Unsymmetrically substituted organotin (IV) N-alkyl, N-hydroxyethyl dithiocarbamates: Synthesis and spectral aspects

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Received 5 December 2006; revised 28 May 2007

Unsymmetrically substituted triphenyltin(IV) N-alkyl, N-hydroxyethyl dithiocarbamates, [(C₆H₅)₃Sn(S)CN(R)CH₂CH₂OH] [R=CH₃ (1), C₂H₅ (2)], diphenyltin(IV) bis(N-alkyl, N-hydroxyethyl dithiocarbamates), [(C₆H₅)₂Sn(S)CN(R)-CH₂CH₂OH]₂, [R=CH₃ (3), C₂H₅ (4)] and chlorodiphenyltin(IV) N-alkyl, N-hydroxyethyl dithiocarbamates, [(C₆H₅)₂Sn(Cl)S(S)CN(R)CH₂CH₂OH] [R=CH₃ (5), C₂H₅ (6)] have been synthesized and characterized on the basis of elemental analysis and spectral data (FAB mass, UV, IR, ¹H, ¹³C and ¹¹⁹Sn NMR). The Sn atom exhibits 5- and 6-coordination in the complexes.

IPC Code: Int. Cl.8 C07F7/22

Due to wide applicability of sulphur bearing ligands in biological and industrial field, a lot of literature is available on the dithiocarbamate complexes of transition and non-transition metals. Various reports have appeared on symmetrically substituted organotin(IV) dithiocarbamates. Although complexes of unsymmetrically substituted organotin(IV) dithiocarbamate are known, no complexes of organotin(IV) with unsymmetrically substituted N-alkyl, N-hydroxy ethyl dithiocarbamate seems to be reported so far.

In continuation of our earlier studies on the organometal dithiocomplexes, we report here the synthesis and characterization of the unsymmetrically substituted organotin (IV) N-alkyl, N-hydroxyethyl dithiocarbamates.

Experimental

Triphenyltin chloride, diphenyltin dichloride and sodium salt of N-alkyl, N-hydroxyethyl dithiocarbamates were prepared by the reported method. Dichloromethane was dried by distillation over P₂O₅ and isopropyl alcohol was purified by distillation over SnCl₂. All other solvents and reagents were obtained commercially and freshly distilled solvents after purification were used due to high sensitivity of organotin halides to air and moisture.

Molar conductances were measured on Decibel conductivity meter model DC610 using a dip type conductivity cell in dry and purified CH₃OH.

FAB mass were recorded on a JEOL SX102/DA-6000 mass spectrometer using Argon/Xenon (6 kV, 10 mA) as the FAB gas at 10 kV accelerating voltage and the spectrum was recorded at room temperature using m-nitrobenzyl alcohol as matrix. Microanalysis was carried out on Elementar Varis EL-III analyzer.

UV spectra of the compounds were recorded on a Systronics 2101 double beam spectrophotometer (200-400 nm, CH₃OH). FTIR spectra were recorded on a Shimadzu Prestige 21 (340-4000 cm⁻¹, KBr) and Bruker IFS66V spectrometer (450-4000 cm⁻¹, KBr), ¹H, ¹³C and ¹¹⁹Sn NMR were recorded using a saturated CDCl₃ solution at 300, 75.45 and 111.95 MHz, respectively on JEOL Al-300 FT NMR spectrometer. Chemical shifts were taken in ppm with respect to tetramethylsilane for ¹H and ¹³C nuclei. Dimethyltin dichloride was taken as an external reference for ¹¹⁹Sn NMR spectra and values were converted with respect to tetramethyltin.

Preparation of complexes

Triphenyltin(IV) N-methyl, N-hydroxyethyl dithiocarbamate [(C₆H₅)₃Sn(S)CN(CH₃)CH₂CH₂OH]

Anhydrous sodium salt of N-methyl, N-hydroxyethyl dithiocarbamate (0.190 g, 1.1 mmol) in 20 mL dichloromethane was added to the dichloromethane solution of triphenyltin chloride (0.385 g, 1 mmol) and stirred for 14-16 h at room temperature. It was filtered and the filtrate was concentrated under reduced pressure. A viscous mass was obtained which was recrystallized with ethanol-petroleum ether mixture (1:10, v/v) and dried in vacuo.

Diphenyltin(IV) bis(N-ethyl, N-hydroxyethyl dithiocarbamate [(C₆H₅)₂Sn(S)CN(C₂H₅)CH₂CH₂OH]₂)

Anhydrous sodium salt of N-ethyl, N-hydroxyethyl dithiocarbamate (0.546 g, 3 mmol) in dichloromethane (5 mL) was added to 25 mL of dichloromethane solution of diphenyltin dichloride (0.343 g, 1 mmol) and stirred for 14 h at 30°C. NaCl was removed by filtration and the filtrate was concentrated under reduced pressure to about 5 mL. On keeping the filtrate in deep freeze, the compound...
separated. Solid residue was recrystallized by ethanol-pet.ether mixture (1:10, v/v) and dried in vacuo.

**Chlorodiphenyltin(IV) N-methyl, N-hydroxyethyl dithiocarbamate**

\[(\text{C}_6\text{H}_5)_2\text{Sn(Cl)}\{\text{S(S)CN(CH}_3\text{)CH}_2\text{CH}_2\text{OH}\}\]

Anhydrous sodium salt of N-methyl, N-hydroxyethyl dithiocarbamate (0.190 g, 1.1 mmol) in dry ethanol (5 mL) was added to the ethanolic solution (10 mL) of diphenyltin dichloride (0.343 g, 1 mmol) and stirred for 14-16 h at room temperature. NaCl was precipitated and removed by filtration. Filtrate was concentrated under reduced pressure. A viscous mass was obtained which was washed with petroleum ether. A solid compound was obtained which was recrystallised with ethanol pet-ether mixture (1:9, v/v) and dried in vacuo.

**Results and discussion**

All the reactions were done under moisture-free dry N\(_2\) atmosphere. Diphenyl and triphenyltin derivatives of unsymmetrically substituted dithiocarbamic acid were prepared by the reaction of corresponding sodium salt with appropriate organotin halide.

\[
\text{(C}_6\text{H}_5\text{n})\text{SnCl}_{4-\text{n}} + \text{x. Na(S)CN(R)CH}_2\text{CH}_2\text{OH} \rightarrow \text{[(C}_6\text{H}_5\text{n})\text{Sn{S(S)CN(R)CH}_2\text{OH}}_\text{x}}
\]

1. \(R = \text{CH}_3, n = 3, x = 1\)
2. \(R = \text{C}_2\text{H}_5, n = 3, x = 1\)
3. \(R = \text{CH}_3, n = 2, x = 2\)
4. \(R = \text{C}_2\text{H}_5, n = 2, x = 2\)

\[
\text{[(C}_6\text{H}_5\text{)Sn(Cl)S(S)CN(R)CH}_2\text{CH}_2\text{OH}}
\]

5. \(R = \text{CH}_3\)
6. \(R = \text{C}_2\text{H}_5\)

Analytical data collected of the complexes (Table 1) agree well with 1:1 and 1:2 stoichiometry (organotin:dtc) for 1, 2, 5 and 6, and 3 and 4, respectively. These are white to coloured compounds and are soluble in common organic solvents. These are slightly affected by atmospheric oxygen, and hence stored under dry N\(_2\) atmosphere.

Molar conductances of 1-6 (1.8-4.6 \(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}\)) indicate non-electrolytic behaviour and absence of ionic species in solution.

In FAB mass spectra of \([(\text{C}_6\text{H}_5\text{)Sn{S(S)CN(CH}_3\text{)CH}_2\text{CH}_2\text{OH}}}_2]\) (3), the molecular ion peak is observed at 574 \(m/z\). The other fragmentation pattern suggested by mass spectra at \(m/z\) value 575 corresponds to M+H, 426 to M-\([\text{N(CH}_3\text{)CH}_2\text{CH}_2\text{OH}}]_2\), 420 to M-Ph\(_2\) and 154 to Ph\(_2\). These data confirm the mononmeric character and presence of 1:1 (triorganotin:dtc) stoichiometry of the complexes.

UV spectra of the complexes show a strong absorption band at 252+3 nm, which is attributed to \(\pi \rightarrow \pi^*\) transition of N=C=S. Another band at 288+1 nm belongs to the medium absorption due to \(\pi - \pi^*\) transition of S=C=S moiety. A weak absorption due to n-\(\pi^*\) transition in CS\(_2\) group appears at 315±2 nm. These data support the presence of CS\(_2\) group in the dithiocarbamate moiety.

In the IR spectra, two intense bands due to \(\nu\)(CS\(_2\)) asy and \(\nu\)(CS\(_2\)) sym appear at 1067±3 and 1016±4 cm\(^{-1}\), respectively. The low \(\Delta\nu\) value of \([\nu\text{(CS}_2\text{)asy}-\nu\text{(CS}_2\text{)sym} (-49 \text{ cm}^{-1})]\) compared to \(\Delta\nu^*\) of sodium salt of dithiocarbamate indicate that dithiocarbamate moiety is coordinated to tin in an anisobidentate fashion. The presence of a strong band in the region 1504±17 cm\(^{-1}\) is assigned \(\nu\text{C…N}\). The relatively high value for C=N suggests that dithiocarbamate moiety is linked to Sn atom in the bidentate manner.

Additional evidence for anisobidentacity of the ligand is provided by the appearance of a splitted band due to Sn-S at 445±5 cm\(^{-1}\). A medium band due to Ph-Sn stretching is observed at 563±3 cm\(^{-1}\).

**\(^1\)H, \(^{13}\)C\(^{\{1\}H}\) and \(^{119}\)Sn\(^{\{1\}H}\) NMR**

\(^1\)H NMR spectra of few representative complexes (1-3, 5, 6) are given in Table 2. Phenyl protons exhibit two multiplets at \(\delta 7.26-7.97\). \(^1\)H NMR spectra of the complexes also show characteristics signals due to CH\(_3\), N-CH\(_2\), N-CH\(_2\) and O-CH\(_2\) protons. N-CH\(_3\) and N-CH\(_2\) signals are shifted downfield (~0.3 ppm) as compared to sodium salt of N-alkyl, N-hydroxyethyl dithiocarbamates. Hydroxyl proton appears as a broad signal as expected (Table 2).

In \(^{13}\)C\(^{\{1\}H}\) spectra of complexes (1-3, 5), signals due to phenyl carbons, CH\(_3\), N-CH\(_2\), O-CH\(_2\), N-CH\(_3\) and NCS\(_2\) are found as expected (Table 2). These values support the findings of IR and \(^1\)H NMR spectra.

In \(^{119}\)Sn\(^{\{1\}H}\) NMR spectra of complex 1, \(^{119}\)Sn chemical shift is observed at (~) 122.60 ppm, which may be interpreted in terms of a penta coordinated Sn atom. However, \(^{119}\)Sn chemical shift for complex 3 is observed at higher field in comparison to 1 and a peak
NOTES

Table 1—Analytical data of organotin (IV) N-alkyl, N-hydroxyethyl dithiocarbamates

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Colour</th>
<th>M.Pt. (°C)</th>
<th>Yield (%)</th>
<th>Elemental analysis % found (calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>White</td>
<td>80</td>
<td>80</td>
<td>C 52.71 (52.82) H 4.70 (4.63) N 2.72 (2.79)</td>
</tr>
<tr>
<td>2</td>
<td>White</td>
<td>66</td>
<td>78</td>
<td>C 53.82 (53.71) H 4.95 (4.89) N 2.79 (2.72)</td>
</tr>
<tr>
<td>3</td>
<td>White</td>
<td>138</td>
<td>74</td>
<td>C 41.79 (41.89) H 4.49 (4.57) N 4.94 (4.88)</td>
</tr>
<tr>
<td>4</td>
<td>Cream</td>
<td>144</td>
<td>76</td>
<td>C 42.86 (42.93) H 4.80 (4.76) N 4.69 (4.76)</td>
</tr>
<tr>
<td>5</td>
<td>Cream</td>
<td>78</td>
<td>80</td>
<td>C 41.98 (41.90) H 3.93 (3.95) N 2.94 (3.05)</td>
</tr>
<tr>
<td>6</td>
<td>White</td>
<td>120</td>
<td>82</td>
<td>C 43.09 (43.20) H 4.32 (4.26) N 3.01 (2.96)</td>
</tr>
</tbody>
</table>

Table 2—^1H, ^13C and ^119Sn NMR spectral data (δ, ppm) of representative compounds

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Aryl protons</th>
<th>Alkyl protons</th>
<th>Aryl carbons</th>
<th>Alkyl carbons</th>
<th>^119Sn NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.26-7.71, m, 15H (C₆H₅-Sn)</td>
<td>3.48, 3H, (N-CH₃), 3.81-3.93, m, 2H, (O-CH₂), 5.1 Hz, 3.77, br, 1H, (OH)</td>
<td>141.97 (Sn-C₆H₅), 136.72 (Ar-C,o to Sn), 129.18 (Ar-C,p to Sn), 128.54 (Ar-C,m to Sn)</td>
<td>45.32 (N-CH₃), 59.97 (N-CH₂), 60.37 (O-CH₂), 197.77 (NCS₂)</td>
<td>(-) 122.60</td>
</tr>
<tr>
<td>2</td>
<td>7.34-7.61, m, 15H (C₆H₅-Sn)</td>
<td>1.30-1.31, t, 3H (CH₃), 3.84-3.93, m, 2H (O-CH₂), 4.10 Hz, 3.91, br, 1H, (OH)</td>
<td>142.18 (Sn-C₆H₅), 136.72 (Ar-C,o to Sn)</td>
<td>11.97 (CH₃), 52.53 [N-CH₂(CH₃)]</td>
<td>----</td>
</tr>
<tr>
<td>3</td>
<td>7.31-7.86, m, 10H (C₆H₅-OCH₃)</td>
<td>3.49, 3H, (N-CH₃), 3.85-3.92, m, 8H, (NCH₂+OCH₂), 3.98, br, 1H, (OH)</td>
<td>150.62 (Sn-C₆H₅), 134.28 (Sn-C₆H₅)</td>
<td>45.06 (N-CH₃), 59.81 (N-CH₂), 60.23 (O-CH₂)</td>
<td>(-) 182.22</td>
</tr>
<tr>
<td>5</td>
<td>7.27-8.06, m, 10H (C₆H₅-Sn)</td>
<td>3.42, 3H, (N-CH₃), 3.76-3.80, m, 2H (N-CH₃), 3.99-4.02, t, 2H (O-CH₂), 3.91, br, 1H, (OH)</td>
<td>141.84 (Sn-C₆H₅), 135.30 (Ar-C,o to Sn), 130.25 (Ar-C,p to Sn), 128.85 (Ar-C,m to Sn)</td>
<td>45.50 (N-CH₃), 59.94 (N-CH₂), 60.18 (O-CH₂)</td>
<td>----</td>
</tr>
<tr>
<td>6</td>
<td>7.27-7.97, m, 10H (C₆H₅-Sn)</td>
<td>1.26, t, 3H, (CH₃), 3.79-3.81, m, 4H (NCH₂+OCH₂), 3.91, 1H, (OH)</td>
<td>---- ---- ----</td>
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</tr>
</tbody>
</table>

at (-) 182.22 ppm is observed which indicates the presence of hexa coordinated tin atom. These results are consistent with the earlier reports of penta and hexa coordinated Sn atom²⁰,²¹.

The above discussions show that all the new derivatives 1, 2, 5 and 6 have trigonal bipyramidal geometry around tin atom, generated by two phenyl groups, a sulphur atom in the equatorial position and one sulphur and one phenyl/chlorine atom in the axial site²². A similar structure has been assigned to [(C₆H₅)₃Sn(S₂CN(C₄H₉)CH₃)] on the basis of single crystal analysis²⁰. But, 3 and 4 possess octahedral geometry having two phenyl groups, two sulphur atoms in the square plane and two sulphur atoms in the axial position. The proposed structure is consistent with the octahedral structure of
[(C₆H₅)₂Sn{S₂CN(C₂H₅)₂}]₂ determined by single crystal X-ray analysis.

Acknowledgement
The authors are thankful to the Director, IIT (Madras), India and the Chairman, CISC, Banaras Hindu University, Varanasi for obtaining IR and ¹H, ¹³C, ¹¹⁹Sn NMR spectra, respectively. Further, we are thankful to the Director, Central Drug Research Institute, Lucknow and the Head, SOS in Chemistry, Jiwaji University, Gwalior for microanalysis, FAB mass and IR, UV spectra, respectively.

References