SOME MIXED LIGAND COMPLEXES OF TIN(II) DERIVED FROM HETEROCYCLIC β-DIKETONES AND THE OXIME OF ACETYL THIOPHENE: SYNTHETIC STRATEGY AND STRUCTURAL FEATURES

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Abstract

Mixed ligand tin(II) complexes of the composition SnLL' have been synthesised by the interaction of ClSnL (where LH=RCO$\overline{\text{C:C(OH)N(C}_6\text{H}_5\text{)N:C}}CH_3$ & R=-CH$_3$,-C$_2$H$_5$, -C$_6$H$_5$ and -p-ClC$_6$H$_4$) and L'Na (where L'H = [(CH$_3$)C:(NOH)$\overline{\text{C:C(H)C(H):C(H)S}}$]. ClSnL in turn was prepared by the ligand redistribution reaction between SnL$_2$ and anhydrous SnCl$_2$. These reactions have been carried out in THF solution under N$_2$ atmosphere and anhydrous conditions and the resulting complexes ClSnL and SnLL' are characterised by physico-chemical and spectral studies.

Introduction

Tin complexes of composition SnL$_2$ have been cited in the literature mainly due to their structural features and stereochemical considerations. In contrast to the SnL$_2$ complexes, the literature available on the chemistry of mixed ligand complexes, SnLL',[1-4] is rather scanty. In continuation to our work on the metal complexes of group IV elements with heterocyclic ß- diketones,[5-8] we are reporting the synthesis, characterisation and structural features of two new classes of complexes viz ClSnL and SnLL' in the present communication.

Results and Discussion

The complexes ClSnL have been synthesised by the following redistribution reaction in dry THF solution under nitrogen atmosphere.

$$\mathrm{SnCl_2 + SnL_2 \xrightarrow[N_2 atm.,]{THF} 2ClSnL}$$

Mono(chloro)(pyrazolonato) tin(II) complexes i.e. ClSnL thus obtained by the ligand exchange reactions are found to be pale yellow to brown solids, soluble in $CHCl_3$ and THF but insoluble in benzene, n-hexane etc. These complexes were recrystallised by chloroform -pet. ether mixture. Molecular weights were determined osmometrically in chloroform solution.

These complexes were subjected to further reaction with the monosodium salt of oxime of acetylthiophene in THF solution under N_2 atmosphere in 1:1 molar ratio.

$$\mathrm{ClSnL + NaL'} \xrightarrow[N_2\ \mathrm{atm.,}]{\mathrm{THF}} \mathrm{SnLL' + NaCl}\downarrow$$

Sodium chloride formed during the reaction was filtered off. After stripping off the volatile fraction from the filtrate under reduced pressure, yellow to brown coloured crystalline solids having sharp melting points and soluble in common organic solvents are obtained. These mixed ligand complexes are recrystallised from chloroform- pet. ether mixture. The osmometric molecular weight measurements in $CHCl_3$ solution at 45°C reveals their monomeric nature.

Spectral data and Structure

IR and NMR(^1H, ^{13}C and ^{119}Sn) spectral studies of the complexes ClSnL and SnLL' were carried out to obtain the structural information. The salient features of these studies have been described and discussed under specific headings.

I.R. data

On comparing the IR spectra of the complexes ClSnL and SnLL' with protonated form of the ligands, the bands observed at 620±25cm^{-1} and 435±20 cm^{-1} may be assigned to νSn-O [1,9]. In free protonated ligands[7], $>$C=O group of pyrazolone moiety is observed at ~1545cm^{-1}. This particular band is shifted from its original position to lower wave number i.e. 1525-1520 cm^{-1} indicating the coordination of the carbonyl oxygen to the central tin atom in the complexes. Two bands observed at 1590±5cm^{-1} and 1570±5cm^{-1} have been assigned to νC_6H_5 and νC=N/C=C, respectively[7]. No significant shift in the position of these bands is observed. Two absorption bands observed in the region 350±30cm^{-1} may be assigned to νSn-Cl[10-13]. Further, in mixed ligand complexes, the appearance of a band at 410±20 cm^{-1} may be assigned to νSn-S [11,12,14,15].

^{1}H NMR

The observed ^{1}H NMR data of the two classes of componds ClSnL and SnLL' have been summarised in experimental part. In the spectra of ClSnL, ring methyl protons are observed at 2.12±0.53 ppm and ring phenyl as well as terminal $-C_6H_5/p-ClC_6H_4$ protons are observed at 7.07-7.95 ppm as complex patterns. Acetyl protons in $CH_3CO\overline{C:C(OH)N(C_6H_5)N:C}CH_3$ derivatives are observed at 2.32±0.09 ppm as singlet and propionyl protons in $C_2H_5CO\overline{C:C(OH)N(C_6H_5)N:C}CH_3$ derivatives as a triplet at ~1.21 and a quartet at 2.70±0.15ppm, respectively.

In SnLL' complexes, the free -OH group which was observed in ligand at ~9.00 ppm as a broad signal has been found to be absent. It suggests the deprotonation of $>$C=N-OH proton. Ring methyl protons observed at 2.04± 0.21 ppm show a downfield shift. Doublet for $-CH_3$ protons observed at ~2.33 ppm in free ligand (L'H) is merged and appears as a broad singlet at 2.25± 0.02 ppm in SnLL' type complexes. Ring phenyl, terminal $-C_6H_5$ /-p-ClC_6H_4 and protons of thiophene ring are merged together and are observed as complex pattern in the region 6.91-8.12 ppm.

^{13}C NMR

The observed ^{13}C NMR spectral data are in agreement with those of ^{1}H NMR data. ^{13}C NMR signals for different carbon atoms are observed at their usual positions. Two ^{13}C signals are observed in ligand moiety i.e. in oxime of acetyl thiophene corresponding to $-CH_3$ carbon atom but in SnLL'complexes only one carbon signal is observed. The fact that the oxime shows two lines for the $CH_3-\overset{|}{C}=N-$ is obviously due to the fact that E and Z isomers are possible for the free oxime but for the complexes only E isomer is possible. However, an upfield shift in the position of C_6' carbon signal indicates the bonding through oxygen atom of $>$C=N–OH group. Carbon atoms of phenyl ring, terminal $-C_6H_5$ / -p-ClC_6H_4 and thiophene ring are observed in the range 120.4 to 149.5 ppm.

^{119}Sn NMR

^{119}Sn NMR spectra of the two classes of complexes ClSnL and SnLL' have been recorded and the observed chemical shift data have been summarised as follows.

	Compound	Chemical shift in δ ppm
(1)	ClSn[OPPMA]	-474.78(THF)
(2)	ClSn[OPPMP]	-471.82(THF)
(3)	ClSn[OPPMB]	-392.02($CHCl_3$)

(4)	(OxAT)Sn[OPPMA]	-726.58($CHCl_3$)
(5)	(OxAT)Sn[OPPMP]	-723.80($CHCl_3$)
(6)	(OxAT)Sn[OPPMB]	-756.11($CHCl_3$)
(7)	(OxAT)Sn[OPPMC]	-792.23(THF)

^{119}Sn NMR chemical shift in ClSnL type of complexes are observed in the range -392.02 to -474.78 ppm, whereas in SnLL' type complexes the chemical shifts are observed in the range -723.80 to -792.23 ppm. The molecular weight measurement indicates that ClSnL type complexes have the following dynamic equilibrium between monomeric and dimeric state (Fig. I).

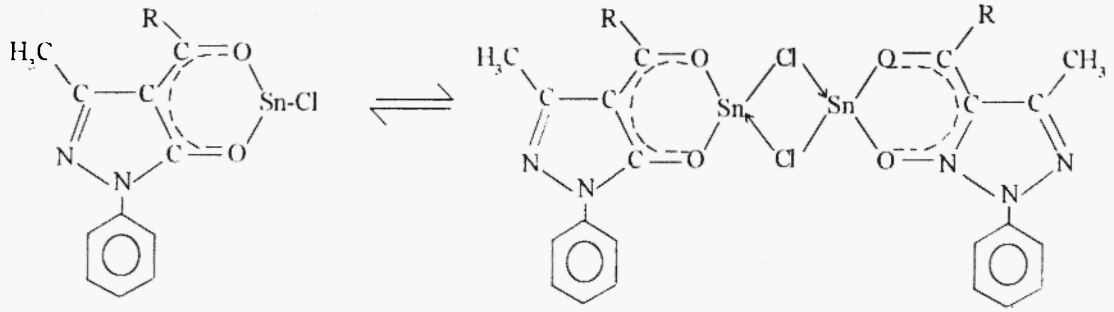

Fig. I

where R=$-CH_3$, $-C_2H_5$, $-C_6H_5$ and -p-ClC_6H_4

The appearance of two absorption bands in the region 350± 30cm^{-1} in the IR spectra of these complexes which have been assigned to νSn-Cl[10-13] also provide additional support for the presence of chlorine in two different environment i.e., bridging and terminal. ^{1}H and ^{13}C NMR signals are observed on expected positions and do not provide any support for the proposed dynamic equilibrium.

Mixed ligand complexes SnLL' are found to be monomeric in nature and may be assigned the following structure (Fig. II).

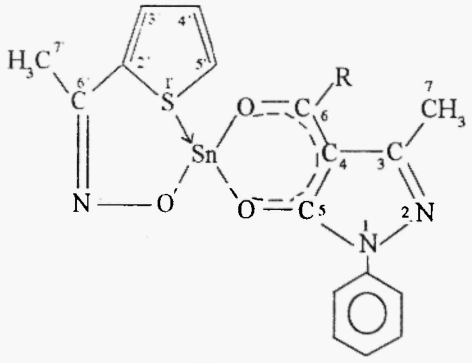

Fig. II

where R=$-CH_3$, $-C_2H_5$, $-C_6H_5$ and -p-ClC_6H_4

The bonding of sulphur atom of thiophene ring with central tin atom has been supported by the appearance of νSn-S absorption band at 410±20 cm^{-1} [11,12,14,15]. Similar structure has earlier been proposed for some mixed ligand tin (II) complexes derived from monofunctional bidentate ligands and the observed ^1H and ^{13}C NMR shift values are in close agreement with the earlier reported data. [16,17]

Experimental Section

Tin(II) chloride dihydrate ($SnCl_2.2H_2O$)(BDH) was treated with acetic anhydride to obtain anhydrous tin (II) chloride. Reactions were carried out under anhydrous conditions in N_2 atmosphere. All the solvents used were dried by standard methods. Heterocyclic ß-diketones were prepared by the procedure reported by Jensen[18] and the oxime of acetyl thiophene was prepared by standard method[19]. Tin was estimated as tin(IV) oxide[19]. Melting points were determined in sealed capillaries. A Knauer vapour pressure osmometer was used to determine the molecular weights in $CHCl_3$ solution at 45°C. IR spectra were recorded in the range 4000-200 cm^{-1} on FT-IR spectrophotometer using CsI pellets. NMR(^1H,^{13}C, ^{119}Sn) spectra were recorded on Jeol FX-90Q spectrometer in $CDCl_3$ and $CHCl_3$ solution using TMS and tetramethyltin as standard references, respectively.

Since the preparation follows same procedure, one representative reaction of each class of compounds i.e. ClSnL & SnLL' is described in detail.

Preparation of ClSnL

Mono(chloro)[4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-onato]tin(II), $ClSn[(C_6H_5)CO\overline{C{:}CON(C_6H_5)N{:}C}CH_3]$

A THF solution of anhydrous $SnCl_2$(3.98 mmol)was added dropwise to THF solution of bis[4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-onato]tin(II) (3.98 mmol), under N_2 atmosphere. The reaction mixture was stirred and refluxed for ~4 hours. The solvent in excess was stripped off from the reaction mixture under reduced pressure at the room temperature and a yellow coloured solid was obtained which was recrystallised from $CHCl_3$-pet. ether mixture in ~68% yield.

Synthesis of SnLL'

$[RCO\overline{C{:}CON(C_6H_5)N{:}C}CH_3]Sn[(CH_3)C{:}(NO)\overline{C{:}C(H)C(H){:}C(H)S}]$

A THF solution of the oxime of acetyl thiophene (1.54 mmol) was added to a solution of sodium methoxide (obtained by dissolving 1.54mmol of sodium in ~5ml of methanol) and was refluxed for ~4 hours. In the above solution, a THF solution of ClSnL (1.54 mmol) was added dropwise and the reaction mixture was refluxed for ~5 hours. The precipitated NaCl was removed by filtration and the solvent in excess was removed from the filtrate by evaporating under reduced pressure. A yellow coloured solid product was obtained and was recrystallised from chloroform-pet. ether mixture in ~76% yield.

The synthetic, analytical and spectral data of these mixed ligand complexes along with other analogous complexes are summarised below.

AMPPOH: Colour - yellow; m.pt. 62 °C; Mol. wt. found (calcd.) 206 (216.2); ^{1}H NMR ($CDCl_3$ in δ ppm) 10.85 bs (1H, -OH), 2.51 s (3H, $-CH_3$), 6.99-8.04 m (5H, $-C_6H_5$), 2.41 s (3H, $-CH_3$); ^{13}C NMR ($CHCl_3$ in δ ppm) 15.4 (C_7), 137.1 (C_3), 104.1 (C_4), 160.4 (C_5), 196.2 (C_6), 26.2 ($-CH_3$), 120.4-147.0 ($-C_6H_5$).

PMPPOH: Colour - brown; m. pt. 48 °C; Mol. wt. found (calcd.) 222 (230.0); ^{1}H NMR ($CDCl_3$ in δ ppm) 11.57 bs (1H, -OH), 2.65 s (3H, $-CH_3$), 7.10 - 7.95 m (5H, $-C_6H_5$), 2.85 q (2H, $-CH_2$), 1.23 t (3H, $-CH_3$); ^{13}C NMR ($CHCl_3$ in δ ppm) 15.9 (C_7), 137.4 (C_3), 103.4 (C_4), 160.4 (C_5), 198.0 (C_6), 8.4 ($-CH_3$), 32.6 (CH_2), 120.8-147.0 ($-C_6H_5$).

BMPPOH: Colour - yellow crystalline; m. pt. 92 °C; Mol. wt. found (calcd.) 292 (278.1); ^{1}H NMR ($CDCl_3$ in δ ppm) 12.05 bs (-1H, -OH), 2.10 s (3H, $-CH_3$), 7.10-8.04 m (10H, $-C_6H_5$); ^{13}C NMR ($CHCl_3$ in δ ppm) 15.7 (C_7), 137.5 (C_3), 103.6 (C_4), 161.5 (C_5), 191.5 (C_6), 120.6-147.9 ($-C_6H_5$).

CMPPOH: Colour - yellow crystalline; m. pt. 118 °C; Mol. wt. found (calcd.) 310 (312.0); ^{1}H NMR ($CDCl_3$ in δ ppm) 12.35 bs (1H, -OH), 2.10 s (3H, $-CH_3$); 7.15-8.00 m (9H, $-C_6H_5/-C_6H_4$); ^{13}C NMR ($CHCl_3$ in δ ppm) 15.8 (C_7), 138.1 (C_3), 103.5 (C_4), 161.1 (C_5), 190.9 (C_6), 120.8-147.6 ($-C_6H_5/-C_6H_4$).

HOxAT: Colour - Shiny white; m. pt. 88 °C; Mol. wt. found (calcd.) 140.0 (141.19); ^{1}H NMR ($CDCl_3$ in δ ppm) 9.00 bs (^{1}H, =NOH), 2.33 d (3H, $-CH_3$), 6.59-7.71 m (3H, $-C_4H_3S$); ^{13}C NMR ($CHCl_3$ in δ ppm) 12.4, 19.5 (C_7'), 151.6, 140.0 (C_6'), 129.8, 130.9 (C_2'), 125.5, 126.4 (C_3'), 126.7, 127.0 (C_5') 126.4, 125.5 (C_4').

ClSn[OPPMA]: Colour - brown crystalline; m. pt. 200 °C; Mol. wt. found (calcd.) 565.0 (369.37); %Sn found (calcd.) 32.10 (32.13); % Cl found (calcd.) 9.58 (9.59); ^{1}H NMR ($CDCl_3$ in δ ppm) 2.49 s (3H, $-CH_3$), 7.15-8.04 m (5H, $-C_6H_5$), 2.41 s (3H, $-CH_3$); ^{13}C NMR (THF in δ ppm) 16.8 (C_7), 139.2 (C_3), 105.9 (C_4), 160.8 (C_5), 193.9 (C_6), 25.3 ($-CH_3$), 121.2-149.2 ($-C_6H_5$); ^{119}Sn NMR (THF in δ ppm) -474.78.

ClSn[OPPMP]: Colour - brown crystalline; m. pt. 158 °C; Mol. wt. found (calcd.) 553.0 (383.40); % Sn found (calcd.) 30.92 (30.95); % Cl found (calcd.) 9.20 (9.25); ^{1}H NMR ($\mathrm{CDCl_3}$ in δ ppm) 2.49s (3H, -$\mathrm{CH_3}$), 7.15-7.70m (5H, -$\mathrm{C_6H_5}$). 2.81q (2H, -$\mathrm{CH_2}$), 1.20t (3H, -$\mathrm{CH_3}$); ^{13}C NMR (THF in δ ppm) 17.7 (C_7), 140.0 (C_3), 105.9 (C_4). 161.6 (C_5), 198.1 (C_6), 9.6 (-$\mathrm{CH_3}$), 33.6 (-$\mathrm{CH_2}$), 122.0 - 149.4 (-$\mathrm{C_6H_5}$); ^{119}Sn NMR (THF in δ ppm) -471.82.

ClSn[OPPMB]: Colour -yellow; m. pt. 152 °C; Mol. wt. found (calcd.) 646.0 (431.45); %Sn found (calcd.) 27.50 (27.51); % Cl found (calcd.) 8.22 (8.22); ^{1}H NMR ($\mathrm{CDCl_3}$ in δ ppm) 1.76s (3H, -$\mathrm{CH_3}$), 7.07 - 8.04m (10H, -$\mathrm{C_6H_5}$); ^{13}C NMR ($\mathrm{CHCl_3}$ in δ ppm) 16.2 (C_7), 137.5 (C_3), 105.4 (C_4), 162.2 (C_5), 190.7 (C_6), 121.4 - 149.5 (-$\mathrm{C_6H_5}$); ^{119}Sn NMR ($\mathrm{CHCl_3}$ in δ ppm) -392.02.

ClSn[OPPMC]: Colour- yellow; m. pt. 230 °C; Mol. wt. found (calcd.) 690.0 (465.89); % Sn found (calcd.) 25.45 (25.48); ^{1}H NMR ($\mathrm{CDCl_3}$ in δ ppm) 1.60 (3H. -$\mathrm{CH_3}$), 7.15 - 7.95 (9H, -$\mathrm{C_6H_5}$/-$\mathrm{C_6H_4}$).

[OxAT]Sn[OPPMA]: Colour - brown; m. pt. 72 °C Mol. wt. found (calcd.) 520.0 (474.11); % Sn found (calcd.) 25.00 (25.03); NaCl found (calcd.) 0.32 (0.34); ^{1}H NMR ($\mathrm{CDCl_3}$ in δ ppm) 2.27 bs (3H. -$\mathrm{CH_3}$). 2.14s (3H, -$\mathrm{CH_3}$); 6.97 - 7.95m (8H. - $\mathrm{C_4H_3S}$/-$\mathrm{C_6H_5}$), 2.23s (3H, -$\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CHCl_3}$ in δ ppm) 16.5 (C_7), 137.7 (C_3), 104.9 (C_4). 160.4 (C_5), 193.5 (C_6), 27.3 (-$\mathrm{CH_3}$), 12.0 (C_7'), 120.9 - 150.9 (-$\mathrm{C_6H_5}$/-$\mathrm{C_4H_3S}$); ^{119}Sn NMR ($\mathrm{CHCl_3}$ in δ ppm) -726.58.

[OxAT]Sn[OPPMP]: Colour - brown; m. pt. 110-112 °C; Mol. wt. found (calcd.) 532.0 (488.13); % Sn found (calcd.) 24.30 (24.32); NaCl found (calcd.) 0.16 (0.16); ^{1}H NMR ($\mathrm{CDCl_3}$ in δ ppm) 2.25bs (3H, -$\mathrm{CH_3}$), 2.25bs (3H, -$\mathrm{CH_3}$), 6.95 - 7.95m (8H, -$\mathrm{C_4H_3S}$/-$\mathrm{C_6H_5}$), 2.57q (2H, -$\mathrm{CH_2}$), 1.20t (3H, -$\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CHCl_3}$ in δ ppm) 16.9 (C_7), 137.9 (C_3), 104.3 (C_4), 162.4 (C_5), 197.0 (C_6), 8.6 (-$\mathrm{CH_3}$). 32.5 (-$\mathrm{CH_2}$), 12.2 (C_7'), 121.0 - 150.4 (-$\mathrm{C_6H_5}$/-$\mathrm{C_4H_3S}$); ^{119}Sn NMR ($\mathrm{CHCl_3}$ in δ ppm) -723.80.

[OxAT]Sn[OPPMB]: Colour - yellow; m. pt. 172 °C; Mol. wt. found (calcd.) 568.0 (536.18); % Sn found (calcd.) 22.12 (22.13); NaCl found (calcd.) 0.085 (0.087); ^{1}H NMR ($\mathrm{CDCl_3}$ in δ ppm) 2.25bs (3H, -$\mathrm{CH_3}$), 1.60s (3H, -$\mathrm{CH_3}$), 6.91-7.95m (13H, -$\mathrm{C_6H_5}$/-$\mathrm{C_4H_3S}$); ^{119}Sn NMR ($\mathrm{CHCl_3}$ in δ ppm) -756.11.

[OxAT]Sn[OPPMC]: Colour - yellow; m. pt. 175 °C; Mol. wt. found (calcd.) 579.0 (570.62); % Sn found (calcd.) 20.80 (20.80); NaCl found (calcd.) 0.095 (0.098); ^{1}H NMR ($\mathrm{CDCl_3}$ in δ ppm) 2.23bs (3H, -$\mathrm{CH_3}$), 1.83s (3H, -$\mathrm{CH_3}$), 6.92 - 7.95m (12H, -$\mathrm{C_6H_5}$/-$\mathrm{C_6H_4}$/-$\mathrm{C_4H_3S}$); ^{13}C NMR (THF in δ ppm) 16.2 (C_7), 134.7 (C_3), 104.1 (C_4), 165.7 (C_5), 187.9 (C_6), 10.4 (C_7') 118.4 - 149.6 (-$\mathrm{C_6H_5}$/-$\mathrm{C_6H_4}$/-$\mathrm{C_4H_3S}$); ^{119}Sn NMR (THF in δ ppm) -792.23.

Where

s=singlet, bs=broad singlet, d=doublet, t=triplet, q=quartet, m=complex pattern

HOxAT = $[(CH_3)C{:}(NOH)\overline{C{:}C(H)C(H){:}C(H)S}]$

AMPPOH=$CH_3CO\overline{C{:}C(OH)N(C_6H_5)N{:}C}CH_3$, PMPPOH=$C_2H_5CO\overline{C{:}C(OH)N(C_6H_5)N{:}C}CH_3$

BMPPOH= $C_6H_5CO\overline{C{:}C(OH)N(C_6H_5)N{:}C}CH_3$, CMPPOH=$ClC_6H_4CO\overline{C{:}C(OH)N(C_6H_5)N{:}C}CH_3$;

C_6H_5/C_6H_4Cl & proton of thiophene ring merged with ring phenyl protons and observed as complex pattern.

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