ASIAN JOURNAL OF CHEMISTRY

First Supramolecular Complexes of Organotin(IV) with Kryptofix 5: Synthesis and Spectral Study

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Four novel organotin(IV) complexes of kryptofix 5 with general formula [(R$_2$SnCl$_2$)$_2$(L)], R = Me(1), Ph(2), Bz(3), [(R$_3$SnOCOCF$_3$)(L)], R = Ph(4), L = kryptofix5, have been prepared. The newly synthesized compounds have been characterized by UV-VIS, FT-IR, multi-nuclear NMR (^{1}H, ^{13}C and ^{119}Sn, ^{19}F) and mass spectrometry. The J = 80 and 120 of methyl group of complex (1) and (4) indicate five and higher than five coordinated central tin atom.

Key Words: Organotin(IV), Supramolecule, Kryptofix, Multi-donor atom, Organotin(IV) carboxylate.

INTRODUCTION

Crown ethers are organic ring compounds, typically larger than 12 atoms in the cycle that contain oxygen, nitrogen, sulfur or other heteroatoms. These heteroatoms alternate with carbon bridges that may be ethylene (CH$_2$CH$_2$) units or they may be part of more complex structures. The key property of crown ethers on which interest has centered for decades is their ability to complex various ions. Initially, studies were focused on such alkali metal ions as sodium and potassium, but ammonium ion, diazonium ion, transition metals and even neutral species were complexed by these versatile macrocycles. Cryptands (trade name of kryptofix) are cyclic or polycyclic molecules which contain three or more binding sites held together by covalent bonds. These molecules are three dimensional analogues of crown ethers. These complexing agents display a wide range of binding specificities. Artificial macrocyclic polyethers, cryptands and crown ethers have demonstrated a remarkable complexing ability for metal ions[1,2] and polar organic species[3,4]. Due to the similarities of open chain polyethylene glycols in many respects to synthetic and naturally occurring antibiotics, there has been a growing interest in the coordination chemistry of these ligands and their metal ion complexes. Organotin(IV) compounds received increasing attention in the recent past years, not only because of their many and differentiate applications in industry as agricultural biocides, wood preservatives, heat stabilizers, marine antifouling paints, flame retardants, smoke suppressants, homogeneous catalysts, but also for their possible biomedical applications as antioxidants, tin-based antimicrobial drugs, potential antitumor drugs, *etc*.[5-13]. Among them organotin macrocycles have attracted significant research interest due to their potential industrial applications and biological activities[14-18]. As reported in these metallo-macrocyclic systems, ligands with multi-coordination or donor atoms and particular stereochemistry may lead to different specific architectures. Especially those carboxylate ligands with additional donor atoms, available for coordination to Sn, have been revealed to help the construction of interesting macrocyclic structures[19-21]. In this paper we report the synthesis of both organotin and organotin carboxylate complexes with Kryptofix 5 (Fig. 1).

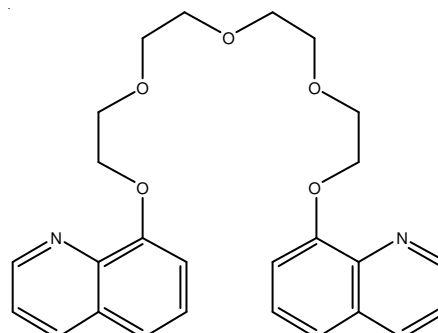Fig. 1. Structure of kryptofix 5

EXPERIMENTAL

Dimethyltin(IV) dichloride, triphenyltin(IV) chloride, silver trifluro acetate, kryptofix 5 (Merck), diphenyltin(IV) dichloride (Aldrich) were used without further purification.

[1]H, ^{13}C, ^{119}Sn and ^{19}F NMR measurements were carried out at room temperature in CDCl$_3$ solution of the compounds on a Bruker 500 spectrometer. Infrared spectra (KBr pellets) were recorded on a Tensor 27 Bruker FT-IR spectrometer (4000-400 cm^{-1} range). The UV-VIS was recorded on Varian Cary 100.

General procedure

Synthesis of [(Me$_2$SnCl$_2$)$_2$(Kry)] (1): Compound (**1**) was prepared by adding a methanolic solution (10 mL) of kryptofix (1.02 g, 2.27 mmol) into Me$_2$SnCl$_2$ (0.50 g, 2.27 mmol) dissolved in methanol (10 mL). The reaction mixture was immediately turn to yellowish colour, which was stirred for 8 h at room temperature. The product was appeared as precipitate in the reaction mixture. The reaction was filtered and the obtained solid was collected as product. m.p.: 171 ± 1 ºC.

Synthesis of [(Ph$_2$SnCl$_2$)$_2$(Kry)] (2): The synthesis of (**3**) was carried out in an identical manner to (**1**). Ph$_2$SnCl$_2$ (0.38 g, 1.11 mmol) and kryptofix (0.5 g, 1.11 mmol). m.p. 184 ± 2 ºC.

Synthesis of [(Bz$_2$SnCl$_2$)$_2$(Kry)] (3): The kryptofix ligand (0.12 g, 0.2 mmol), was refluxed for 8 h with dibenzyltin(IV) dichloride (0.10 g, 0.2 mmol) under argon atmosphere in methanol solution contained in a 100 mL two necked round bottom flask. The reaction mixture was then filtered and by the slow evaporation of solvent, the crystalline product obtained. m.p. 138 ± 2 ºC.

Synthesis of [(Ph$_3$SnOCOCF$_3$)$_2$(Kry)] (4): An ethanolic solution of CF$_3$COOAg (0.14 g, 0.63 mmol) was added dropwise into an ethanolic solution of Ph$_3$SnCl (0.24 g, 0.63 mmol) and stirred for 2 h. The AgCl precipitate was removed by filtering the reaction mixture. An ethanolic solution of kryptofix (0.28 g, 0.63mmol) was added to filtrate and stirring was continued for further 6 h. The crystalline product obtained by the slow evaporation of solvent. m.p. 116 ± 2 ºC.

The compounds were characterized by UV-VIS, FT-IR, ^{1}H, ^{13}C, ^{119}Sn, ^{19}F NMR and mass spectral studies. All the spectroscopic data are gathered in Tables 1 and 2.

RESULTS AND DISCUSSION

UV-VIS spectra: The electronic spectra analysis of kryptofix-5 and its organotin(IV) complexes (**1**, **2** and **4**) were carried out in DMSO (10^{-4} M) at room temperature ranging from 200-800 nm. The bands at 256 and 304 nm in the

TABLE-1 INFRARED SPECTRAL DATA				
Compound	ν(C-H) (cm^{-1})	ν(COC) (cm^{-1})	ν(Sn-N) (cm^{-1})	ν(C=O) (cm^{-1})
Ligand (Kry)	2877-3041	1103	–	–
(1)	2884-3065	1106	460	–
(2)	2879-3047	1107	420	–
(3)	2880-3056	1114	454	
(4)	2923-3048	1105	453	1711, 1404

kryptofix-5 and its organotin(IV) complexes spectra are assigned to be the π-π* of quinoline ring. λ$_{max}$ in complexes and ligand was the same. UV spectra have been shown in Fig. 2.
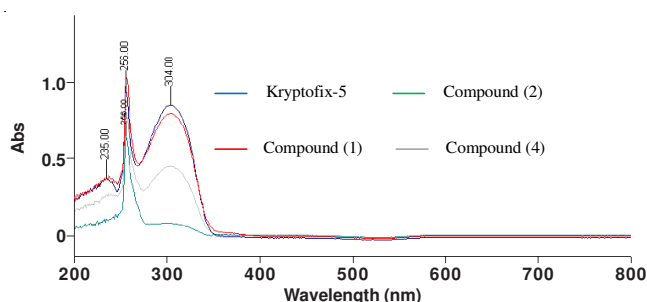

Fig. 2. UV spectrometry of the ligand and the complexes

Infrared spectroscopy: The most important IR absorption frequencies, along with the relative assignments of tin(II) complexes are summarized in Table-1. The ν(COC) has a strong band in 1100 cm^{-1} that it appears in 1103 cm^{-1} for the ligand. In the infrared spectra of [(Me$_2$SnCl$_2$)$_2$(Kry)], [(Ph$_2$SnCl$_2$)$_2$(Kry)], [(Bz$_2$SnCl$_2$)$_2$(Kry)] and [(Ph$_3$SnOCOCF$_3$)$_2$(Kry)], the ν(C-O) appear at 1106, 1107, 1114 and 1105 cm^{-1}, respectively. These bands are shifted to the higher energy region in comparison with the ligand. The ν$_{asym}$(CO$_2$) and ν$_{sym}$(CO$_2$) modes of [(Ph$_3$SnOCOCF$_3$)$_2$(Kry)] appear at 1711 and 1404 cm^{-1}, respectively (Table-1).

^{1}H NMR spectra: The ^{1}H, ^{13}C and ^{119}Sn NMR data for all supramolecular tin complexes are given in Table-2. The ^{1}H NMR spectrum of the kryptofix-5 shows four important resonance signals in aliphatic range at 3.70-4.46 and another four signals in aromatic range at 7.14-8.97 ppm. Four resonance signals in aliphatic range assigned to etheric protons which two of them are triplet and two another multiple.

TABLE-2 NMR SPECTROSCOPIC DATA			
Compound	^{1}H NMR	^{13}C NMR	^{119}Sn NMR
(1)	1.23-1.39 (s, 12H, CH$_3$), 3.72-3.79 (m, 8H, CH$_2$), 4.07-4, 49 (tt, 8H, CH$_2$), 7.26-9.07 (m, 12H, Ph)	24.18 (CH$_3$), 69.41, 69.63, 70.74, 79.87 (CH$_2$), 112, 120, 122, 128, 130, 136, 141(Ph), 147 (C-N), 152 (C-O)	-229.49
(2)	3.60-3.66 (m, 8H, CH$_2$), 3.92-4.39 (tt, 8H, CH$_2$), 7.15-8.90 (m, 32H, Ph)	68, 69, 70,71 (CH$_2$), 109.7, 120.2, 121.9, 127.1, 128.7, 129.1, 129.7, 129.9, 135.6, 136.5(Ph), 140, 149(C-N), 154 (C-O of Ph)	-402.06
(3)	2.79-3.05 (s, 4H, CH$_2$-Sn), 3.37-3.47 (m, 8H), 3.76-4.20 (tt, 8H, CH$_2$), 6.79-8.86 (m, 32 H)	41.36 (CH$_2$-Sn), 68.8, 69.3, 70.4, 70.7(CH$_2$), 111.4, 120.0, 122.0, 125.0, 128.1, 128.4, 128.5, 128.8, 129.6, 136.3 (Ph), 140.5, 140.6 (C-N), 152.0 (C-O)	-258.50
(4)	3.48-3.58 (m, 8H, CH$_2$), 3.96-4.34 (tt, 8H, CH$_2$), 7.07- 8.51 (m, 42 H, Ph)	68, 69, 70, 71(CH$_2$), 109.7, 120.2, 121.9, 127.1, 128.6, 128.9, 129.1, 129.8, 136.5, 136.7 (Ph), 136.8-140.1 (C-N), 141.49 (C-O of Ph), 149.3 (C-F), 154.6 (C=O)	-258.50

Existence of the multiple groups is because of the coupling with quinoline ring's protons. The three signals in 7.14-7.15, 8.13-8.15, 8.96-8.97 are related to ring which contains nitrogen atom and the multiple signal at 7.40-7.47 is attributed to aromatic ring. In the complexes (1-4) these structures remain and the chemical shift of the quinoline's protons depicts that coordination is from the nitrogen site of the quinoline part of the kryptofix. It is interested that coordination number for some of the compounds can be predict by ^2J(Sn-H) coupling constant. The coupling constant up to 90 shows the coordination number five. Hence The available $^2J(^{119}$Sn-C-^{1}H) coupling constant about 80 and 120 and splitting pattern of methyl group and intensity of resonances of complex (1) and(3) reveals five and seven coordinated tin atom. In initial compound, Me_2SnCl_2, coupling constant was 60 and $^2J(^{119}$Sn-^{1}H) increasing from 60 to 80 indicates structural change and coordination of kryptofix from one coordination site to Sn atom (Table-2).

^{13}C NMR spectra: Two sets of key resonance signals were observed from the spectrum of all complexes. They are δ(O-CH_2-CH_2-O) (4 signals, 67-80 ppm), δ(quinoline ring) (9 signals, 109-154 ppm). In the complex (1) one signal in 24.18 shows the Me group and in complex (4) the signals at 41.36, 141.49 and 158.23 concern to δ(CH_2-Sn), δ(C-F) and δ(C=O), respectively.

^{119}Sn NMR spectra: ^{119}Sn NMR spectra of the complexes give signals at δ-229.49, -402.06, -424.17 and -258.50 which concern to complexes (1),(2), (3) and (4), respectively. Existence of a single peak for all complexes shows the high purity of the synthesized complexes.

Mass spectrometry: The mass spectra of the ligand's fragment for all complexes were same: m/e 128 $[C_9H_6N]^+$ (quinoline), 144 $[C_9H_6NO]^+$ 172 $[C_9H_6NOCH_2CH_2OCH_2]^+$, 216 $[C_9H_6NOCH_2CH_2OCH_2CH_2]^+$, 244 $[C_9H_6NOCH_2CH_2OCH_2CH_2OC]^+$ and whole mass of kryptofix ligand appears at 448. In the compound (**1**) these fragments are characterized: m/e 135 $[SnMe]^+$, 150 $[SnMe_2]^+$, 155 $[Sn\ ^{35}Cl]^+$, 157 $[Sn\ ^{37}Cl]^+$, 190 $[SnCl_2]^+$, 205 $[Me_2SnCl_2]^+$ and 220 $[Me_2SnCl_2]^+$. In the compound (**2**) these fragment are determined: m/e 35 $[Cl]^+$, 77 $[Ph]^+$, 155 $[SnCl]^+$, 190 $[SnCl_2]^+$, 197 $[PhSn]^+$ and 264 $[Ph_2Sn]^+$. In compound (**3**) these fragments are found: 77 $[Ph]^+$, 274 $[Ph_2Sn]^+$, 233 $[SnOCOCF_3]^+$, 310 $[PhSnOCOCF_3]^+$ and 387 $[Ph_2SnOCOCF_3]^+$.

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