



## Design of organotin (IV) complexes derived from ciprofloxacin

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### Abstract

Organotin compounds find a bigger range of technological and industrial applications. Many of these applications involve catalysis, often in polymer chemistry as stabilizers and in a biological application as well. In this research three organotin (IV) complexes were synthesized of the type  $\text{Ph}_3\text{SnL}$ ,  $\text{Me}_2\text{SnL}_2$  and  $\text{Bu}_2\text{SnL}_2$  of the ligand ciprofloxacin (**1**-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid). The prepared complexes were characterized by infrared spectral data and elemental analysis. From the FTIR spectral data octahedral geometry was proposed for  $\text{Me}_2\text{SnL}_2$  and  $\text{Bu}_2\text{SnL}_2$ , while  $\text{Ph}_3\text{SnL}$  complex has trigonal bipyramid geometry. The symmetric and asymmetric stretching vibrations band of carboxylate group showed ( $\Delta\nu \text{COO}^-$ ) values were less than  $200 \text{ cm}^{-1}$  gave an indication for the ligand to show bidentate characteristic

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### 1. Introduction

The chemistry of organotin (IV) complexes has developed considerably during last 30 years, highlighting the syntheses of a number of complexes with interesting characteristics [1–3]. Tin can be present as an element in a wide variety of both inorganic and organometallic compounds. Organometallic tin compounds or organotin are characterized by the presence of at least one covalent carbon - tin bond. Although tin may exist either in the  $\text{Sn}^{2+}$  or in the  $\text{Sn}^{4+}$  oxidation state, almost all organotin have a tetravalent structure. Depending on the number of organic moieties, the organotin compounds are classified as mono-, di-, tri-, and tetraorganotins. In compounds of industrial importance, methyl, butyl, octyl and phenyl groups form the organic substituents, while the anion is usually chloride, fluoride, oxide, hydroxide, carboxylate, or thiolate [4]. Organotin carboxylates have attracted considerable attention due to their widely used applications in many fields such as biological activity and potential antineoplastic and anti-tuberculosis agents [5], and cytotoxicity [6] as well as their industrial and agricultural applications [7–10]. Crystallographic studies have reveal that organotin carboxylates adopt structures which are dependent on both the nature of the substitute bond to the tin atom and on the type of carboxylate ligand [11, 12]. Studies on organotin (IV) derivatives containing carboxylate ligands with additional

donor atom, such as nitrogen, have revealed new structural types which may lead to complexes with different activity [13]. Ciprofloxacin (CFL) is a synthetic, broad-spectrum fluoroquinolone antibacterial agent for oral administration [14]. It is active against a wide variety of aerobic gram-negative and gram-positive bacteria. Fluoroquinolones are an important class of antibacterial compounds which possess a fluorine atom at position-6 and a piperazine ring at position-7 of the quinolinone-carboxylic acid (Figure 1). These drugs are known to possess an appreciable antibacterial activity [15].

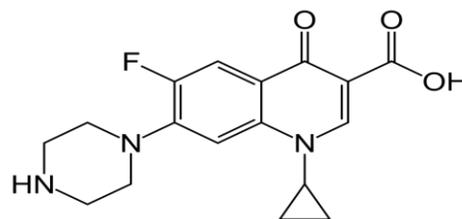


Figure 1. Structure of ciprofloxacin

### 2. Methods and Materials

Ciprofloxacin, reagent and solvents were supplied from

Sigma-Aldrich Chemical Company (Gillingham, UK) and used without any further purification. The Fourier Transform Infrared Spectroscopy (FT-IR) spectra frequencies were recorded in the range of (400-4000)  $\text{cm}^{-1}$  as KBr disc by using FTIR 8300 Shimadzu spectrophotometer. The Elemental analysis (CHN) of the percentage compositions of the elements (C%, H%, N%) for the prepared compounds were determined using EM-017mth instrument.

### 2.1 Synthesis of Triphenyltin (IV) complex

Triphenyltin (IV) complex were synthesized by dissolving the free ligand (0.33 g, 1 mmol) in hot methanol (15 ml) and adding drop wise a methanolic solution of  $\text{Ph}_3\text{SnCl}$  (0.39 g, 1 mmol) in (10 ml) with stirring. The resulting solution was stirred at room temperature for 10 min and then refluxed for 6 h. It was filtered and the volatiles were removed in vacuum, which on recrystallization from methanol afforded white powder.

### 2.2 Synthesis of Diorganotin (IV) complexes

The free ligand (2 mmol) dissolved in 20 ml of methanol was slowly added, with constant stirring, to methanolic solution of  $\text{Me}_2\text{SnCl}_2$  or  $\text{Bu}_2\text{SnCl}_2$  (1 mmol). The mixture was refluxed for 8 h. The resulting solution was filtered and concentrated in vacuum. On the recrystallization from methanol gave an off white to pale yellow powder.

## 3. Result and discussion

### 3.1 Synthesis

Four organotin complexes,  $\text{Ph}_3\text{SnL}$ ,  $\text{Me}_2\text{SnL}_2$ ,  $\text{Bu}_2\text{SnL}_2$  and  $\text{Bu}_2\text{SnOL}$  were synthesized from reactions between diorganotin dichlorides or triorganotin chloride with ciprofloxacin as a ligand (L) in methanol under reflux conditions for 6–8 h (figure 2 and 3). a 1:1 molar ratio of L and  $\text{Ph}_3\text{SnCl}$  was used In the case of  $\text{Ph}_3\text{SnL}$ , while, a 2:1 molar ratio of L and  $\text{R}_2\text{SnCl}_2$  (R = Me, Bu) was used for the production of  $\text{Me}_2\text{SnL}_2$  and  $\text{Bu}_2\text{SnL}_2$ . The structures of Sn (IV) complexes were characterized by and FTIR spectroscopy and elemental analysis.

Table 1. FTIR spectroscopic data for L and organotin (IV) complexes.

Band Assignment	L	$\text{Ph}_3\text{SnL}$	$\text{Me}_2\text{SnL}_2$	$\text{Bu}_2\text{SnL}_2$
O-H	3529	—	—	—
N-H	3433	3406	3448	3444
C=O carboxyl group	1708	1732	1730	1733
C=O ketone group	1624	1627	1628	1627
$\nu(\text{COO})_{\text{asym}}$	1575	1589	1590	1587
$\nu(\text{COO})_{\text{sym}}$	1509	1508	1507	1510
$(\text{COO})\nu\Delta$	66	81	83	77
Sn-C	—	540	520	525
Sn-O	—	440	447	432
Sn-N	—	410	415	408

### 3.2 Infrared Spectroscopy

By comparing the main FTIR frequencies of the ciprofloxacin and that of tin complexes it shows that there were two very strong absorptions peaks in the spectrum of the ligand at (1708) $\text{cm}^{-1}$  due to the carboxylic group and (1624) $\text{cm}^{-1}$  for ketone group. The sharp absorption peak at (3529)  $\text{cm}^{-1}$  in the spectrum of the ligand that stands for (OH) group was not detected in the spectrum of the complexes, indicating that this moiety participated in the bonding to the metal. The symmetric and asymmetric modes of the carboxylic group would account for the bands around (1590-1500)  $\text{cm}^{-1}$  [16]. The  $\Delta\nu(\text{COO})$  values were obtained by the following equation [ $\Delta\nu(\text{COO}) = \nu_{\text{asym}}(\text{COO}) - \nu_{\text{sym}}(\text{COO})$ ] and the result showed  $\Delta\nu(\text{COO}) < 200 \text{ cm}^{-1}$ , in this case the (COO) considered as bidentate [17]. The IR spectral data for the organotin complexes showed new absorption bands. These bands are assigned for  $\nu(\text{Sn-C})$ ,  $\nu(\text{Sn-O})$ , and  $\nu(\text{Sn-N})$  that resonate within the 516-540, 447-426, and 408-416  $\text{cm}^{-1}$  regions respectively. The appearance of such bands give approve for the coordination between ligand and Sn (IV). The coordination takes place between secondary amine, carboxylate and alkyl or phenyl group [18, 19]. From the FTIR spectral data an octahedral geometry was proposed for  $\text{Me}_2\text{SnL}_2$  and  $\text{Bu}_2\text{SnL}_2$ , while  $\text{Ph}_3\text{SnL}$  complex has trigonal bipyramid geometry. The elemental content of the Sn (IV) complexes were observed by elemental analysis. The result shows generally an agreement with the calculated values of the ligand and its complexes.

Table 2. Melting points and Elemental Analyses (%) Calcd (Found) for L and Sn(IV) complexes.

Compound	Color	Melting point	C%	H%	N%
L	White	> 300	61.56 (61.93)	5.48 (6.02)	12.67 (12.59)
$\text{Ph}_3\text{SnL}$	White	> 300	61.7 (56.58)	4.88 (5.15)	6.17 (6.54)
$\text{Me}_2\text{SnL}_2$	Pale yellow	> 300	53.28 (53.98)	5.22 (5.60)	10.33 (10.51)
$\text{Bu}_2\text{SnL}_2$	Off white	> 300	56.32 (56.65)	6.08 (6.70)	9.38 (10.14)

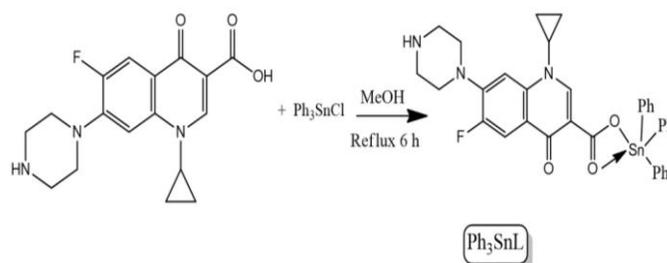


Figure 2: Synthesis of triphenyltin (IV) complex

