Synthetic Pathway, Structural Chemistry and Structural Elucidation Based Upon Spectral Studies [IR, NMR (^{1}H, ^{13}C and ^{119}Sn)] of Some Mixed Ligand Complexes of Diorganotin (IV) Derived from Sterically Demanding Heterocyclic β-Diketones and N-Protected Amino Acids.

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ABSTRACT

A series of new mixed ligand diorganotin (IV) complexes of general formula Bu_2SnLA [where LH = RCOC:C(OH)N(C_6H_5)N:CCH$_3$; R = -C_6H_5, -C_2H_5, -CH_3 and AH = C(O)C_6H_4C(O)NCHR'COOH; R' = -H, -CH_3, -$CH(CH_3)_2$, -$CH_2C_6H_5$, -CHR' = -CH_2CH_2- was synthesized by the interaction of dibutyltin (IV) dichloride with the corresponding ligands in the presence of triethylamine in 1:1:1:2 molar ratios in dry refluxing benzene solution. The plausible structures of these newly synthesized complexes have been proposed on the basis of physico-chemical and spectral studies. The central tin atom is bonded by heterocyclic β-diketone and N-protected amino acid ligands. The ^{119}Sn NMR spectral studies of some of these complexes reveal the presence of hexacoordinated tin centres in these complexes.

INTRODUCTION

The chemistry of organotin (IV) complexes derived from various organic ligands such as Schiff bases /1,2/, β-diketones /3/, dithiocarbazates /4/, mono and dithiophosphates /5,6/, dipeptides /7/, semi- and thiosemicarbazones /8/, N-protected amino acids /9,10/ and oximes /11,12/ has been extensively studied during the last few decades. There has been continuous interest in the chemistry of organotin (IV) complexes /13-16/ and the studies on organotin (IV) complexes are mainly concerned with their synthetic and structural aspects. The modern physical techniques may be applied for the study of the structural aspects of organotin(IV) complexes.

The organotin(IV) complexes exhibit significant biological activities /17-23/ and find applications as biocides /24,25/, industrial catalysts /26,27/ and polymers /28/. N-protected amino acids and sterically demanding heterocyclic β-diketones are the potential organic ligands because of their interesting bonding patterns /29-31/ and potential biological applications of their metal complexes /17,32,33/. A good deal of

work has been reported on the chemistry of complexes of these potential ligands with group IV and XIV metals /34-39/. However, the synthesis of mixed ligand complexes of dibutyltin(IV) dichloride derived from these ligands has not been cited in the literature. It was interestingly relevant to investigate the interaction of these potential organic ligands with dibutyltin(IV) dichloride, to study the comparative coordination behaviour of these ligands towards diorganotin(IV). We now report the preparation and structural considerations of some mixed ligand complexes of dibutyltin(IV) derived from these potential organic ligands in the present communication.

EXPERIMENTAL

Precautions were taken to exclude moisture throughout the experiments. Dibutyltin (IV) dichloride (Lancaster) was used after distillation (135°/10 mm). All solvents were dried by standard methods. Analytical grade chemicals were used for all experiments. Tin was estimated as tin(IV) oxide. Melting points were determined in sealed capillaries. Molecular weight measurements were carried out by determining depression in freezing point and were found to be in agreement with calculated values (Table 1). The ligands, sterically demanding heterocyclic β-diketones, have been synthesized by the procedure reported by Jensen /40/ and the other ligands, N-protected amino acids, were synthesized by the procedure reported by Sheehan /41/.

Table 1

Synthetic and Analytical Data of Diorganotin(IV) Complexes of Sterically Demanding Heterocyclic β-Diketones (LH) and N-Protected Amino Acids (AH).

S. No.	Reagents in g (mmol)				Product Formula	% Yield*	M.P. (°C)	% Sn Found (Calc.)	Mol. wt. Found (Calc.)
	Bu_2SnCl_2	LH	AH	$(C_2H_5)_3N$					
1.	0.78 (2.5)	L_1H 0.71 (2.5)	A_1H 0.53 (2.5)	0.52 (5.1)	$Bu_2SnL_1A_1$	87	100	16.55 (16.61)	701 (714.4)
2.	0.80 (2.6)	0.73 (2.6)	A_2H 0.53 (2.5)	0.53 (5.2)	$Bu_2SnL_1A_2$	91	78	16.21 (16.29)	715 (728.4)
3.	1.37 (4.5)	1.26 (4.5)	A_3H 1.12 (4.5)	0.91 (9.0)	$Bu_2SnL_1A_3$	81	67	15.60 (15.68)	756 (745.4)
4.	1.38 (4.5)	1.26 (4.5)	A_4H 1.35 (4.5)	0.92 (9.1)	$Bu_2SnL_1A_4$	78	85	14.67 (14.75)	790 (804.5)
5.	1.42 (4.6)	1.30 (4.6)	A_5H 1.03 (4.6)	0.95 (9.3)	$Bu_2SnL_1A_5$	92	72	16.20 (16.29)	718 (728.4)

Table 1 (continued)

Synthetic and Analytical Data of Diorganotin(IV) Complexes of Sterically Demanding Heterocyclic β-Diketones (LH) and N-Protected Amino Acids (AH).

6.	1.04 (3.4)	L_2H 0.79 (3.4)	A_1H 0.71 (3.4)	0.69 (6.9)	$Bu_2SnL_2A_1$	67	98	17.80 (17.81)	642 (633.3)
7.	1.31 (4.3)	0.99 (4.3)	A_2H 0.95 (4.3)	0.87 (8.6)	$Bu_2SnL_2A_2$	72	90	17.39 (17.44)	671 (680.4)
8.	1.12 (3.6)	0.85 (3.6)	A_3H 0.91 (3.6)	0.74 (7.3)	$Bu_2SnL_2A_3$	74	75	16.65 (16.75)	691 (708.4)
9.	1.51 (4.9)	1.15 (4.9)	A_4H 1.5 (4.9)	1.01 (9.9)	$Bu_2SnL_2A_4$	63	97	15.55 (15.68)	740 (756.5)
10.	1.56 (5.1)	1.18 (5.1)	A_5H 1.13 (5.1)	1.04 (10.3)	$Bu_2SnL_2A_5$	76	81	17.39 (17.44)	669 (680.4)
11.	1.06 (3.4)	L_3H 0.75 (3.4)	A_1H 0.71 (3.4)	0.70 (6.9)	$Bu_2SnL_3A_1$	85	95	18.10 (18.19)	642 (652.3)
12.	1.12 (3.6)	0.79 (3.6)	A_2H 0.81 (3.6)	0.74 (7.3)	$Bu_2SnL_3A_2$	89	81	17.72 (17.81)	656 (666.3)
13.	1.13 (3.7)	0.81 (3.7)	A_3H 0.92 (3.7)	0.75 (7.4)	$Bu_2SnL_3A_3$	90	77	17.00 (17.09)	686 (694.4)
14.	1.05 (3.4)	0.75 (3.4)	A_4H 1.02 (3.4)	0.70 (6.9)	$Bu_2SnL_3A_4$	71	92	15.95 (15.98)	735 (742.5)
15.	1.62 (5.3)	1.15 (5.3)	A_5H 1.17 (5.3)	1.08 (10.6)	$Bu_2SnL_3A_5$	67	83	17.69 (17.81)	658 (666.3)

* Yields of the recrystallised products.

Synthesis of Dibutyltin(IV) Complexes

All these derivatives are synthesized by the same procedure and, therefore, synthesis of one representative complex is described in detail and the data for the rest have been summarized in Table 1.

Ligand (L_1H), 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (0.71 g, 2.5 mmol) and another ligand (A_1H), 1,3-dihydro-1,3-dioxo-2H-isoindole-2-acetic acid (0.53 g, 2.5 mmol) were dissolved in dry benzene and were mixed with Bu_2SnCl_2 (0.78 g, 2.5 mmol) in dry benzene; immediately after this, triethylamine (0.52 g, 5.1 mmol) in dry benzene was added dropwise. The yellow brown colour of the reaction mixture changed to dark brown. No heat change was observed during the mixing of all the reactants. After refluxing this solution ~ 8-10 hrs, the precipitated triethylamine hydrochloride was filtered off. On stripping the volatile fraction under reduced pressure, a coloured product was obtained which was recrystallised from THF/Pet.-ether mixture. The physical data and analytical data of this and other complexes are given in Table 1 along with analogous complexes.

RESULTS AND DISUCUSSION

Dibutytin(IV) complexes of general formula, Bu2Sn[RCOC:C(O)N(C6H5)N:CCH3][O2CCHR'NC(O)C6H4C(O)] (where R = -C6H5, -C2H5, -CH3; R' = -H, -CH3, -CH(CH3)2, -CH2C6H5 and –CHR'= -CH2CH2- have been synthesized by the interaction of dibutyltin (IV) dichloride with sterically demanding heterocyclic β-diketones (LH) and N-protected amino acids (AH) in the presence of triethylamine in 1:1:1:2 molar ratios in refluxing benzene solution.

$$Bu_2SnCl_2 + RCOC{:}C(OH)N(C_6H_5)N{:}CCH_3 + C(O)C_6H_4C(O)NCHR'COOH + 2(C_2H_5)_3N \xrightarrow[\text{Reflux}]{C_6H_6}$$

$$Bu_2Sn[RCOC{:}C(O)N(C_6H_5)N{:}CCH_3][O_2CCHR'NC(O)C_6H_4C(O)] + 2(C_2H_5)_3N.HCl\downarrow$$

where

R = -C_6H_5,	R' = -H;	Complex 1, ($Bu_2SnL_1A_1$)
R = -C_6H_5,	R' = -CH_3;	Complex 2, ($Bu_2SnL_1A_2$)
R = -C_6H_5,	R' = -$CH(CH_3)_2$;	Complex 3, ($Bu_2SnL_1A_3$)
R = -C_6H_5,	R' = -$CH_2C_6H_5$;	Complex 4, ($Bu_2SnL_1A_4$)
R = -C_6H_5,	-CHR' = -CH_2CH_2-;	Complex 5, ($Bu_2SnL_1A_5$)
R = -C_2H_5,	R' = -H;	Complex 6, ($Bu_2SnL_2A_1$)
R = -C_2H_5,	R' = -CH_3;	Complex 7, ($Bu_2SnL_2A_2$)
R = -C_2H_5,	R' = -$CH(CH_3)_2$;	Complex 8, ($Bu_2SnL_2A_3$)
R = -C_2H_5,	R' = -$CH_2C_6H_5$;	Complex 9, ($Bu_2SnL_2A_4$)
R = -C_2H_5,	-CHR' = -CH_2CH_2-;	Complex 10, ($Bu_2SnL_2A_5$)
R = -CH_3,	R' = -H;	Complex 11, ($Bu_2SnL_3A_1$)

R = $-CH_3$,	R′ = $-CH_3$;	Complex 12, ($Bu_2SnL_3A_2$)
R = $-CH_3$,	R′ = $-CH(CH_3)_2$;	Complex 13, ($Bu_2SnL_3A_3$)
R = $-CH_3$,	R′ = $-CH_2C_6H_5$;	Complex 14, ($Bu_2SnL_3A_4$)
R = $-CH_3$	$-CHR' = -CH_2CH_2$;	Complex 15, ($Bu_2SnL_3A_5$)

After filtering off the triethylamine hydrochloride formed during the reaction and stripping off the volatile fraction, coloured solids were obtained. These derivatives were found to be soluble in common organic solvents like benzene, chloroform, THF etc. and were recrystallised from THF/Pet.-ether mixture in 63 to 92 % yields. The molecular weight measurements of these complexes show their monomeric nature. They have been further characterized by IR and NMR (^1H, ^{13}C and ^{119}Sn) spectral studies.

Spectral Studies

The plausible structures of the newly synthesized mixed ligand dibutyltin (IV) complexes derived from heterocyclic β-diketones and N-protected amino acids have been proposed on the basis of spectral studies [IR and NMR (^1H, ^{13}C and ^{119}Sn)].

IR Spectra

A comparative study of the IR spectra of these mixed ligand organotin(IV) complexes with their parent ligands provided useful information for structural elucidation of these complexes. The IR spectra of these complexes exhibit two medium intensity bands in the region 610-515 and 745-625 cm^{-1} for Sn-O bond /42/. A new band was observed at ~1520 ± 20 cm^{-1}, which may be assigned to ν(C O) stretching vibrations in the complexes. A shift of the order of ~ 35-15 cm^{-1} in the carbonyl frequency, to a lower wave number in comparison with its position in the parent ligands (~ 1545 cm^{-1}), suggests that coordination is through carbonyl oxygen and heterocyclic β-diketone is behaving as bidentate ligand. There is no significant shifting in the positions of other bands observed at ~ 1590 and 1570 cm^{-1}, which may be assigned to phenyl and ν(C=C/C=N) stretchings, respectively.

No significant shift is observed in the position of a band appearing around 1760 cm^{-1} due to $\nu CO_{(asym)}$ as compared to its position in the parent ligands, which rules out the possibility of the involvement of this group in bonding. A broad band appearing around 1700-1705 cm^{-1} due to [$\nu CO_{(sym)}$ + $\nu COO_{(asym)}$] in the IR spectra of the ligands is split into two after complexation /35,43/. The sharp band at ~ 1700 cm^{-1} and a medium intensity band at 1600-1570 cm^{-1} may be due to $\nu CO_{(sym)}$ and $\nu COO_{(asym)}$ vibrations, respectively. The lower shift of the order of 165-105 cm^{-1} in the $\nu COO_{(asym)}$ frequency [$\Delta\nu = \nu COO_{(asym)} - \nu COO_{(sym)}$] upon complexation indicates chelating nature of the carboxylate group of N-protected amino acids. This observation is in agreement with the earlier reported values /44/. The bands appearing in the region 550-427 cm^{-1} and 458-425 cm^{-1} may be attributed to Sn-C vibrations /45/

^1H NMR Spectra

The ^1H NMR spectra of these complexes have been recorded in $CDCl_3$ solution using TMS as an internal standard and are summarized in Table 2.

Table 2

^{1}H NMR data of Sterically Demanding Heterocyclic β-Diketones and N-Protected Amino Acids and their Dibutyltin(IV) Complexes (in δ ppm).

Complex No.	Ligands and complexes	RCOC:C(OH)N(C$_6$H$_5$)N:CCH$_3$ (LH)						C(O)C$_6$H$_4$C(O)NCHR'COOH (AH)					
		OH	Ring CH$_3$	Ring Phenyl	CH$_2$	Terminal CH$_3$		OH	C$_6$H$_4$ C$_6$H$_5$	CH	CH$_2$	CH$_3$	Sn-Butyl
	[a]L$_1$H	12.05 (b)	2.10 (s)	7.10-8.04 (m)	-	-	*						
	[b]A$_1$H							**	8.05-7.60 (m)	-	4.47 (s)	-	
1	Bu$_1$SnL$_1$A$_1$	-	1.96 (s)	7.03-8.24 (m)	-	-	*	-	*	-	4.43 (s)	-	2.53-0.66 (m)
	[c]A$_2$H							9.27 (s)	7.87 (m)	5.08 (q)	-	1.74 (d)	
2	Bu$_2$SnL$_1$A$_2$	-	1.80 (s)	7.1-8.2 (m)	-	-	*	-	*	4.9 (q)	-	***	2.02-0.63 (m)
	[c]A$_1$H							8.94 (s)	7.80 (m)	4.60 (d) 2.70 (st)	-	1.15 (d) 0.95 (d)	
3	Bu$_2$SnL$_1$A$_1$	-	1.93 (s)	7.1-8.2 (m)	-	-	*	-	*	4.6 (d) 2.7 (st)	-	***	2.09-0.63 (m)
	[c]A$_1$H							9.10 (s)	7.61 (m) / 7.11 (s)	5.15 (t)	3.50 (d)	-	
4	Bu$_2$SnL$_1$A$_4$	-	1.87 (s)	7.03-8.21 (m)	-	-	*	-	*	5.19 (t)	3.64 (d)	-	2.47-0.66 (m)
	[c]A$_1$H							8.80 (s)	7.76 (m)	-	2.81 (t) 4.00 (t)	-	
5	Bu$_2$SnL$_1$A$_3$	-	1.93 (s)	7.2-8.20 (m)	-	-	*	-	*	-	2.82 (t) 4.05 (t)	-	2.06-0.73 (m)
	[a]L$_1$H	11.57 (b)	2.65 (s)	7.39-8.12 (m)	2.75 (q)	1.23 (t)							
6	Bu$_2$SnL$_1$A$_1$	-	2.40 (s)	7.05-8.17 (m)	2.74 (q)	***	-	-	*	-	4.37 (s)	-	2.06-0.51 (m)
7	Bu$_1$SnL$_1$A$_2$	-	2.50 (s)	7.06-8.17 (m)	2.74 (q)	***	-	-	*	5.00 (q)	-	1.74 (d)	2.21-0.63 (m)

Table 2 continued

8	$Bu_2SnL_2A_3$	-	2.44 (s)	7.06-8.17 (m)	2.75 (q)	***	-	-	*	4.59 (d) 3.13 (m)	-	***	2.15-0.50 (m)
10	$Bu_2SnL_2A_3$	-	2.50 (s)	7.06-8.17 (m)	3.1 (q)	***	-	-	*	-	4.05 (t) 2.82 (t)	-	2.02-0.57 (m)
	^aL_3H	10.85 (b)	2.51 (s)	6.99-8.04 (m)	-	2.41 (s)							
11	$Bu_2SnL_2A_1$	-	2.51 (s)	6.97-8.17 (m)	-	2.40 (s)	-	-	*	-	4.31 (s)	-	2.18-0.60 (m)
12	$Bu_2SnL_2A_2$	-	2.44 (s)	7.03-8.21 (m)	-	2.40 (s)	-	-	*	5.00 (q)	-	***	2.06-0.53 (m)
13	$Bu_2SnL_3A_3$	-	2.40 (s)	7.03-8.21 (m)	-	2.34 (s)	-	-	*	4.53 (d) 2.72 (m)	-	***	2.09-0.34 (m)
14	$Bu_2SnL_3A_4$	-	2.44 (s)	7.03-8.21 (m)	-	2.40 (s)	-	-	*	5.19 (t)	3.57 (t)		2.05-0.47 (m)
15	$Bu_2SnL_1A_1$	-	2.50 (m)	7.03-8.21 (m)	-	2.47 (s)	-	-	*	-	4.02 (t) 2.78 (t)	-	2.06-0.53 (m)

Note : (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (st) = septet

* merged with phenyl region ; ** NH^+ signal appeared at δ 4.2 ppm ; *** merged with butyl region

a = Ref. 39 ; b = Ref. 43 ; c = Ref. 35

The ^{1}H NMR spectra display the expected signals of different types of protons present in the complexes. The butyl protons attached to tin exhibit a complex pattern in the region δ 2.58-0.34 ppm. The aromatic protons are observed as a complex pattern δ 8.24-6.97 ppm. The other ^{1}H NMR signals of heterocyclic β-diketones and N-protected amino acids, which do not show significant shifting, are summarized in Table 2.

^{13}C NMR Spectra

The ^{13}C NMR of a few representative complexes have been recorded in $CHCl_3$ and are summarized in Table 3.

These mixed ligand complexes have two organic ligands, N-protected amino acids and heterocyclic β-diketones. It is of interest to study the comparative coordination behaviour of these two organic ligands towards dibutyltin(IV). The ^{13}C NMR spectra of some of the complexes show a downfield shift of δ 2-7 ppm in the position of carboxylic carbon signal as compared to its position in the parent N-protected amino acid ligands, revealing the bidentate nature of COO group of the ligands. The delocalisation of electrons takes place during the complex formation in the heterocyclic β-diketone ligands of these complexes. The complex has a six-membered quasi aromatic ring involving C_3, C_4, C_6 and the two oxygen atoms. There is some shifting in the positions of these carbon signals due to delocalisation of electrons. The bidentate nature of heterocyclic β-diketone ligands is suggested. The ^{13}C NMR spectra of some of the complexes exhibit signals at δ 13.27-27.63 ppm, which may be attributed to the butyl carbons attached to tin.

^{119}Sn NMR Spectra

^{119}Sn NMR spectra of the mixed ligand organotin (IV) complexes of the type $Bu_2Sn[RCOC{:}C(O)N(C_6H_5)N{:}CCH_3][O_2CCHR'NC(O)C_6H_4C(O)]$, where R = $-C_6H_5$; R′ = –H, $-CH_3$, $-CH(CH_3)_2$ and $-CH_2C_6H_5$, exhibit signals in the region δ 217.49-317.33 ppm and are summarized in Table 4.

Table 4

^{119}Sn NMR data of Some Diorganotin(IV) Complexes Derived from Heterocyclic β-Diketones and N-Protected Amino Acids (in δ ppm).

Complex No.	Complex formula	Chemical shift values
1	$Bu_2SnL_1A_1$	- 217.49
2	$Bu_2SnL_1A_2$	- 317.33
3	$Bu_2SnL_1A_3$	- 219.83
4	$Bu_2SnL_1A_4$	- 224.36

^{119}Sn NMR chemical shifts have been found to be influenced by the coordination number of the tin atom /46/. ^{119}Sn NMR data support the hexa-coordinated tin centers in these complexes. The ^{119}Sn chemical shift values are consistent with the earlier reported /47/ values for hexacoordinated diorganotin (IV) complexes.

Table 3

^{13}C NMR data of Sterically Demanding Heterocyclic β-Diketone and N-Protected Amino Acids and their Dibutyltin (IV) Complexes (in δ ppm).

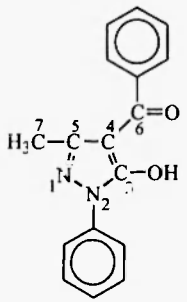
Complex No.	RCC(=O)CH(OH)N(C$_6$H$_5$)NCCH$_3$ (LH)								C$_6$H$_4$(CO)$_2$NCHR'COOH (AH)						Sn-Butyl
	Ligands and Complexes	C_1	C_4	C_5	C_6	C_7	N-Ph	Ph	COO	CO	CH	CH_2	CH_3	Ph	
	[a]L_1H	161.5	103.6	137.5	191.5	15.7	147.9, 128.9 126.5, 120.6	131.7, 128.9, 128.3, 127.8							
	[b]A_1H								170.46	167.29	-	40.25	-	136.03, 134.29, 125.25	
1	$Bu_2SnL_1A_1$	162.3	104.5	137.62	193.20	16.20	149.14, 128.71 127.58, 120.70	*	174.84	167.50	-	39.65	-	133.86, 132.13, 123.35	13.44, 26.11, 26.60, 27.63
	[c]A_2H								174.87	167.28	47.13	-	14.85	133.14, 131.59, 123.41	
2	$Bu_2SnL_1A_2$	162.15	104.20	137.57	192.38	16.03	148.95, 128.48 127.48, 120.46	*	177.31	167.21	47.66	-	15.47	133.73, 131.79, 123.06	13.34, 25.38 26.47, 27.04
	[c]A_3H								174.44	167.67	57.43 28.34	-	20.86 19.45	134.24, 131.81, 123.25	
3	$Bu_2SnL_1A_3$	162.34	104.32	137.84	192.26	16.16	149.00, 128.58 127.49, 120.46	*	176.92	167.75	58.09 28.84	-	21.16 19.59	133.77, 131.74, 123.16	13.40, 25.36 26.61, 27.20
	[c]A_5H								172.28	167.22	-	34.14 32.46	-	134.25, 133.17, 123.42	
5	$Bu_2SnL_1A_5$	162.48	104.45	137.10	191.40	16.15	148.87, 128.58 127.33, 120.40	*	179.23	167.50	-	34.00 33.18	-	133.49, 131.68, 122.74	13.27, 25.73 26.67, 28.65

Note : * merged with N-Ph

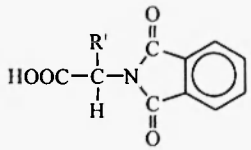
a = Ref. 39

b = Ref. 43

c = Ref. 35



(L_1H)



(AH)

R' = -H, (A_1H)

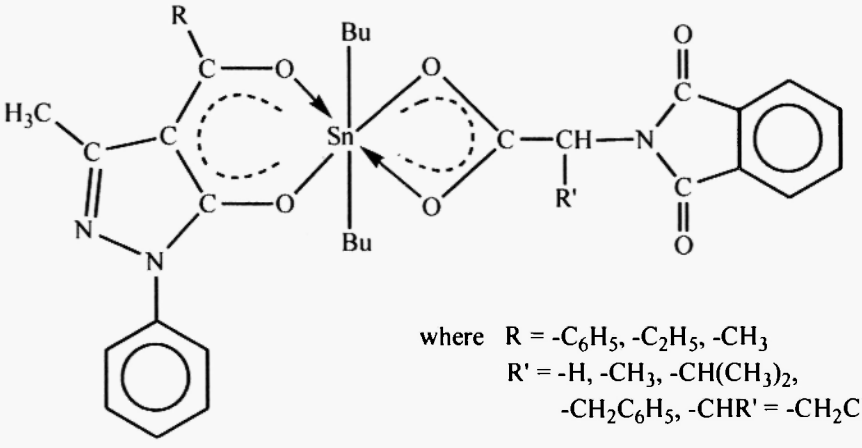
R' = -CH_3, (A_2H)

R' = -$CH(CH_3)_2$, (A_3H)

-CHR' = -CH_2CH_2-, A_1H

CONCLUSION

The complexes of the type $Bu_2Sn[RC\overline{OC:C(O)N(C_6H_5)N}:CCH_3][O_2CCHR'\overline{NC(O)C_6H_4C}(O)]$, where R = $-CH_3$, $-C_2H_5$, $-C_6H_5$ and R′ = -H, $-CH_3$, $-CH(CH_3)_2$, $-CH_2C_6H_5$ and –CHR′ = $-CH_2CH_2-$, are found to be monomeric in nature. The bidentate nature of N-protected amino acids and heterocyclic β-diketones has been suggested on the basis of spectral evidences. The physico-chemical and spectral evidences suggest an octahedral geometry (**Structure 1**) for these complexes in which the two butyl groups are present trans to each other.



where R = $-C_6H_5$, $-C_2H_5$, $-CH_3$
R' = -H, $-CH_3$, $-CH(CH_3)_2$,
$-CH_2C_6H_5$, -CHR' = $-CH_2CH_2-$

Structure 1

Structure 1 is further supported by ^{119}Sn NMR chemical shift values in the region δ 217.49-317.33 ppm recorded for some of these complexes, which are consistent with octahedral geometry/47/.

REFERENCES

1. D. Agustin, G. Rima, H. Gornitzka and J. Barrau, *Inorg. Chem.*, **39**, 5492 (2000).
2. S. Gopinathan, M.P. Degaonkar, A.M. Hundekar and C. Gopinathan, *Indian J. Chem.*, **32A**, 262 (1993).
3. B.K. Agarwal, Y.P. Singh, R. Bohra, G. Srivastava and A.K. Rai, *J. Organomet. Chem.*, **444**, 47 (1993).
4. M.T.H. Tarafder, A.M. Ali, Y.W. Wong and S.H. Wong, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 115 (2001).
5. A.A.S. El. Khaldy, *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 643 (1999).
6. A.A.S. El. Khaldy, *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 653 (1999).
7. M. Nath, R. Yadav and A. Kumar, *J. Organomet. Chem.*, **577**, 1 (1999).
8. S.N. Dobey and J.P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.*, **23**, 1251 (1993).
9. A.K. Saxena, S. Saxena and A.K. Rai, *Indian J. Chem.*, **31A**, 469 (1992).
10. G.K. Sandhu and G. Kaur, *J. Organomet. Chem.*, **388**, 63 (1990).
11. M.S. Singh and K. Tawade, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 157 (2001).
12. A. Meddour, F. Mercier, J.C. Martins, M. Gielen, M. Biesemans and R. Willem, *Inorg. Chem.*, **36**, 5712 (1997).
13. C. Pettinari, *Main Group Met. Chem.*, **22**, 661 (1999).
14. M.A. Beswick, J.S. Palmer and D.S. Wright, *Chem. Soc. Rev.*, **27**, 225 (1998).
15. V.K. Jain, *Coord. Chem. Rev.*, **135/136**, 809 (1994).
16. B. Bovio, A. Cingolani, F. Machete and C. Pettinari, *J. Organomet. Chem.*, **458**, 39 (1993).
17. A. Jain, S. Saxena, A.K. Rai, P.N. Saxena and J.V. Rao, *Metal Based Drugs*, **6**, 183 (1999).
18. M.S. Singh, M.D. Raju, A.K. Singh and P. Narayan, *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 73 (1999).
19. S. Sonika, S. Sharma, S. Gupta and A.K. Narula, *Indian J. Chem.*, **33A**, 1119 (1994).
20. M. Gielen, *Coord. Chem. Rev.*, **151**, 41 (1996).
21. J.J. Bonire, G.A. Ayoko, P.F. Olurinola, J.O. Ehinmidu, N.S.N. Jalil and A.A. Omachi, *Metal Based Drugs*, **5**, 233 (1998).
22. L. Pellerito and L. Nagy, *Coord. Chem. Rev.*, **224**, 111 (2001).
23. M. Gielen, H. Dalil, M. Biesemans, B. Mahieu, D. Devos and R. Willem, *Appl. Organomet. Chem.*, **13**, 515 (1993).
24. X.Q. Sang, Z.Q. Yang, Q.L. Xie and J.S. Li, *J. Organomet. Chem.*, **103**, 566 (1998).
25. Ji Li, G. Zhao, C. Xiong and Y. Ma, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 85 (2001).
26. R. Apodaka and W. Xiao, *Org. Lett.*, **3**, 1745 (2001).
27. W.P. Neumann, *J. Organomet. Chem.*, **437**, 23 (1992).
28. R.J. Davey and A.M.M. Rebello, *J. Cryst. J. Cryst. Growth*, **1**, 187 (2001).
29. A. Jain, S. Saxena and A.K. Rai, *Main Group Met. Chem.*, **17**, 641 (1994).

30. F. Machete, C. Pettinari, A. Cingolani, G.G. Lobbia, A. Cassetta and L. Barba, *J. Organomet. Chem.*, **517**, 141 (1996).
31. A. Jain, S. Saxena, A.K. Rai, R. Bohra and H. Wang, *Main Group Met. Chem.*, **26**, 1 (2003).
32. I.C. Torniporth-Oetting and P.S. White, *Organometallics*, **14**, 1632 (1995).
33. P.N. Saxena, A.K. Saxena, S. Saxena and A.K. Rai, *Appl. Organomet. Chem.*, **5**, 65 (1991).
34. A. Jain, S. Saxena and A.K. Rai, *Indian J. Chem.*, **32A**, 439 (1993).
35. A.K. Saxena, S. Saxena and A.K. Rai, *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 21 (1990).
36. A. Jain, S. Saxena and A.K. Rai, *Indian J. Chem.*, **30A**, 881 (1991).
37. A. Jain, S. Saxena, R. Bohra and A.K. Rai, *Main Group Met. Chem.*, **18**, 139 (1995).
38. A. Jain, S. Saxena, R. Bohra and A.K. Rai, *Main Group Met. Chem.*, **18**, 661 (1995).
39. A. Jain, S. Saxena and A.K. Rai, *Main Group Met. Chem.*, **14**, 329 (1991).
40. B.S. Jensen, *Acta. Chem. Scand.*, **13**, 1668 (1959).
41. J.C. Sheehan, D.W. Chapman and R.W. Roth, *J. Am. Chem. Soc.*, **74**, 3822 (1952).
42. K. Kawakami and R. Okawara, *J. Organomet. Chem.*, **6**, 249 (1966).
43. A.K. Saxena, S. Saxena and A.K. Rai, *Indian J. Chem.*, **29A**, 255 (1990).
44. J. Catterick and P. Thornium, Adv. *Inorg. Chem.* Radiochem., **20**, 291 (1977).
45. M.M. McGrady and R.S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).
46. W.F. Howard, R.W. Creely and W.H. Nelson, *Inorg. Chem.*, **24**, 2204 (1985).
47. V.K. Jain, J. Mason, B.S. Saraswat and R.C. Mehrotra, *Polyhedron*, 4, 2089 (1985).