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 Ph$_3$SnL and Bu$_2$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 $^1$H and $^{13}$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 $^{13}$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.
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. ¹H and ¹³C NMR spectra were recorded using a Jeol FX Fourier Transform Multinuclear NMR spectrometer and solutions in DMSO-δ₆ 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-Kα₁ 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 SnO₂ and BaSO₄, 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 Pb₂SnL and Bu₂SnL 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 ohm⁻¹ mol⁻¹ cm² 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 cm⁻¹ which are assigned to ν(N–H), ν(NH₂), ν(NH) (ArNH₂) and ν(N–H) (–NH–NH–), respectively [1]. These bands appear at 3400, 3380, 3220, and 3140 cm⁻¹, respectively, in HETOPhthc and at 3410, 3370, 3250, and 3180 cm⁻¹, respectively, in Hbzthc. The position of the first two bands is almost unaffected by complexation indicating that the primary amino (–NH₂) 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 hydrazinic nitrogen involves in coordination and formation of the complexes. The β(NH₂) and ν(N–N) absorption bands of strong intensity in the spectra of the ligand appearing at 1600–1640 and 980 cm⁻¹, respectively, show lower and higher energy shifts of 10–20 and 20–40 cm⁻¹, respectively, on complexation indicating that one of the hydrazinic nitrogen atoms is involved in coordination [1]. The thioamide band I [β(NH) + ν(CN)] and thioamide band II [ν(CN) + β(NH)] appearing for the ligands at approximately 1500 and 1300 cm⁻¹, respectively, undergo shifts of higher energy 20–90 cm⁻¹ upon complexation due to the reduction of the >C=S bond order from two to one and an increase in the >C=N bond order from one to two as a result of thienoanalysis.

The position of absorption for the thioamide IV bands appearing at 880–840 cm⁻¹ in the ligands remains almost unchanged in the spectra of the complexes and a new band around 810–770 cm⁻¹ due to the ν(C–S) stretching vibration is present, suggesting that one of the >C=S groups is not involved in the coordination. The appearance of a new band in the region 810–770 cm⁻¹ in the spectra of the complexes
**Table 1: Analytical data and behavior of organotin(IV) dithiohydrazodicarbonamide complexes.**

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

**Table 2: IR spectral bands (cm$^{-1}$) and their assignments.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\gamma$(N–H)</th>
<th>$\gamma$(NH$_2$)</th>
<th>$\beta$(N–H) + $\gamma$(CN)</th>
<th>$\gamma$(CN) + $\beta$(N–H)</th>
<th>$\beta$(CN) + $\gamma$(N–H)</th>
<th>$\beta$(N–H) + $\gamma$(CN)</th>
<th>$\gamma$(C=S)/C–S</th>
<th>$\gamma$(Sn–C)</th>
<th>$\gamma$(Sn–N)</th>
<th>$\gamma$(N–N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPhthc</td>
<td>3420 3390</td>
<td>3210 3210</td>
<td>1500 1300</td>
<td>1385 840</td>
<td>1640 1640</td>
<td>840 1640</td>
<td>1500 1385</td>
<td>840 1640</td>
<td>840 1640</td>
<td>840 1640</td>
</tr>
<tr>
<td>$\text{Ph}_3\text{Sn(Phthc)}$</td>
<td>3410 3380</td>
<td>3200 3150</td>
<td>1555 1385</td>
<td>770 1650</td>
<td>600 384</td>
<td>354 1005</td>
<td>980</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Bu}_2\text{Sn(Phthc)}_2$</td>
<td>3400 3364</td>
<td>3180 3140</td>
<td>1560 1390</td>
<td>760 1645</td>
<td>590 370</td>
<td>360 1000</td>
<td>980</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HEtOPhthc</td>
<td>3400 3380</td>
<td>3220 3370</td>
<td>1520 1300</td>
<td>810 1610</td>
<td>1500 1385</td>
<td>840 1640</td>
<td>1500 1385</td>
<td>840 1640</td>
<td>1500 1385</td>
<td>840 1640</td>
</tr>
<tr>
<td>$\text{Ph}_3\text{Sn(EtOPhthc)}$</td>
<td>3390 3370</td>
<td>3210 3210</td>
<td>1570 1365</td>
<td>720 1605</td>
<td>585 380</td>
<td>340 980</td>
<td>980</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Bu}_2\text{Sn(EtOPhthc)}_2$</td>
<td>3400 3360</td>
<td>3220 3210</td>
<td>1580 1360</td>
<td>710 1610</td>
<td>610 397</td>
<td>350 985</td>
<td>980</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>HBzthc</td>
<td>3410 3370</td>
<td>3250 3180</td>
<td>1510 1320</td>
<td>880 1600</td>
<td>600 384</td>
<td>354 1005</td>
<td>900</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ph}_3\text{Sn(Bzthc)}$</td>
<td>3400 3365</td>
<td>3240 3160</td>
<td>1535 1380</td>
<td>805 1590</td>
<td>611 390</td>
<td>310 940</td>
<td>940</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Bu}_2\text{Sn(Bzthc)}_2$</td>
<td>3400 3360</td>
<td>3250 3150</td>
<td>1540 1370</td>
<td>810 1580</td>
<td>605 380</td>
<td>315 950</td>
<td>950</td>
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</tbody>
</table>

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 cm$^{-1}$ may be tentatively assigned to $\gamma$(Sn–C), $\gamma$(Sn–N), and $\gamma$(Sn–S) modes, respectively [28].

4.2. $^1$H NMR Spectra. $^1$H NMR spectrum of the ligand HPhthc recorded in DMSO-d$_6$ exhibits D$_2$O exchangeable resonance signals at $\delta$ 9.93 (–NH–NH) and $\delta$ 2.36 (s, –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. $^{13}$C NMR Spectra. The $^{13}$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 >C=S carbon atoms. The spectra of $\text{Ph}_3\text{SnPhthc}$ and $\text{Bu}_2\text{Sn(Phthc)}_2$ indicate greater deshielding of the >C=S carbon as compared to the ligand which may arise due to the presence of –N=C–S from –HN–C=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
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 $\text{Bu}_2\text{Sn}($EtOPhtc$)_2$ 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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**References**


