	3140								
HEtOPhthc	3400	3220	1520	1300	810	1610	—	—	—	960
	3380	3140								
$\text{Ph}_3\text{Sn}(\text{EtOPhthc})$	3390	3210	1570	1365	720	1605	585	380	340	980
	3370	3120								
$\text{Bu}_2\text{Sn}(\text{EtOPhthc})_2$	3400	3220	1580	1360	710	1610	610	397	350	985
	3360	3110								
HBzthc	3410	3250	1510	1320	880	1600	—	—	—	900
	3370	3180								
$\text{Ph}_3\text{Sn}(\text{Bzthc})$	3400	3240	1535	1380	805	1590	617	390	310	940
	3365	3160								
$\text{Bu}_2\text{Sn}(\text{Bzthc})_2$	3400	3250	1540	1370	810	1580	605	380	315	950
	3360	3150								

indicates that coordination of the metal through the “thiolo” sulfur has occurred.

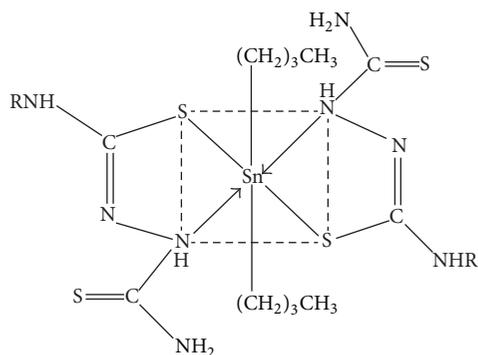
New bands appearing in the far-IR spectra of all the complexes in the region 580–620, 310–360, and 370–390  $\text{cm}^{-1}$  may be tentatively assigned to  $\nu(\text{Sn-C})$ ,  $\nu(\text{Sn-N})$ , and  $\nu(\text{Sn-S})$  modes, respectively [28].

**4.2.  $^1\text{H}$  NMR Spectra.**  $^1\text{H}$  NMR spectrum of the ligand HPhthc recorded in  $\text{DMSO-d}_6$  exhibits  $\text{D}_2\text{O}$  exchangeable resonance signals at  $\delta$  9.93 (–NH–NH) and  $\delta$  2.36 (s, – $\text{NH}_2$ ) ppm. Aromatic protons, together with the –NH proton, are observed as a multiplet between  $\delta$  7.74 and 7.06 ppm. However, the complexes of the ligand HPhthc show a –NH–NH proton signal at  $\delta$  9.70 ppm due to one proton only, supporting the view that one proton has undergone deprotonation after thioenolisation to form the complex. Other proton signals of the ligand appear at more deshielded

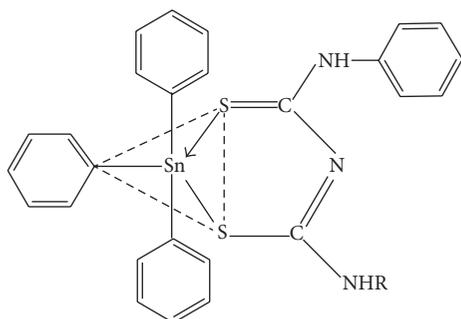
positions in the complexes. The electronic environment around these protons has changed to some extent as a consequence of complexation.

**4.3.  $^{13}\text{C}$  NMR Spectra.** The  $^{13}\text{C}$  NMR spectrum of HBzthc displays resonance signals between  $\delta$  120.0 and 131.8 ppm corresponding to the carbon atoms of the benzyl group and a single peak at  $\delta$  170.6 and  $\delta$  171.3 ppm due to  $>\text{C}=\text{S}$  carbon atoms. The spectra of  $\text{Ph}_3\text{SnPhthc}$  and  $\text{Bu}_2\text{Sn}(\text{Phthc})_2$  indicate greater deshielding of the  $>\text{C}=\text{S}$  carbon as compared to the ligand which may arise due to the presence of  $-\text{N}=\text{C}-\text{S}$  from  $-\text{HN}-\text{C}=\text{S}$  after the removal of proton upon thioenolisation.

**4.4. FAB Mass Spectra.** The FAB mass spectrum of  $\text{Ph}_3\text{SnPhthc}$  shows several peaks due to various fragments resulting from its ionization. The presence of a prominent



Dibutyltin bis(1-aryl-2,5-dithiohydrazodicarbonamide)



Triphenyltin 1-aryl-2,5-dithiohydrazodicarbonamide

Where R =

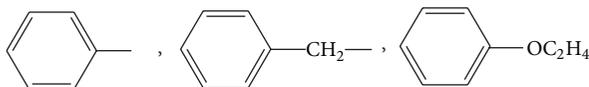


FIGURE 2: Proposed structure of organotin (IV) complexes.

peak at  $m/z = 226$  for the ligand HPhthc and an intense molecular ion peak at  $m/z = 570$  ( $-4H^+$ ), (59) reflects its monomeric nature. The spectrum of  $Bu_2Sn(EtOPhthc)_2$  contains a low intensity peak at  $m/z = 766$  ( $-4H^+$ ), (11) which corresponds to the molecular ion peak of complex.

Based on analytical data and the physicochemical studies noted, structures for the proposed complexes have been proposed. These structures are shown in Figure 2.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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