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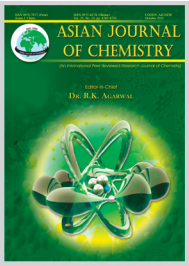

Synthesis, Characterization and *in vitro* Cytotoxic Assay on Human Promyelocytic Leukemia Cells (HL60) of Organotin(IV) Complexes Derived of 4-(methylamino) benzoic Acid and 4-(Dimethylamino)benzoic Acid

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Organotin(IV) carboxylate complexes derived from 4-(methylamino)benzoic acid, 4-($NHCH_3$)C_6H_4COOH and 4-(dimethylamino)benzoic acid, 4-[$N(CH_3)_2$]C_6H_4COOH have been successfully synthesized. Two dibutyltin(IV) complexes with the general formulae [4-(R')$C_6H_4COO]_2Bu_2Sn$ [R' = $NHCH_3$ **1**; R' = $N(CH_3)_2$ **3**] and another two triphenyltin(IV) complexes with the general formulae 4-(R')$C_6H_4COO(C_6H_5)_3Sn$ [R' = $NHCH_3$ **2**; R' = $N(CH_3)_2$ **4**] were successfully synthesized. The acids and complexes **1-4** obtained were characterized quantitatively and qualitatively. Results of the infrared and NMR spectroscopy on the acids and complexes showed that the coordination took place *via* oxygen atoms from the carboxylate anions. From the cytotoxic assay study, complex **2** revealed a significant result compared to complexes **1**, **3** and **4**.

Key Words: Organotin complexes, Carboxylate, *In vitro* cytotoxic activity.

INTRODUCTION

Numerous studies on organotin(IV) complexes have been carried out in order to study its biological properties against bacterial, fungal and cancer cells line[1-5]. Based on literature review, which are well documented over the past 20 years, there are many different types of tri- and diorganotin(IV) carboxylate compounds that have been tested for their *in vitro* activities against a large array of tumor cell lines[1,6,7]. In fact, up to date, organotin(IV) complexes are extensively studied due to its coordination geometries as well as structural diversity (monomer, dimeric, hexameric and oligomeric)[8-11].

As part of our interest and research on organotin(IV) work, we have synthesized and characterized organotin(IV) complexes derived of 4-(methylamino)benzoic acid and 4-(dimethylamino)benzoic acid. In addition, the cytotoxic assay of the complexes were screened against human promyelocytic leukemia cells, HL60 and the results are reported herein.

EXPERIMENTAL

All the reagents and solvents were purchased commercially and used without any further purification. Infrared spectra were recorded using a Perkin-Elmer FTIR GX Spectrophotometer as KBr disc in the frequency range of 4000-400 cm^{-1}. The spectra for ^1H and ^{119}Sn NMR were recorded on a Bruker AC-P 400 MHz FTNMR spectrometer and ^{13}C NMR was recorded on a Bruker AC-P 300 MHz FTNMR spectrometer using deuterated $CDCl_3$ as the solvent and tetramethylsilane, TMS as the internal standard. Elemental C, H and N analyses were carried out on a Fison EA 1108 CHNS-O analyzer. Tin was determined gravimetrically by igniting a known quantity of each complex to SnO_2. The melting points were determined in an open capillary and were uncorrected.

***In vitro* cytotoxic assay:** Cytotoxic assay was carried out against human promyelocetic leukemic cells, HL60, which was obtained from RIKEN Cell Bank, Tsukuba, Japan. The cells were maintained in RMPI-1640 medium supplemented with 10 % fetal calf serum and 100 IU/mL penicillin and 100 µg/mL streptomycin. Cytotoxicity was determined using the microtitration 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay[12,13]. The assay for each concentration of compound was performed in triplicate. The fraction of surviving cells was measured relative to the untreated cells

TABLE-1
SELECTED INFRARED DATA OF ORGANIC ACIDS AND COMPLEXES **1-4**

Compounds	Wavelength (cm^{-1})						
	ν(OH)	$\nu(COO)_{as}$	$\nu(COO)_{s}$	Δν	ν(Sn-O)	ν(Sn-O-Sn)	ν(Sn-C)
4-$(NHCH_3)C_6H_4COOH$	2888 - 2551	1670	1318	352	-	-	-
4-$(NHCH_3)C_6H_4COONa$	-	1615	1421	194	-	-	-
1	-	1608	1364	244	508	629	549
2	-	1599	1319	280	586	-	-
4-$[N(CH_3)_2]C_6H_4COOH$	2807 - 2558	1668	1319	349	-	-	-
4-$[N(CH_3)_2]C_6H_4COONa$	-	1614	1383	231	-	-	-
3	-	1603	1360	243	511	678	548
4	-	1604	1343	261	565	-	-

$\Delta\nu = [\nu(COO)_{as} - \nu(COO)_{s}]$

populations by measuring the absorbance values at 550 nm with the references at 630 nm using ELISA microplate reader (Bio Tek EL 340, USA). Cytotoxicity was expressed as fifty percent cytotoxic dose (CD_{50}), *i.e*. the concentration to reduce the absorbance of treated cells by 50 % with reference to the control (untreated cells). The CD_{50} and the SEM (standard error of the mean) was determined using Probit analysis (SPSS, version 12.0.1).

Preparation of sodium salt and complexes: The sodium salts of the respective acids were obtained by heating under reflux a 1:1 molar mixture of sodium hydroxide, NaOH (3 mmol) and acid (3 mmol) in ethanol (50 mL) for 2 h. After a few days, white precipitates were obtained.

***Bis*[4-(methylamino)benzoato]dibutyltin(IV),[4-$(NHCH_3)C_6H_4COO]_2(C_4H_9)_2Sn$ (1):** This complex was obtained by heating under reflux a 1:2 molar mixture of dibutyltin(IV) oxide, (3 mmol) and 4-(methylamino)benzoic acid (6 mmol) in toluene/ethanol (50 mL) for 4 h. A clear solution was separated by filtration and kept in a bottle. After two weeks, some transparent crystals (0.54 g, 34 % yield) were collected, m.p.: 154.6-155.2 ºC. Anal. found for $C_{24}H_{34}N_2O_4Sn_1$: C, 55.63; H, 5.89; N, 5.48; Sn, 22.61 %. Calcd. for $C_{24}H_{34}N_2O_4Sn_1$: C, 54.06; H, 6.43; N, 5.25; Sn, 29.61 %.

4-(Methylamino)benzoatotriphenyltin(IV),4-$(NCH_3)C_6H_4COO(C_6H_5)_3Sn$ (2): Complex **2** was prepared by heating under reflux a 1:1 molar mixture of triphenyltin(IV) hydroxide (3 mmol) and 4-(methylamino)benzoic acid (3 mmol) in acetonitrile (60 mL) for 2 h. Colourless solution was isolated by filtration and kept in a bottle. After two weeks, transparent crystals (0.41 g, 27 % yield) were collected. m.p.: 102.8-105.2 ºC. Anal. found for $C_{26}H_{23}NO_2Sn_1$: C, 63.47; H, 5.19; N, 2.55; Sn, 22.10 %. Calcd. for $C_{26}H_{23}N_1O_2Sn_1$: C, 62.44; H, 4.64; N, 2.80; Sn, 23.73 %.

***Bis*[4-(dimethylamino)benzoato]dibutyltin(IV),{4-$[N(CH_3)_2]C_6H_4COO\}_2(C_4H_9)_2Sn$ (3):** Complex **3** was prepared by a similar method to those described for complex **1**, except substituting 4-(methylamino)benzoic acid with 4-(dimethylamino)benzoic acid. Methanol (60 mL) was used as solvent and the mixture was heated under reflux for 3 h. A clear transparent solution was isolated by filtration and kept in a bottle. After two weeks, transparent crystals (1.13 g, 67 % yield) were collected. m.p.: 131.5-132.8 ºC. Anal. found for $C_{26}H_{38}N_2O_4Sn_1$: C, 55.03; H, 7.37; N, 7.43; Sn, 22.87 %. Calcd. for $C_{26}H_{38}N_2O_4Sn_1$: C, 54.64; H, 6.82; N, 4.99; Sn, 21.15 %.

4-(Dimethylamino)benzoatotriphenyltin(IV), 4-$[N(CH_3)_2]C_6H_4COO(C_6H_5)_3Sn$ (4): Complex **4** was prepared by heating under reflux a 1:1 molar mixture of triphenyltin(IV) hydroxide (2 mmol) and 4-(dimethylamino)benzoic acid (2 mmol) in acetone (50 mL) for 2 h. A clear transparent solution was isolated by filtration and kept in a bottle. After a few days, transparent crystals (0.91 g, 59 % yield) were obtained. m.p.: 131.5-132.8 ºC. Anal. found for $C_{27}H_{25}NO_2Sn_1$: C, 63.04; H, 5.55; N, 5.15; Sn, 23.41 %. Calc. for $C_{27}H_{25}N_1O_2Sn_1$: C, 63.07; H, 4.90; N, 2.72; Sn, 23.08 %.

RESULTS AND DISCUSSION

In this study, complexes **1-4** have been obtained in solid state as a single crystal. However, only single crystal of complex **1** was suitable for single crystal X-ray crystal structure determination and the respective data of complex **1** has been reported[14]. Elemental analysis C, H, N and Sn data obtained were in agreement with the predicted formula and complexes **1-4** gave a sharp melting point indicated the isolation of fairly pure complexes. An outline of the proposed structure for complexes **1-4** are depicted in Fig. 1.

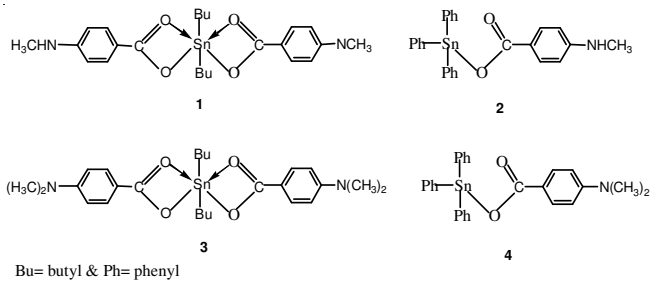


Fig. 1. Proposed structure of complexes **1-4**

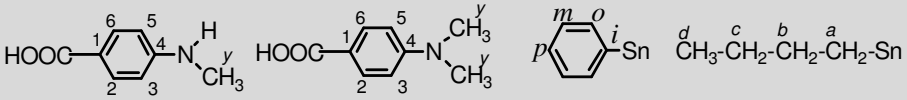
The characteristic infrared absorption frequencies (cm^{-1}) and assignments of important absorption bands of the acids, sodium salts and complexes **1-4** are listed in Table-1. The ν(O-H) bands, which appeared in the range 2888-2551 cm^{-1} for the acids, were absent in the infrared spectra of salts and complexes **1-4** showed the deprotonation and coordination of the carboxylate anion[4,5]. The infrared spectra of complexes **1-4** revealed that the $\nu(COO)_{as}$ was shifted to a lower wavelength number compared to the parent acids, which signify that the coordination took place *via* the oxygen atoms of the carboxylate anions.

The magnitude of $\Delta\nu = [\nu(COO)_{as}\text{-}\nu(COO)_{s}]$ is a useful indicator in the correlation of the coordination modes of the carboxylate anions to the tin atoms. Sandhu and Verma[15] have shown that the Δν value of complexes greater by 65-90 cm^{-1}

TABLE-2
^{1}H NMR DATA OF ORGANIC ACIDS AND COMPLEXES **1-4**

Compounds	Chemical shift, δ(ppm)		
	Benzene	Amino group [$NHCH_3$, $N(CH_3)_2$]	-R (R= Bu & Ph)
4-($NHCH_3$)C_6H_4COOH ($CDCl_3$)	6.59 (d, 8.8 Hz, 2H) H3 & H5; 7.97 (d, 8.9 Hz, 2H) H2 & H6	2.93 (s, 3H) H*y*	-
1 ($CDCl_3$)	6.64 (d, 8.9 Hz, 4H) H3 & H5; 8.04 (d, 8.8 Hz, 4H) H2 & H6	2.92 (s, 6H) H*y*	0.95 (t, 7.3 Hz, 6H) H*d;* 1.44-1.45 *(m, 4H) H*c;* 1.77-1.80 *(m, 8H) H*a* & H*b*
2 ($CDCl_3$)	6.54 (d, 8.9 Hz, 2H) H3 & H5; 8.00 (d, 8.8 Hz, 2H) H2 & H6	2.88 (s, 3H) H*y*	7.44-7.47 *(m, 9H) H*m* & H*p* 7.79-7.87 *(m, 6H) H*o*
4-[$N(CH_3)_2$]C_6H_4COOH ($CDCl_3$)	6.72 (d, 8.9 Hz, 2H) H3 & H5; 8.00 (d, 9.0 Hz, 2H) H2 & H6	3.09 (s, 6H) H*y*	-
3 ($CDCl_3$)	6.67 (d, 8.8 Hz, 4H) H3 & H5; 8.03 (d, 7.4 Hz, 4H) H2 & H6	3.06 (s, 12H) H*y*	0.89 (t, 7.3 Hz, 6H) H*d;* 1.35-1.44 *(m, 4H) H*c;* 1.73-1.78 *(m, 8H) H*a* & H*b*
4 ($CDCl_3$)	6.65 (d, 8.8 Hz, 2H) H3 & H5; 8.01 (d, 7.4 Hz, 2H) H2 & H6	3.04 (s, 6H) H*y*	7.45-7.49 *(m, 9H) H*m* & H*p* 7.74-7.91 *(m, 6H) H*o*

s= singlet, d= doublet, t= triplet, m= multiplet; Coupling constant= Hz, *= overlap



than in their sodium salts indicated either asymmetric or monodentate bonding of the carboxylate group to tin(IV) atom. The $\Delta\nu$ value indicated that the carboxylate anions were bonded to tin(IV) atom moiety in a bidentate mode in complexes **1** and **3**. Moreover, for complexes derived of triphenyltin(IV) carboxylate, $\Delta\nu$ below 200 cm^{-1} would be expected for bridging or chelating carboxylates, but greater than 200 cm^{-1} for the monodentate bonding carboxylate anions[16]. Hence, carboxylate anions in complexes **2** and **4** would be expected to bond to the tin atom in monodentate manner since the $\Delta\nu$ above 200 cm^{-1}. Further evidence for the coordination to Sn(IV) *via* O atoms was revealed by the presence of the Sn-O stretching bands in the spectra of complexes **1-4** in the region of 586-508 cm^{-1}.

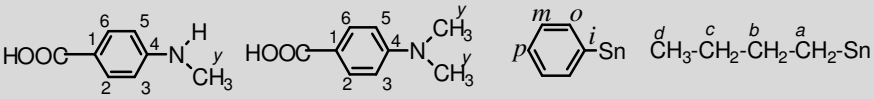
The ^{1}H NMR spectra of complexes **1-4** revealed similarities to their parent acids and the spectral data of complexes **1-4** are summarized in Table-2. The ^{1}H NMR spectrum of 4-(methylamino)benzoic acid exhibited two sets of signals at downfield region [6.59 ppm and 7.97 ppm] with the integration values of 2:2, which was also observed in the ^{1}H NMR spectra of complexes **1** and **2** arising from the aromatic protons of the benzene ring. Similar observation also found in complexes **3-4** and 4-(dimethylamino)benzoic acid. In the upfield regions of the ^{1}H NMR spectra of the complexes **1** and **3** showed the signals of butyl protons in the range of 0.89-1.78 ppm respectively[4,5]. For complexes **2** and **4**, the occurrence of multiplets in the downfield region at the range of 7.44-7.49 and 7.74-7.91 ppm with integration values of 9:6 respectively were ascribed to the aromatic protons of the phenyl group[4,5].

The formation of complexes were evident from the δ(COO) value in the ^{13}C NMR spectra. Complexes **1-4** exhibited a δ(COO) signal in the range of 173.41-176.32 ppm. The ^{13}C NMR spectra of complexes **1-4** showed that the chemical shift of the δ(COO) signal in each complexes was shifted downfield compared to that of their parent acids indicating the participation of the carboxylate anions in the coordination to the tin(IV) atom[4,5]. The occurrence of four resonance signals in the range of 110.58-154.08 ppm defined as benzene signals of the parent acids and complexes. In addition, the alkylamino signals of complexes appears in the range of 30.25-40.07 ppm were similar to that of the parent acids indicative of non-coordination of alkylamino groups to the tin(IV) moieties. Complexes **1** and **3** were derivative of dibutyltin(IV) showed the occurrence of CH_3 and CH_2 in the range of 13.55-13.65 and 25.25-26.80 ppm respectively (Table-3). Complexes **2** and **4** revealed the chemical shifts of the $\delta(^{13}C)_{ipso}$ at 139.30 and 139.17 ppm respectively indicative of a four-coordinated Sn(IV) atom[17-19]. Generally, the ^{1}H and ^{13}C NMR spectra of the complexes obtained were found to exhibit no additional resonance and thus reflects the purity of the complexes. Based on the integration values, the number of protons in complexes **1-4** were in accordance with the number of protons proposed.

The $\delta(^{119}Sn)$ values define the region with different coordination number of the tin(IV) atom moiety and the $\delta(^{119}Sn)$ values are summarized in Table-3. For diorganotin(IV) carboxylate complexes, the $\delta(^{119}Sn)$ value for five-coordinated complexes between -90 to -190 ppm and for six-coordinated complexes between -210 to -400 ppm[20]. From the ^{119}Sn NMR solution study, the tin(IV) atom of complexes **1** and **3** were five-coordinated (predominantly). Based on the infrared spectroscopy study, both complexes **1** and **3** were pure and the tin(IV) atoms were six-coordinated and existed in a distorted octahedral geometry. This might be upon dilution, the crystal lattice were broken up resulting the carboxylate anions assembly self-arrangement (in dynamic state). Hence, one of the carboxylate anions was located close to the tin(IV) atom and exhibited bidentate chelation while the other carboxylate anion exhibited monodentate chelation resulting five-coordinated tin atom in complexes **1** and **3**. Complexes **2** and **4** derivatives of triphenyltin(IV) exhibited $\delta(^{119}Sn)$ values at -122.64 and -123.78 ppm respectively, which lie slightly upfield in the range of -40 to -120 ppm [for triphenyltin(IV) complexes] and did not lie in the range of five-coordinated tin atom [-180

TABLE-3
^{119}Sn AND ^{13}C NMR DATA OF ORGANIC ACIDS AND COMPLEXES **1-4**

Compounds	Chemical shift (ppm)				
	^{119}Sn	Benzene	Amino group [$NHCH_3$, $N(CH_3)_2$]	-R (R= Bu & Ph)	COO
4-$(NHCH_3)C_6H_4COOH$ ($CDCl_3$)	-	111.51 (C3 & C5), 117.61 (C1), 132.61 (C2 & C6), 153.89 (C4)	30.50 (C*y*)	-	172.44
1 ($CDCl_3$)	-160.03	111.33 (C3 & C5), 117.98 (C1), 132.14 (C2 & C6), 153.17 (C4)	30.25 (C*y*)	13.65 (C*d*), 25.34 (C*b*), 26.48 (C*c*), 26.80 (C*a*)	176.30
2 ($CDCl_3$)	-122.64	111.17 (C3 & C5), 118.18 (C1), 132.96 (C2 & C6), 153.96 (C4)	30.40 (C*y*)	139.30 (C*i*), 137.15 (C*o*), 128.98 (C*m*), 130.10 (C*p*)	173.64
4-$[N(CH_3)_2]C_6H_4COOH$ ($CDCl_3$)	-	111.29 (C3 & C5), 116.61 (C1), 132.44 (C2 & C6), 154.08 (C4)	40.57 (C*y*)	-	172.64
3 ($CDCl_3$)	-161.19	110.52 (C3 & C5), 116.56 (C1), 132.26 (C2 & C6), 153.42 (C4)	40.06 (C*y*)	13.55 (C*d*), 25.25 (C*b*), 26.39 (C*c*), 26.70 (C*a*)	176.32
4 ($CDCl_3$)	-123.78	110.58 (C3 & C5), 116.80 (C1), 132.47 (C2 & C6), 153.30 (C4)	40.07 (C*y*)	139.17 (C*i*), 136.94 (C*o*), 128.75 (C*m*), 129.86 (C*p*)	173.41



to -260 ppm for triphenyltin(IV) complexes]. Hence, indicating that the tin(IV) atom in complexes **2** and **4** remained as four-coordinated and have a distorted tetrahedral geometry[17,18].

The CD_{50} values for the complexes **1-4** are given in Table-4. From the data in Table-4, it was found that all the complexes obtained showed significant results against HL60 cells with the cytotoxic assay value less than 1 µg/mL. In addition complexes **1-4** showed a better cytotoxic activity compared to etoposide (0.60 µg/mL). Among the complexes obtained, complex **2** (0.28 µg/mL) showed a better *in vitro* cytotoxic assay against HL60 cells with the lower value compared to complexes **1, 3** and **4**.

TABLE-4
CYTOTOXICITY ASSAYS, CD_{50} VALUE OF COMPLEXES **1-4**

Complexes	CD_{50} (µg/mL)
	Human promyelocetic leukemic cells, HL60
1	0.50 ± 0.018
2	0.28 ± 0.039
3	0.37 ± 0.014
4	0.40 ± 0.036
Etoposide (reference)	0.60 ± 0.051

Cytotoxicity values are expressed as mean ± SEM from the triplicate

Conclusion

Complexes **1-4** have been successfully synthesized and characterized. Elemental analysis C, H, N and Sn data obtained were in agreement with the predicted formula. Results of the infrared and NMR spectroscopy on the acids and complexes showed that the coordination took place via oxygen atoms from the carboxylate anions. With the exceptional case, the tin(IV) atoms in complexes **1** and **3** are six-coordinated in solid state and exhibited five-coordinated in solution which may attributed from the dynamic stage and self-rearrangement of one carboxylate anion. Overall, all the four complexes obtained show promising *in vitro* cytotoxic activity compared to reference drug (etoposide). Based on the *in vitro* cytotoxic assay, complex **2** showed better activity compared to complexes **1**, **3** and **4**.

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