SYNTHESIS AND SPECTROSCOPIC STUDY OF SOME ORGANOTIN(IV) DERIVATIVES OF BENZILMONOTHIOSEMICARBAZONE

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ABSTRACT

Some di-and triorganotin(IV) derivatives of benzilmono thiosemicarbazone (HBMTS) have been synthesised by the reactions of the corresponding di-and triorganotin(IV) chlorides with the sodium salt of benzilmono thiosemicarbazone in different molar ratios. These derivatives have been characterised by elemental analyses, molecular weights, conductivity measurements and spectral (IR, ^{1}H, ^{13}C and ^{119}Sn NMR) studies.

INTRODUCTION

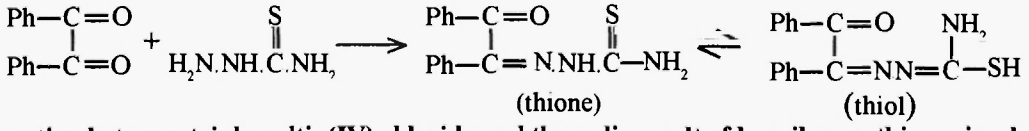
Organotin(IV) chelates with N,O and S donor ligands[1-3] have received much attention during the last few years. Thiosemicarbazones possess important antiinflammatory[4], antifungal[5] and antibacterial[6] activity and transition metal complexes containing them have been screened for medicinal properties[7]. Thiosemicarbazones containing different functional groups have been extensively studied in order to assess their ability to form complexes with many metals[8]. Moreover, they are valuable synthons for a wide variety of useful chemicals. Thus in view of the pharmacological importance of the ligand[9] and in continuation of our studies on ligand[10] and organotin(IV) derivatives,[11] we report here the syntheses and characterisation of some new organotin(IV) complexes of benzilmono thiosemicarbazone.

EXPERIMENTAL

All the reactions were carried out under an anhydrous and oxygen free nitrogen atmosphere. The solvents were purified, dried[12] and stored under nitrogen. Anal R grade chemicals were used as received for all experiments. The melting points were determined on a Toshniwal capillary melting-point apparatus and are uncorrected. Tin, sulfur and chlorine in the complexes have been determined by gravimetric, and Messenger's methods, respectively.[12] The details concerning the molar conductance measurements are similar to those reported previously.[11] Infrared and far-infrared spectra are recorded on an FTIR spectrophotometer model FTS 165, 4000-200 cm^{-1} at the Institute of Exploration and Petroleum, Dehradun. ^{1}H, ^{13}C (75 MHz, $CDCl_3$) and ^{119}Sn spectra are recorded on Bruker AC 200 MHz spectrophotometer at the National Chemical Laboratory, Pune, using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. Chemical shifts are recorded in ppm (δ) relative to TMS.

Synthesis of Benzilmonothiosemicarbazone[13] :

To the boiling solution of thiosemicarbazide (3.46g, 4 mmol) in ethanol (100ml), was added benzil (8.40g, 4 mmol) in a round bottom flask. The contents were stirred and heated for one hour. After cooling, thiosemicarbazone readily crystallised, which was filtered off and dried under reduced pressure. It was recrystallised from ethanol to give yellow coloured crystals, 10.28g (85%), m.p. 80°C. It can, in principle exhibit thione-thiol tautomerism in solution, since it contains a thioamide -HN-C=S functional group.[14] Both act as bidentate ligands, the thiol form yielding a singly charged anion with the loss of the thiol proton.
Analysis found : C, 63.24; H, 4.35; N, 14.68; S, 11.08%. Calcd for $C_{15}H_{13}N_3OS$: C, 63.60; H, 4.59; N, 14.84; S, 11.31 %.



Reaction between triphenyltin(IV) chloride and the sodium salt of benzil monothiosemicarbazone in a 1:1 molar ratio :

0.11g (4.80 mmol) of sodium metal and 15 ml of isopropanol were taken in a round bottom flask fitted with a dried and cooled water condenser and guard tube. It was refluxed for about half an hour till a clear solution of sodium isopropoxide was obtained. After cooling, 1.36g (4.80 mmol) of benzilmonothiosemicarbazone was added and the mixture was further refluxed for two hours. 1.56g, (4.80 mmol) of triphenyltin(IV) chloride was added and the mixture was further refluxed for 2 hours to ensure the

This article is dedicated to (late) Dr.R.J.Rao, School of Studies in Chemistry, Vikram University, Ujjain.

completion of the reaction. The desired product (70%) was isolated by evaporation of the solvent under reduced pressure, after filtering off the precipitated sodium chloride. The product was further purified by crystallisation from benzene-petroleum ether (40-60°) mixtures. All other organotin(IV) derivatives of benzilmonothiosemicarbazone were synthesised analogously. The pertinent data for this compound and other derivatives are listed below.

Compound 1. $Ph_3Sn[SC(NH_2)=N-N=C(Ph).COPh]$:

Yield 70%; Mol.Wt.[C(F)] : 632(644); light brown solid; M.P.143-145°C. Analysis [%F(C)] : C,62.36(62.65); H,4.02(4.27); N,6.42(6.65); Sn,18.56(18.82); S, 5.23(5.06). IR(cm^{-1}) : ν (C=O), 1660; ν (C=N), 1615; ν (Sn-S), 380; ν (Sn-N), 450; ν (NH_2), 3370, 3460. PMR (δ ppm) : 6.40-7.5, [m, 25H, (Arom.)]; 8.15; [S, 2H, (NH_2)]; ^{13}C NMR (δ ppm) : 169.46, C-1; 190.32, C-2; 133.90, C-3; 130.62, C-4;128.23, C-5; 125.23, C-6; 126.19, C-7; 129.33, C-8; 198.83, C-9; 131.27, C-3'; 130.21, C-4'; 127.15, C-5'; 126.19, C-6'; 127.14, C-7'; 128.59, C-8'; 122.46-129.47 (Sn-Ph); ^{119}SnNMR (δ ppm) : - 333.6.

Compound 2 : **$Bu_2Sn[SC(NH_2)=N-N=C(Ph)COPh]$** :

Yield 71%; Mol.Wt.[C(F)] . 572(586); brown solid; M.P 140-142°C. Analysis [%F(C)] : C,56.48(56.64); H,6.64(6.82); N,7.12(7.34); Sn,20.63(20.80); S, 5.35(5.59). IR(cm^{-1}) : ν (C=O), 1655; ν (C=N), 1625; ν (Sn-S), 390; ν (Sn-N), 445; ν (NH_2), 3380, 3470. PMR (δ ppm) : 6.35-7.80, [m, 10H (Arom.)]; 8.25; [S, 2H, (NH_2)], 1.10-1.25, [m, 18H(CH_2)], 0.85, (J=8Hz), [t, 9H,(CH_3)];^{13}C NMR (δ ppm) : 168.22, C-1; 189.67, C-2; 132.89, C-3; 131.26, C-4; 128.68, C-5; 124.21, C-6; 126.87, C-7; 129.31, C-8; 197.92, C-9; 130.81, C-3'; 131.16, C-4'; 128.07, C-5'; 126.85, C-6'; 126.97, C-7'; 129.17, C-8'; 8.68, 13.57, 26.79, 27.31 (Sn-Bu); ^{119}SnNMR(δ ppm) -239.23.

Compound 3 : $Bu_2Sn[SC(NH_2)=N-N=C(Ph)COPh]Cl$:

Yield 74%; Mol.Wt.[C(F)] : 550.50(562); brown solid; M.P 123-125°C. Analysis [%F(C)] : C,50.30(50.14); H,5.62 (5.45); N,7.42 (7.63); Sn,21.44(21.62); S, 5.66(5.81); Cl, 6.22 (6.45); IR(cm^{-1}) : ν (C=O), 1650, ν (C=N), 1625, ν (Sn-S), 385, ν (NH_2,) 3365, 3460., ν (Sn-N), 450; PMR (δ ppm) : 6.65-7.90, [m, 10H (Arom.)]; 8.10; [S, 2H, (NH_2)]; 1.30-1.45 [m,12H (CH_2)], 0.60(J=8H), [t, 6H,(CH_3)]; ^{13}C NMR (δ ppm) : 169.71, C-1; 189.79, C-2; 131.37, C-3; 131.53, C-4; 129.41, C-5; 124.48, C-6; 125.37, C-7; 128.94, C-8; 197.83, C-9; 130.72, C-3'; 130.87, C-4'; 129.23, C-5'; 126.63, C-6'; 127.27, C-7'; 129.49, C-8'; 8.80, 13.60, 27.31, 29.12 (Sn-Bu); ^{119}SnNMR (δ ppm) : -235.46.

Compound 4 : $Bu_2Sn[SC(NH_2)=N-N=C(Ph)COPh]_2$:

Yield 71%; Mol.Wt.[C(F)] : 797(804); light brown solid; M P 151-153°C. Analysis [%F(C)] : C,57.08(57.21); H,(5.27); N,10.31(10.54); Sn,14.72(14.93); S, 7.86(8.03). IR(cm^{-1}) : ν (C=O), 1665, ν (C=N), 1620, ν (Sn-S), 375, ν (NH_2), 3375, 3485., ν (Sn-N), 440. PMR (δ ppm) : 6.50-7.90, [m, 20H (Arom.)]; 8.05; [S, 4H, (NH_2)]; 0.76, (J=8Hz), [t, 6H(CH_3)]; ^{13}C NMR (δ ppm) : 169.23, C-1; 190.58, C-2; 131.97, C-3; 130.49, C-4; 129.23, C-5; 124.67, C-6; 126.43, C-7; 129.91, C-8; 197.76, C-9; 130.42, C-3'; 131.37, C-4'; 128.19, C-5'; 126.76, C-6'; 127.13, C-7'; 129.43, C-8'; 19.37, 9.11, 13.54, 27.26, 29.00 (Sn-Bu); ^{119}SnNMR (δ ppm) : - 676.16

Compound 5 $Me_2Sn[SC(NH_2)=N-N=C(Ph)COPh]Cl$:

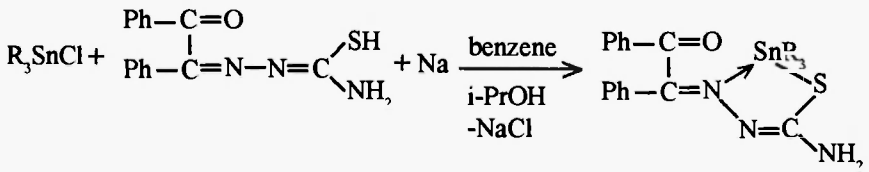
Yield 77%; Mol.Wt.[C(F)] : 466.50(476); brown solid; M.P 80-83°C. Analysis [%F(C)] : C,43.56(43.73); H, 3.68 (3.86); N,8.78(9.00); Sn,23.30(25.51); S, 6.62(6.86), Cl, 7.43 (7.61); IR(cm^{-1}) : ν (C=O), 1645, ν (C=N), 1615, ν (Sn-S), 395, ν (NH_2), 3390, 3485, ν (Sn-N), 444. PMR (δ ppm) : 6.40-7.85, [m, 10H (Arom.)]; 8.15; [S, 2H, (NH_2)]; 0.90, [S, 6H(CH_3)]; ^{13}C NMR (δ ppm) : 168.67, C-1; 190.47, C-2; 131.29, C-3; 131.89, C-4; 127.88, C-5; 124.67, C-6; 127.20, C-7; 129.81, C-8; 197.87, C-9; 131.21, C-3'; 130.86, C-4'; 128.16, C-5'; 127.53, C-6'; 126.66, C-7'; 129.72, C-8'; 6.67, (Sn-Me), ^{119}SnNMR (δ ppm) : - 232.

Compound 6 $Me_2Sn[SC(NH_2)=N-N=C(Ph)COPh]_2$:

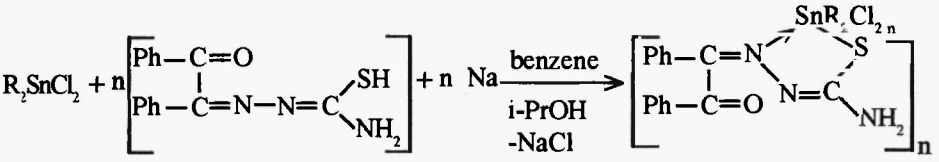
Yield 75%; Mol.Wt.[C(F)] : 713(728); brown solid; M.P 115-117°C. Analysis [%F(C)] : C,53.85(53.65); H,4.20 (4.18); N,11.61 (11.78); Sn,16.41(16.69); S, 8.92(8.91). IR(cm^{-1}) : ν (C=O), 1660, ν (C=N), 1620, ν (Sn-S), 380, ν (NH_2), 3385, 3470, ν (Sn-N), 440. PMR (δ ppm) : 6.55-7.60, [m, 20H (Arom.)]; 8.10; [S, 4H, (NH_2)]; 0.55, [S,6H,(CH_3)]; ^{13}C NMR (δ ppm) : 169.23, C-1; 190.47, C-2; 131.66, C-3; 130.75, C-4; 129.43, C-5; 124.29, C-6; 125.49, C-7; 128.69, C-8; 197.19, C-9; 130.54, C-3'; 131.29, C-4'; 129.43, C-5'; 126.47, C-6'; 128.19, C-7'; 129.69, C-8'; 6.43, (Sn-Me); ^{119}SnNMR (δ ppm) : - 642.13

RESULTS AND DISCUSSION

Triorganotin(IV) and diorganotin(IV) derivatives of benzilmonothiosemicarbazone have been synthesized by the reaction of the corresponding triorganotin(IV) and diorganotin(IV) chlorides with the conjugate base of the ligand (prepared *in situ* by the reaction of sodium isopropoxide with the ligand) in 1:1 and 1:2 molar ratios, respectively.



(Where R=Ph, **Compd.1**; R= n-Bu, **Compd.2**)



(Where, R=n-Bu, n=1, **Compd.3**; R=n-Bu, n=2, **Compd.4**; R=Me, n=1, **Compd.5**; R=Me, n=2, **Compd.6**)

All these new complexes have been prepared by refluxing the reactants in dry benzene for about 3-4 hours to ensure the completion of the reaction. Intermolecular nucleophilic substitution with elimination of chloride ion leads to the formation of the products. All these derivatives are brown crystalline solids which are further purified by crystallization from benzene-petroleum ether (40-60°C) mixtures. All these compounds are more or less soluble in common organic and coordinating solvents like $CHCl_3$, CCl_4, C_6H_6, DMF and DMSO etc. Conductance measurements in DMF have been made at room temperature using a Digisum Electronic conductivity bridge. Molar conductance values (< 40 ohm^{-1} cm^2 mole^{-1}) reveal the non electrolytic[15] nature of the complexes. Molecular weight determination in chloroform solution shows the monomeric nature of these complexes.

IR Spectral Data :

The IR spectrum of the ligand shows a broad band in the region 3320-2950 cm^{-1} due to ν(NH) and two strong bands due to ν_{as} and ν_s of NH_2 in the 3490-3350 cm^{-1} region[16]. Strong bands at 1660 cm^{-1} of ν(C=O) and at Ca. 1050 ± 10 cm^{-1} of ν(C=S) are observed. In the IR spectrum of the ligand in solution, bands due to ν(C=S) and ν(NH), which are observed in the IR spectrum in KBr optics, do not appear. This may be attributed to the existence of an tautomeric forms[17], viz. a thione form in the solid state and thiol form in solution, which is further confirmed by ν(S-H) band at 2570 cm^{-1} is absent in the IR spectrum in KBr optics, but ν(NH) at Ca.3135 cm^{-1} is present. This result finds support further from the fact that new bands appear at Ca.1660, 1550 and 780 cm^{-1} in the complexes due to ν(N=C-S), ν(C=N-N=C) and ν(C-S) vibrations, respectively[18]. A band at 2570 cm^{-1} attributable to ν(S-H) does not appear in the complexes and a new band in the region 395-370 cm^{-1}, ν(Sn-S) appears indicating to the formation of Tin-Sulfur bond[19,20]. A strong band at 1600 cm^{-1} assignable to ν(C=N) (in ligand), gets shifted to the higher frequency side (Ca.1620 cm^{-1}) in the spectra of complexes on coordination through azomethine nitrogen, which may be due to an increase in the bond order of C=N,[21] which is further supported by the presence of a new band in the far IR spectra of the complexes, at Ca.437±17 cm^{-1}, which may be assigned to Sn-N.[22] A strong band at 1660 cm^{-1} ν(C=O) and two bands in the region 3490-3350 cm^{-1} $\nu(NH_2)$ in the spectrum of the ligand, remain unaltered in the spectra of all the complexes and thus clearly indicating the non-involvement of carbonyl and NH_2 group in coordination.[23]

NMR Spectral Data :

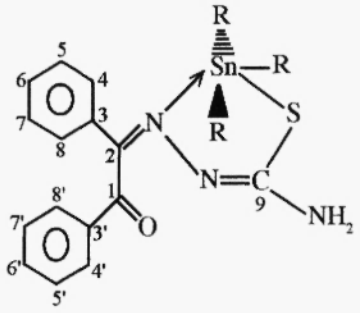
The ^{1}H NMR spectrum of HBMTC shows signals at δ 9.94, 8.21 and 7.85- 6.50 ppm downfield from TMS, assigned to the SH, NH_2 and phenyl protons, respectively[24]. The chemical shifts of SH and NH_2 protons are concentration dependent and are shifted to lower δ values in dilute solutions. The SH signal is absent in the spectra of complexes, confirming deprotonation and its subsequent involvement in coordination. Since ^{32}S is non-magnetic, no coupling with this nucleus is observed. The resonance due to the phenyl moiety remains almost unaffected in the complexes. The protons of the butyl groups appear in the range of δ 0.55-1.45 ppm. The methyl protons of the dimethyltin(IV) derivatives appear as a sharp singlet at δ 0.95 ppm with ^2J (^{119}Sn-^{1}H) = 87 ± 1 Hz and multiplets for butyl and phenyl protons. The magnitude of ^2J (^{119}Sn - ^{1}H) = 85± 7 for other complexes have been observed. The magnitude of ^2J (^{119}Sn-^{1}H) (87 ± 1Hz) is indicative of higher coordination number (>4) of tin in these complexes,[25] suggesting the bidentate behaviour of the ligand.

The ^{13}C NMR data are given in the experimental section. The ^{13}C {^{1}H} NMR resonances are assigned by comparison with the ^{13}C NMR shifts of the ligand and the complexes of organotin(IV). The R groups attached to tin display single resonance for chemically equivalent carbons, however, the butyl compounds display three resonances (resonances for two carbons being overlapped). The tin-carbon couplings ^1J (^{119}Sn-

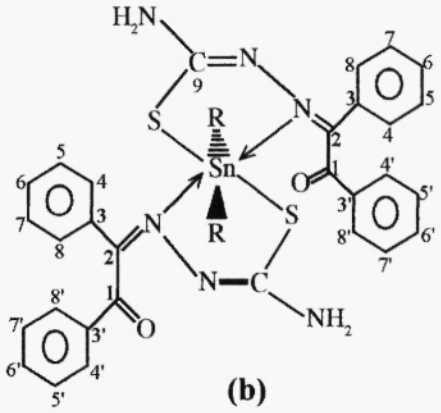
^{13}C) 625-700 Hz for five coordinate tin and 976-978 Hz for six coordinate Tin have been observed. The absolute $J(^{119}Sn - ^{13}C)$ values in alkyltin groups usually decrease as $^1J > ^3J > ^2J > ^4J$. These are comparable to the corresponding five and six coordinate organotin(IV) derivatives.[26] ^1H and ^{13}C data suggest bidentate behaviour of the ligand.

The ^{119}Sn NMR chemical shifts of all the derivatives have been observed and occur in the range of five and six- coordinate organotin(IV) compounds.[27,28] These ^{119}Sn NMR chemical shifts of triphenyltin(IV)[1] and tributyltin(IV)[2], mixed chlorodibutyltin(IV)[3] and mixed chloro-dimethyltin(IV)[5] derivatives suggest that these compounds contain five- coordinate tin, whereas dimethyl[6] and dibutyltin(IV)[4] derivatives contain six-coordinate tin.

Thus based on the above studies, five coordinate (a) and six coordinate (b) structures may be tentatively proposed for triorganotin(IV) and diorganotin(IV) derivatives of ligand, respectively.



(a)



(b)

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