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Synthesize and Characterize Dibutyltin (IV) Oxide Complex by Utilizing New Ligand

Emad Alhaydary and Emad Yousif*

Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

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Abstract

Herein successfully synthesized new organotin (IV) complex Bu_2SnOL by reacting sulfamethoxazole drug as a ligand with dibutyltin (IV) oxide. The synthesized complex was fully characterized by Fourier transform infrared, ^{1}proton nuclear magnetic resonance, ^{13}carbon nuclear magnetic resonance, ^{119}tin nuclear magnetic resonance and ultraviolet-visible spectroscopies. Field emission scanning electronic microscopy was also applied to study the surface morphology of synthesized complex. The above techniques have demonstrated that the complex was prepared with high percentage of purity. This type of compound has various applications in medicine and industry. For example, using it as photo–stabilizer of different plastic polymers (polyvinyl chloride, polystyrene and polyvinyl alcohol).

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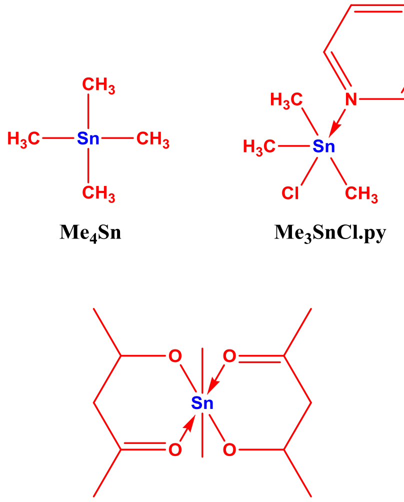
*Corresponding author: emad_yousif@hotmail.com

1. Introduction

Tin is located in group 14 in a post-transition element in the periodic table and it has same chemical features of neighbor elements germanium and lead within the same group. In addition, it has two oxidation states the most stable one is +2 and the least stable one is +4. Thus, the electronic configuration of tin is [Kr] $4d^{10}$ $5s^2$ $5p^2$. Tin isotope (^{119}sn) can be identify by NMR machine due to it has 1/2 spin [1]. Both oxidation states of tin can react with halides, oxygen, and sulfur to make inorganic compounds. The most famous reaction is tin metal with hydrochloric acid to form tin (II) chloride and release hydrogen gas [2]. Another important reaction is with oxygen when heated the tin up in the air to make tin (IV) dioxide. Tin^{+2} materials have one unbounded pair of electrons and their divalent are mainly depending on the coordination number normally sp^3d-distorted tetrahedral, sp^2-trigonal, and sp^3-pyramidal geometry structures [3]. Tin has ability to make covalent bond with carbon atom to form organotin materials, which has a unique property make them quite important in both industrial and medicine applications especially as a photo-stabilizers of plastic polymers such as Poly (vinyl chloride) PVC [4].

Organotin materials are important part of organometallic field and they consist of metallic tin linked to hydrocarbon groups by covalent bonds. In 1849, $(C_2H_5)_2SnI_2$ (diethyltin diiodide) was the first organotin discovered by Frankland [5,6]. This field was grown quickly in the last century especially after Grignard reaction discovery which exhibits the ability of formation tin carbon covalent bond. Nowadays this field still rich because its huge applications in industry and medicine [7,8]. The most famous organotin compounds are tetrabutyltin, trimethyltin chloride, triphenyltin acetate, triphenyltin chloride and triphenyl hydroxide [9].

Organotin (IV) can easily obtained by oxidizing organotin (II) that is more stable. Organotin (IV) can be designed in different forms depending on the number of organic and anion groups connected to the tin such as mono-organotin, di-, tri- and tetra- compounds [10]. As shown in Figure 1, the proposed geometry structure of organotin materials having molecular formula X_4Sn (hence X is an organic unit) for example Me_4Sn with sp^3-tetrahedral coordination. However, with lower electronegative for the bonded ligands to the metallic tin which prefers to coordinate to groups more than four for example sp^3d-trigonalbipyramidal five-coordination ($Me_3SnCl.py$) and sp^3d^2-octahedral six-coordination ($Me_2Sn(acac)_2$) [11].



Me_4Sn **$Me_3SnCl.py$**

$Me_2Sn(acac)_2$

Figure 1. Proposed geometrical structure of organotin compounds with coordination more than four.

There are several applications of organotin materials in both industrial and medicine areas [12-14] and some of these applications and we going to highlight the using of organotin materials as photo-stabilizers of plastic polymers especially the PVC polymeric films [15-19]. Herein we are introducing new organotin photo-stabilizers with using sulfamethoxazole drug as a ligand. Sulfamethoxazole is used as antibiotic against bacterial infections for example *E. coli* and *Listeria*. Yet nobody has utilized this drug to prepare organotin materials which are suitable for different applications such as PVC photo-stabilizers [20-24].

2. Chemicals and Procedures

2.1 Chemicals

All reagents and chemicals were uitilized in this project have been got from Fluka, GCC, Sigma Aldrich, BDH, Scharlau, and Romil companies and utilized without any further purification. The IUPAC name of sulfamethoxazole is 4-amino-N-(5-methylisoxazol-3-yl)benzenesulfonamide.

2.2 Techniques and instruments:

The FTIR spectra were determined using a modern machine (Bruker Alpha ATR-FTIR) at range between 4000 cm^{-1} to 400 cm^{-1} frequency. The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded by using 400 MHz Bruker Avance spectrophotometer. Hence 119-tin nuclear magnetic resonance (^{119}Sn-NMR) spectra were determined by utilizing 107 MHz Bruker DRX300NMR spectrophotometer. 13-C nuclear magnetic resonance (^{13C}-NMR) spectra were determined by. The tetramethylsilane (TMS) was used as internal standard of measured compounds ($\delta = 0.00$ ppm). Dimethyl sulfoxide (DMSO-d_6) deuterated solvent was used to dissolve the prepared compound. Shimadzu UV-1601 machine was used to record the Ultraviolet and visible spectra for range 200-700 nm and using quartz cell (1 cm) at ambient temperature for ligand and prepared complexes. Several suitable solvents have been used to dissolve the synthesized compound with very dilute concentration range between 0.6–1 a. u absorption intensity. Flame Atomic Microscopy (FAM) was utilized to study the surface morphology of PVC films by taking two- and three-dimensions images. AA-6880 Shimadzu flame atomic microscopic (Japan) was applied for this study. TESCAN MIRA3 LMU system (Kohoutovice, Czech Republic) was utilized to perform Field Emission Scanning Electron Microscopy (FESEM) field emission scanning electron microscopy and (EDX) energy dispersive X-ray elemental analyses of synthesized complexes using an accelerating voltage (15 kV). However, the morphology measurement of PVC films after irradiation were done using a ZEISS and at accelerating voltage 10 kV. Accelerated weather-meter QUV tester (Philips, Saarbücken, Germany) provided by UV-lamp 313 nm was utilized to expose the PVC films for 300 hours by UV light at room temperature with lambda maximum 313 nm and (1.052×10^{-8} $ein.dm^{-3}.s^{-1}$) light intensity.

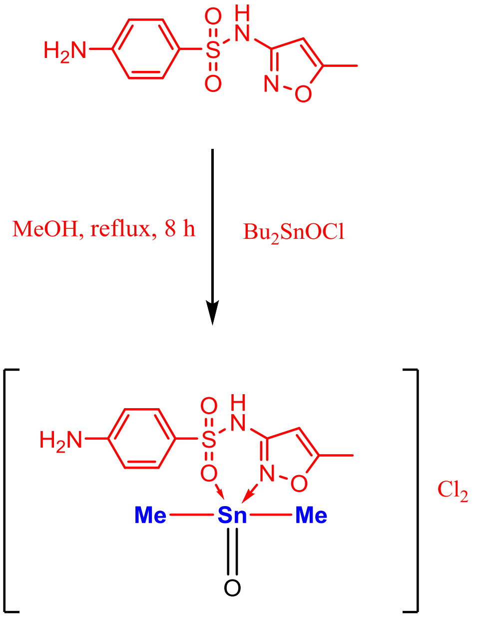
2.3 Synthesis of di-methyltin (IV) complex

The Dibutyltin (IV) oxide complex were synthesized by utilizing 1:1 ratio molar percentage of metal:ligand. 0.253 g (1.0 mmol) of sulfamethoxazole ligand was dissolved in 10 ml of methanol and left to stir at room temperature until full dissolve. Separately0.3038 g (1.0 mmol) of Bu_2SnOCl was dissolved in 5 ml of methanol. The last was added to the stirred sulfamethoxazole mixture and left to stir at reflux for 8 hours. The precipitations were filtered off, washed and dried. Then the crude product was recrystallized from methanol produce pure target product as shown by ^{1}H NMR, ^{13}C NMR, ^{119}Sn NMR and FTIR analysis.

3. Results and Discussions

3.1 Synthesis of organotin (IV) complex:

The di-organotin complex was synthesized by reacting one to one ratio of metal:ligand. The reactions were done by refluxing the reactants for 8 hours using methanol as a solvent. The crude products were purified by recrystallization from methanol and pure target products were got in very good percentage yield 83%. All products were characterized by ^{1}H NMR, ^{13}C NMR, ^{119}Sn NMR and FTIR analysis to demonstrate the chemical structures of synthesized compound. Scheme 1 shows the reaction scheme of formation di-organotin complex.



Scheme 1. Synthesis of di-butyltin (IV) oxide complex.

3.2 Characterization of dibutyltin (IV) oxide complexes

Flame atomic absorption spectrophotometer was used to determine the metal content of complexes. Thus, it has been demonstrated that the experimental results in agreement with theoretical calculations. Thus, the metal percentage demonstrated by Flame atomic absorption is 25.07% and the theoretical percent is 25.10%.

Field-emission microscopy (FESEM) technique was utilized to exhibit the surface morphology of synthesized complex. Using this approach, it can take microscopic images to the surface of synthesized materials and have an idea about their particles shape and size. This method works by focusing beam electrons and scanning the surface structure to get information about topographic features of complex surface. Furthermore, it can be getting clear, high resolution and less distorted images of examined particles by using FESEM. Figure 2 shows the FESEM images of the surface of synthesized complex as the image show the agglomerated of very small particles in homogenous way.

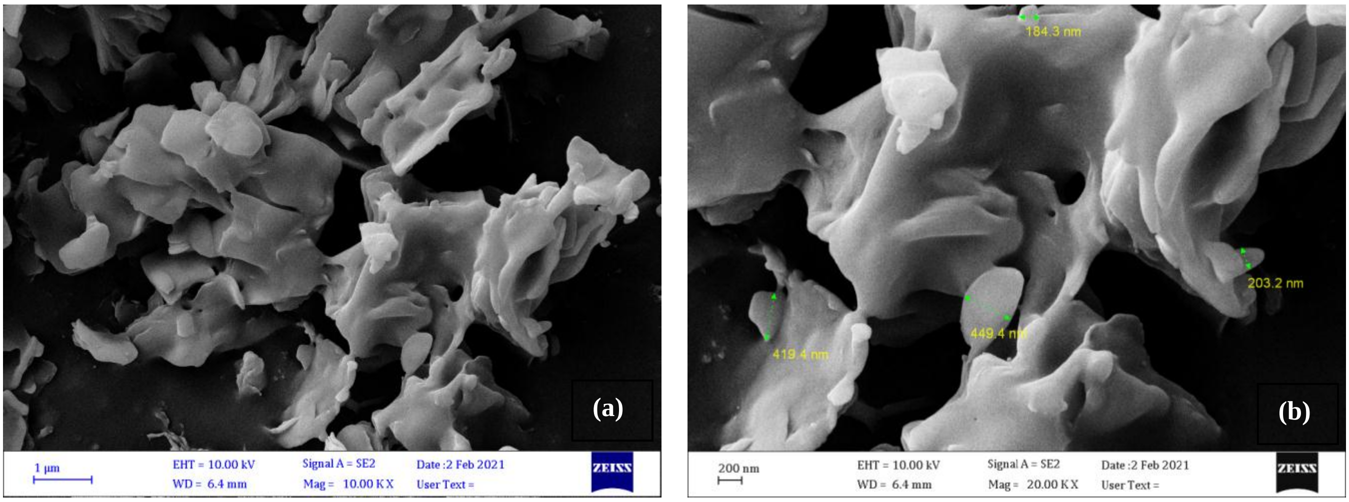


Figure 2. FE-SEM images of Bu_2SnOL_2 complex. (a) 1 micro magnification. (b) 200 nm magnification.

Energy dispersive X-ray (EDX) was utilized to provide information about elemental composition of solid surface for synthesized organotin (IV) complexes [25]. To obtain the chemical formula of synthesized material. EDX is linked to field emission scanning electron microscopy (FESEM) and this is a common chemical microanalysis procedure to determine the chemical formula. As shown in Figure 3, the EDX mapping of complex demonstrate the elemental composition of di-butyltin (IV) oxide complex.

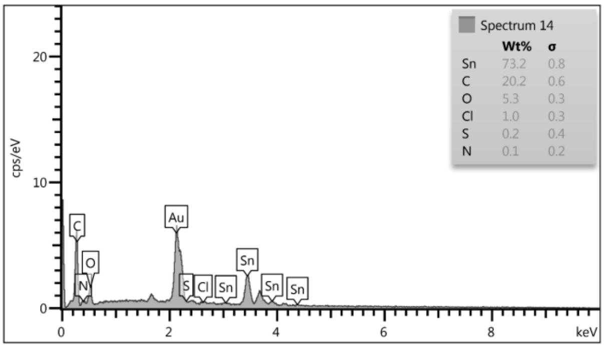


Figure 3. EDX mapping of di-butyltin(IV) oxide complex.

FTIR is considered one of the most important techniques to study the chemical or functional change of chemical structures [26]. Using this approach, it can be identify the formation of new functional groups or breaking existence functional group which gives clear evidence about the direction of the chemical reaction. Furthermore, FTIR spectrum shows the intensity of functional group absorption peak which give us indication about number of groups within the chemical structure. Di-butyltin (IV) oxide complex was characterized by FTIR and the spectrum showed all required peaks to prove the chemical structure. The most significant peaks to prove the structure of ligand and complex have been summarized in Table 1. As shown in the ligand FTIR spectrum, where NH_2 group shows two peaks symmetric and anti-symmetric between 3373 cm^{-1} and 3473 cm^{-1} where it is supposed to be. While NH showed peak around 3294 cm^{-1}, Schiff base group (C=N) around 1501 cm^{-1} and SO_2 two peaks between 1127 cm^{-1} to 1379 cm^{-1}. Figures 5 shows the FTIR spectra of synthesized complex, where observed shifting in C=N and SO_2 peaks due to the formation of coordination bonds, N–Sn and O–Sn [27].

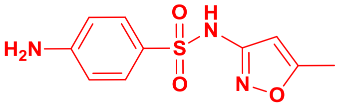
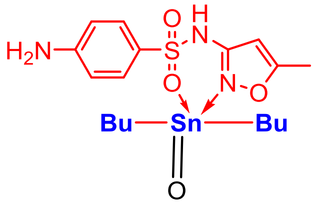
Table 1. FTIR spectroscopic data for ligand and complex.

Compounds	**Wave number cm^{-1}**			
	NH_2	N–H	C=N	SO_2
L	3463.64 3372.65	3294.91	1501	1127 1337

Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy was also applied to identify the chemical structure of synthesized materials. It considers one of the most important technique to characterize the chemical structure by determining the hydrogen atoms within the compound structure according to their environment [28, 29]. The ^{1}H-NMR spectra of synthesized complexes show all required peaks to demonstrate the chemical structure of resulting compounds. Thus DMSO-d_6 was used as a good solvent to prepare the ^{1}H-NMR samples. As shown in the ^{1}H-NMR spectrum of ligand, where showed broad singlet peak that resonate at 11.07 ppm due to the exchange proton of NH group. They also show all the aromatic protons with the expected multiplicity and chemical shifts. It has also showed a multiple peak at 6.23-6.19 ppm which is related to hetro-aromatic hydrogen close to higher electronegative atoms (nitrogen, and oxygen) which causes de-shielding of the proton.

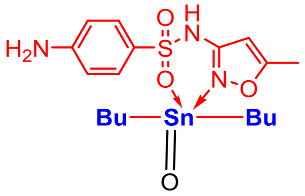
^{1}H NMR spectrum of synthesized compound shows clearly reveal the shift of NH group signal value toward 3.5 ppm. All ^{1}H NMR data have been summarized in Table 2. For Bu_2SnOL complex the spectrum shows extra peaks at 1.3 ppm and 0.9 ppm for butyl groups linked to tin with ratio 1:2 ligand to alkyl groups and that's clear evidence that one unit of ligand linked to tin.

Table 2. ^{1}H-NMR spectral data for ligand and metal complexes.

Compound	**^{1}H-NMR (400 MHz: DMSO-d_6, δ, ppm, *J* in Hz)**
	11.07 (s, exch 1H, NH), 7.58 (d, *J* = 8.0 Hz, 2H, Ar), 6.70 (d, *J* = 8.0 Hz, 2H, Ar), 6.23-6.19 (m, exch 2H, NH_2, and 1H, Ar), 2.41 (s, 3H, CH_3).
	11.07 (s, exch 1H, NH), 7.58 (d, *J* = 8.0 Hz, 2H, Ar), 6.70 (d, *J* = 8.0 Hz, 2H, Ar), 6.23-6.19 (m, exch 2H, NH_2, and 1H, Ar), 2.40 (s, 3H, CH_3), 1.30 (m, 12H, $6CH_2$), 0.90 (t, *J* = 6.7, 6H, $2CH_3$).

The ^{13}C NMR spectra of synthesized complex were analyzed and demonstrated the existence of needed peaks to prove their chemical structures and all data of ^{13}C NMR are summarized in Table 3. The ligand ^{13}C NMR spectrum shows 8 peaks which is related to eight carbon atom environments. One peak at aliphatic region (11.86 ppm) returns to the side CH_3 group. While Bu_2SnOL complex spectrum shows extra four peaks in aliphatic region return to butyl groups linked to tin.

Table 3. ^{1}H-NMR spectral data for ligand and metal complexes.

Compound	**^{1}H-NMR (400 MHz: DMSO-d_6, δ, ppm, *J* in Hz)**
	169.74, 157.79, 153.14, 128.67, 123.90, 112.40, 95.12, 11.89
	169.72, 157.78, 153.13, 128.66, 123.89, 112.39, 95.12, 27.4, 25.3, 22.51, 14.1, 13.80.

119-Tin nuclear magnetic resonance technique is widely utilized to identify the organotin compounds and also tin inorganic materials in both solid and liquid states. The importance of ^{119}Sn-NMR spectrum is demonstrating the tin coordination number and also proves the existence of single organotin compound when the spectrum shows only one sharp singlet peak [30-32]. DMSO-d_6 was used as deuterated solvent to record the ^{119}Sn-NMR spectra of synthesized complex. The ^{119}Sn-NMR spectra show peaks at -231.02 for Bu_2SnOL complex. Hence this is the region of hexa-coordinated organotin (IV) complexes [33-36].

The ultraviolet technique was utilized to characterize the ligand and prepared complexes using DMSO as a polar solvent. The spectrum of synthesized complex shows peak at lambda maximum around 300 nm which could belongs to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ electronic transition but they are overlapped. It does not notice a peak at visible region because Sn (IV) complexes are diamagnetic and there is no d-d transition. The UV adsorption region for all measured compounds were around 270-340 nm and this makes these aromatic materials very important as photo-stabilizers as will be explained in more details next section.

4. Conclusion

To summarize di-organotin (IV) complex was successfully synthesized using sulfamethoxazole drug as a ligand. The chemical structures of new complexes (Bu_2SnOL) were demonstrated using various spectroscopic techniques such as Fourier transform infrared, ^{1}proton nuclear magnetic resonance, ^{13}carbon nuclear magnetic resonance, and ^{119}tin nuclear magnetic resonance, ultraviolet-visible spectroscopies. The surface features of complexes have also exhibited by field emission scanning electronic microscopy. In future it is going to use this complex as a photo-stabilizer of various plastic polymers such as polyvinyl chloride and polystyrene.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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