

Communication

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Keywords: Di-Carboxylate; Pyrazole; Tin Sn(VI); Crystal Structures; Oxidation Reaction.



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Communication

# New Catalysts based on Carboxylate Sn(IV) Complexes Used in the Oxidation Reaction of 3,5-di-tert-butylcatechol to 3,5-di-tert-butyl-o-benzoquinone

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**Abstract:** It is at the chemistry-biology interface that this work that we have carried out takes place. Indeed, the expected goal is to develop simple molecules, capable of activating the catalytic action of certain metalloenzymes such as tyrosinase. The official name of an enzyme includes the type of reaction catalyzed, the name of the substrates involved. In this work, we carried out the study of the catalytic activity of the complexes of organotin carboxylates synthesized vis-à-vis the oxidation of 3,5-di-tert-butylcatechol. The results obtained show that the various complexes exhibit good catalytic activity for the oxidation of 3,5-di-tert-butylcatechol under mild conditions. The complexes that showed good catalytic activity are the compounds C<sub>1</sub> and C<sub>2</sub>.

**Keywords:** Di-Carboxylate ; Pyrazole; Tin Sn(VI); Crystal Structures; Oxidation Reaction

## 1. Introduction

In recent decades, organotin compounds have attracted the attention of researchers in various fields such as the fundamental field (synthesis, structure, hybridization) [1–5], as well as in the field of applications (agriculture, chemical industry, pharmacology) [6–9].

Organometallic chemistry plays a very important role in exploring the properties of metal ions for the design of new drugs [10,11]. This area has been stimulated by the success of various platinum-based complexes. Thus, cis-platinum or carboplatin is still considered to be the best-selling anticancer drug in the world, thanks to its reduced toxicity compared to other organometallic compounds [10–12]. However, the use of these platinum complexes is severely limited by their side effects. This has prompted chemists to employ different strategies to develop new anti-cancer agents based on the other metals. The use of organometallic compounds as drugs is very common these days because they offer potential advantages over organic-based drugs [13].

New organotin (IV) carboxylate complexes are being synthesized with the aim of obtaining new anti-cancer agents with more effective activity than cis-platinum or other clinically approved drugs [13]. In addition to the advantages of high activity over the platinum compound, tin complexes are much cheaper. Thus, reduction of doses and enhancement of effects will be achieved [13–16].

During the last decades, organotin compounds are widely used in many industrial and agricultural applications. The most important applications are those related to the catalytic activity of organic reactions [6], as well as their use as biocides due to their antifungal properties [7,8]. For

some time, organotin compounds have been studied for their antitumor activity [9]. Today, a number of interesting biological applications have been found for organotin complexes with amino acids [17,18], thiols [19], o-phenanthroline, bipyridine, histidine, azomethines and carboxylates [13,20–23], which are effective against various tumors.

Organotins are compounds containing at least one covalent tin-carbon bond (Sn-C), they are represented by the general formula  $R_nSnX_{4-n}$ , with  $n$  between 1 and 4. Organotin compounds are classified as mono-, di-, tri- and tetraorganotins, which are represented by  $RSnX_3$ ,  $R_2SnX_2$ ,  $R_3SnX$  and  $R_4Sn$  respectively. With  $R$  can be an alkyl, or aryl group, and  $X$  can be an anionic species (halide, oxide, hydroxide, carboxylates or thiolates). The carbon-tin (C-Sn) bond is weaker than the carbon-carbon (C-C) or silicon-carbon (Si-C) bond, it is relatively non-polar, but it is stable in the presence of air and humidity, moreover the stability increases by the presence of anionic groups linked to the tin atom [1–5].

In the literature, we noted studies concerning the synthesis of biomimetic oxidation catalysts to reproduce catecholase activity [24–30]. Most of the results described use catalysts with the aim of mimicking the metallic active site environment of the catecholase enzyme and also understanding the catalytic properties for activating molecular oxygen.

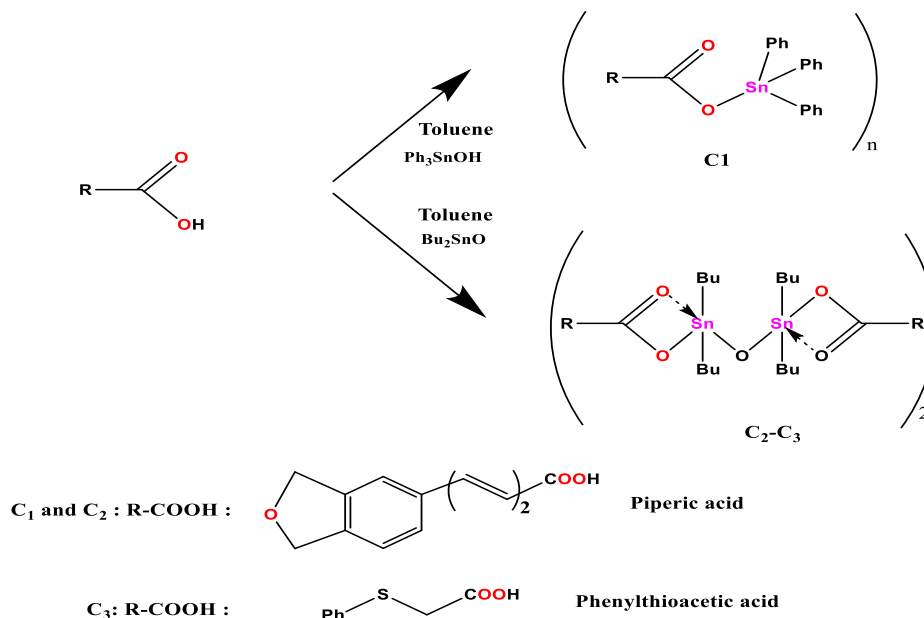
Several studies have been carried out in the field of catecholase activity of catechol derivatives in o-quinone [26,31–35].

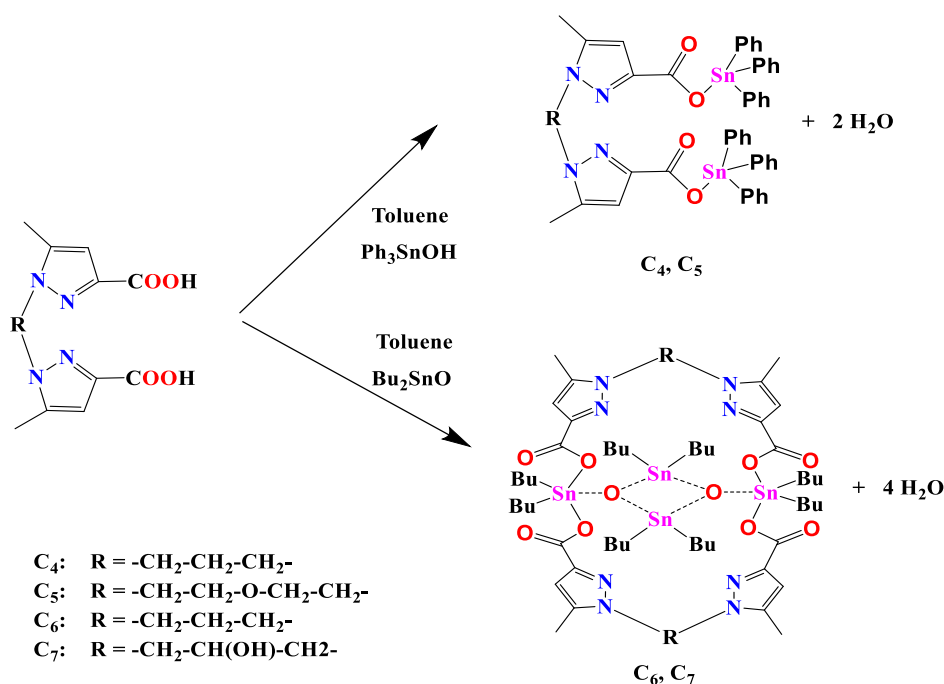
In this work, we studied the catalytic activity of certain organotin derivatives in the oxidation of 3,5-di-tert-butylcatechol to 3,5-di-tert-butyl-o-benzoquinone.

## 2. Methods and Materials

### 2.1. Synthesis of Organotin (IV) Carboxylates C1-C7

The elaboration of the target compounds **C1-C7** was performed as showed in the Scheme 1 [36–38].





**Scheme 1.** Synthesis pathway of tin complexes **C1-C7** [36–38].

## 2.2. Synthesis of Complex (C<sub>1</sub>):

A mixture of triphenyltin hydroxide (1 mmol) and piperic acid **L** (1 mmol) was heated under reflux in toluene (50 mL) for 10h in a Dean-Stark apparatus for azeotropic removal of the water formed in the reaction (Scheme 1). After cooling to room temperature, the solution was filtered. Yellow crystals, suitable for X-ray analysis, formed upon slow evaporation of the solvent after one week. (Yield = 75%); mp =143-145°C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 5.90 (s, 2H, O-CH<sub>2</sub>-O); 6.00 (d, 1H, CH-COO); 6.69 (d, 1H, C-CH=CH), 6.71 (d, 1H, C-CH=CH-C), 6.81 (dd, 2H, C-CH=CH-CH), 6.91 (s, 1H, C-CH=C), 7.6 (dd, 1H, CH=CH-COO); 7.38-7.69 (m, 15H, SnPh<sub>3</sub>), <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ:101.54 (O-CH<sub>2</sub>-O); 120.67 (CH-COO); 122.90 (C-CH=CH), 108.53 (C-CH=CH-C), 139.92 (C-CH=CH-CH), 124.80 (C-CH=CH-CH), 105.9 (C-CH=C), 146.00 (CH=CH-COO), 173.58 (COO), Sn-phenyl skeleton: 138.28 (C<sub>ipso</sub>); 137.06 (C<sub>ortho</sub>); 128.86 (C<sub>meta</sub>); 130.13 (C<sub>para</sub>). IR (cm<sup>-1</sup>): 1630 ν<sub>as</sub>(COO); 1420 ν<sub>s</sub>(COO); 560 ν(Sn-C); 465 ν(Sn-O).

## 2.3. Synthesis of Complex (C<sub>2</sub>):

The complex **C2** was synthesized in a similar way to that of **C1**, Dibutyltin oxide n-Bu<sub>2</sub>SnO (1 mmol) and piperic acid (1 mmol) in toluene (50 mL) were refluxed for 8h under azeotropic removal of H<sub>2</sub>O by a Dean-Stark trap (Scheme 1). After cooling down to the room temperature, the solution was filtered. The filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then dissolved in minimum amount of ethanol and dichloromethane. Yellow crystals, suitable for X-ray analysis, formed up on slow evaporation of the solvent after one week. (Yield = 68%); mp =126-128°C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 0.84 (t, 24 H, *J* = 8 Hz, CH<sub>3</sub>); 1.18–1.32 (m, 48H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 5.92 (s, 8H, O-CH<sub>2</sub>-O); 7.87 (d, 4H, CH-COO); 5.84 (d, 4H, C-CH=CH); 7.86 (d, 4H, C-CH=CH-C); 6.68 (dd, 8H, C-CH=CH-CH); 6.94 (s, 4H, C-CH=C); 7.24 (dd, 4H, CH=CH-COO), <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ: 101.37 (O-CH<sub>2</sub>-O); 122.60 (CH-COO); 124.09 (C-CH=CH); 108.71 (C-CH=CH-C); 138.97 (C-CH=CH-CH); 124.09 (C-CH=CH-CH); 105.91 (C-CH=C); 143.83 (CH=CH-COO); 174.60 (COO); 14.03 (CH<sub>2</sub>-CH<sub>3</sub>); 26.91, 27.07, 27.47, 28.3, 28.44 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>). IR (cm<sup>-1</sup>): 1638 ν<sub>as</sub>(COO); 1425 ν<sub>s</sub>(COO); 563 ν(Sn-C); 467 ν(Sn-O).

#### 2.4. Synthesis of Complex (C<sub>3</sub>):

The synthesis of the title compound was carried out in an identical manner as described for **1** by using di-*n*-butyltin oxide (1mmol) and phenyl thioacetic acid (1mmol) (Scheme 3). After work-up, the solid was recrystallized from ethanol and dichloromethane, which up on slow evaporation afforded colorless crystals. (Yield = 65%); mp =142-144°C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 1.33 (t, 24 H, *J* = 8 Hz, CH<sub>3</sub>); 1.11–1.30 (m, 48H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 7.87 (d, 4H, CH-COO); 5.84 (m, 12H, C-CH=CH-CH=CH, Ph); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ: 37.62 (S-CH<sub>2</sub>-COO); 125.86 (=CH-CH=CH-CH); 127.74 (=CH-CH=CH-CH); 128.94 (CH=C-S); 136.51 (CH=C-S); 174.74 (COO); 14.03 (-CH<sub>2</sub>-CH<sub>3</sub>); 26.91, 27.07, 27.47, 28.3, 28.44 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>). IR (cm<sup>-1</sup>): 1638 ν<sub>as</sub>(COO); 1425 ν<sub>s</sub>(COO); 563 ν(Sn-C); 467 ν(Sn-O).

#### 2.5. Synthesis of Complex (C<sub>4</sub>):

A mixture of triphenyltin hydroxide (2 mmol) and **L** (1 mmol) was heated under reflux in toluene (50 mL) for 10h in a Dean-Stark apparatus for azeotropic removal of the water formed in the reaction. After cooling to room temperature, the solution was filtered. Suitable colorless crystals were obtained by a slow evaporation of solvent (Yield = 68%); mp = 199-200°C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 2.13 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-N); 2.24 (s, 6H, CH<sub>3</sub>-Pz); 3.88 (t, 4H, -CH<sub>2</sub>-N); 6.65 (s, 2H, HPz); 7.63-7.81 (m, 30 H, SnPh). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ: 10.83(CH<sub>3</sub>-Pz); 58.5 (-CH<sub>2</sub>-N); 29.5 (CH<sub>2</sub>-CH<sub>2</sub>-N); 108.45 (CH-Pz); 142.20 (CH<sub>3</sub>-C=C); 143.69 (C-C=O); 166.08 (C=O), Sn-phenyl skeleton: 128.86 (C<sub>meta</sub>); 136.98 (C<sub>ipso</sub>); 136.75 (C<sub>ortho</sub>); 130.3 (C<sub>para</sub>). IR(cm<sup>-1</sup>): 1650 ν<sub>as</sub>(COO); 1400 ν<sub>s</sub>(COO); 530 ν(Sn-C); 460 ν(Sn-O).

#### 2.6. Synthesis of Complex (C<sub>5</sub>):

The complex **C5** was synthesized in a similar way to that of **C4**. Suitable colorless crystals were obtained by a slow evaporation of solvent. (Yield = 65%); mp = 206-207°C; <sup>1</sup>H NMR(300 MHz, DMSO-*d*<sub>6</sub>) δ: 2.10 (s, 6H, CH<sub>3</sub>-Pz); 3.6 (t, 4H, -CH<sub>2</sub>-N); 4.03 (t, 4H, -O-CH<sub>2</sub>-CH<sub>2</sub>-N); 6.25 (s, 2H, H-Pz); 7.19-7.93 (m, 30H, SnPh). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) □: 10.59 (CH<sub>3</sub>-Pz); 47.78(-CH<sub>2</sub>-N); 69.45 (-O-CH<sub>2</sub>-CH<sub>2</sub>-N); 108.55 (CH-Pz); 144.53 (CH<sub>3</sub>-C=C); 143.97 (C-C=O); 168.17(C=O), Sn-phenyl skeleton: 138.38 (C<sub>ipso</sub>); 136.47 (C<sub>ortho</sub>); 128.71 (C<sub>meta</sub>); 130.13 (C<sub>para</sub>). IR (cm<sup>-1</sup>): 1650 ν<sub>as</sub>(COO); 1400 ν<sub>s</sub>(COO); 530 ν(Sn-C); 460 ν(Sn-O).

#### 2.7. Synthesis of Macrocyclic Complex (C<sub>6</sub>):

A mixture of di-*n*-butyltin oxide (2 mmol) and **L1** (1 mmol) was heated under reflux in toluene (50 mL) for 10 h in a Dean-Stark apparatus for azeotropic removal of the water formed in the reaction. After cooling to room temperature, the solution was filtered. Suitable colorless crystals were obtained by slow evaporation of the solvent. Yield = 67%. mp = 104-105 °C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 0.62-0.81 (t, 24 H, *J* = 8 Hz, CH<sub>3</sub>); 1.29–1.60 (m, 48H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 2.25 (s, 12H, CH<sub>3</sub>-Pz); 2.41 (m, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-N); 4.10 (t, 8H, *J* = 6 Hz, -CH<sub>2</sub>-N); 6.53 (s, 4H, HPz). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ: 11.27 (CH<sub>3</sub>-Pz); 14.03 (CH<sub>2</sub>-CH<sub>3</sub>); 26.06 (CH<sub>2</sub>-CH<sub>2</sub>-N); 26.91, 27.07, 27.47, 28.3, 28.44 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>); 46.43 (-CH<sub>2</sub>-N); 108.42 (CH-Pz); 138.85 (CH<sub>3</sub>-C=C); 145.30 (C-C=O); 166.28 (C=O). <sup>119</sup>Sn NMR (150 MHz, CDCl<sub>3</sub>): -29.2, -183.4. IR (cm<sup>-1</sup>): 1630 ν<sub>as</sub>(COO); 1420 ν<sub>s</sub>(COO); 560 ν(Sn-C); 465 ν(Sn-O).

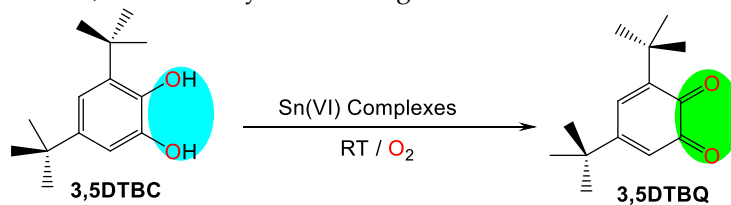
#### 2.8. Synthesis of Macrocyclic Complex (C<sub>7</sub>)

The complex **C7** was synthesized in a similar way to **C6**. Di-*n*-butyltin oxide (2 mmol) and **L** (1 mmol)]. Suitable colorless crystals were obtained by slow evaporation of the solvent. Yield = 62%. mp = 97-98 °C. <sup>1</sup>H NMR (250 MHz, DMSO-*d*<sub>6</sub>) δ: 0.6–1.60 (m, 72H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 1.75 (s, 8H, H<sub>2</sub>O); 2.27 (s, 12 H, CH<sub>3</sub>Pz); 3.95-4.24 (m, 8H, CH<sub>2</sub>-CH(HO)-CH<sub>2</sub>); 4.73 (m, 2H, HO-CH-CH<sub>2</sub>-Pz); 5.57 (d, 2H, *J* = 6Hz, HO-CH-CH<sub>2</sub>); 6.45 (s, 4H, HPz). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ: 11.37 (CH<sub>3</sub>Pz); 13.62, 13.64 (CH<sub>2</sub>-CH<sub>3</sub>); 25.85, 26.74, 26.95, 27.45 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>); 52.45 (CH<sub>2</sub>-CH(HO)-CH<sub>2</sub>); 56.48 (CH<sub>2</sub>-CH(HO)-CH<sub>2</sub>); 108.42 (CH-Pz); 141.63 (CH<sub>3</sub>-C=C); 144.55 (C-C=O); 165.92 (C=O). <sup>119</sup>Sn NMR (150 MHz, DMSO-*d*<sub>6</sub>): -31.7, -184.8. IR (cm<sup>-1</sup>): 1630 ν<sub>as</sub>(COO); 1420 ν<sub>s</sub>(COO); 560 ν(Sn-C); 465 ν(Sn-O).



## 2.9. Physical Measurements

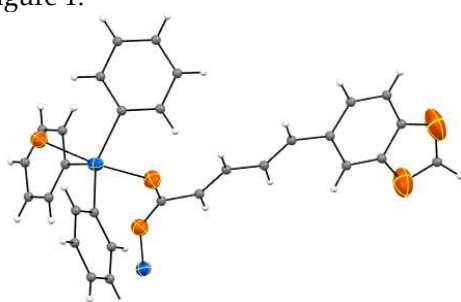
The device used is a UV-visible spectrophotometer of the PyeUnicam UV 300 type with double beams. This will allow the monitoring of the formation of 3,5-di-tert-butyl-o-benzoquinone as a function of time at room temperature. The characteristic band of this compound is 400 nm. The oxidation reaction of 3,5-di-tert-butylcatechol is given in Scheme 1.



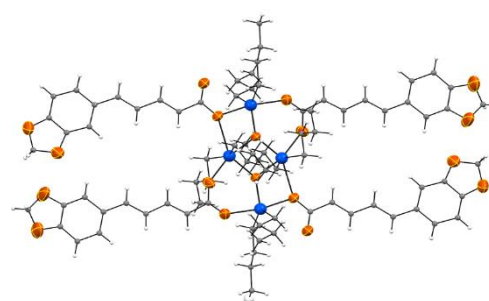
Scheme 1 : Oxidation of 3,5-di-tert-butylcatechol to 3,5-di-tert-butyl-o-benzoquinone.

## 2.10. Organotin Complexes

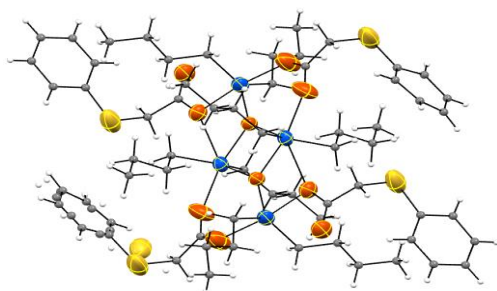
The tridimensional structures of organotin complexes that tested in this study are schemed in Figure 1.



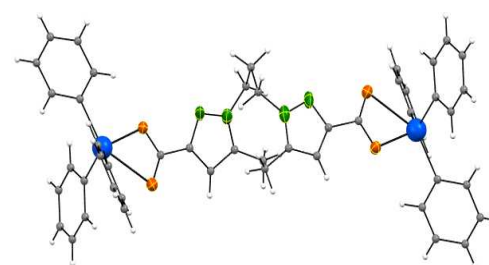
**C1:  $\alpha=90$ ,  $\beta=108.572$ ,  $\gamma=90$**



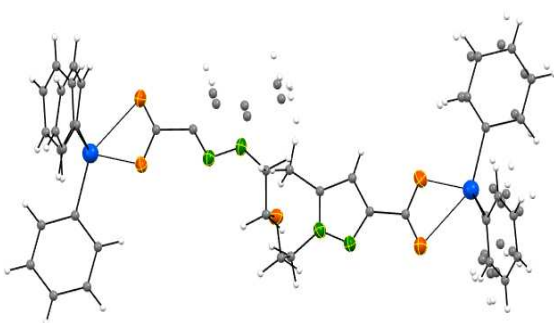
**C2:  $\alpha=76.840$ ,  $\beta=85.130$ ,  $\gamma=87.278$**



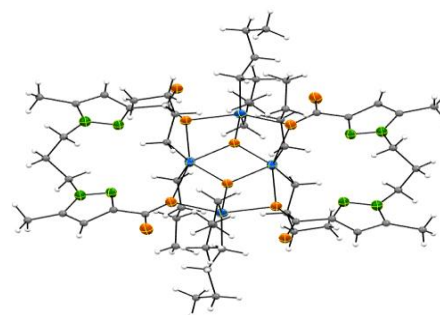
**C3:  $\alpha=91.146$ ,  $\beta=104.916$ ,  $\gamma=111.307$**



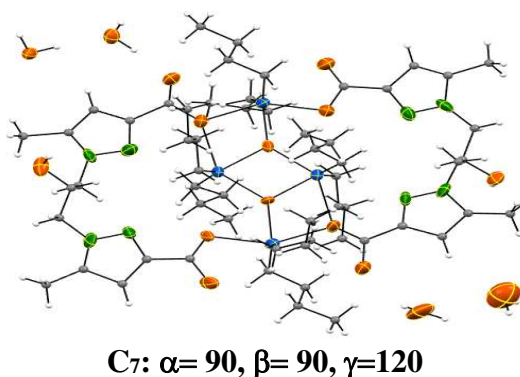
**C4:  $\alpha=90$ ,  $\beta=100.459$ ,  $\gamma=90$**



**C5 :  $\alpha=90$ ,  $\beta=101.4208$ ,  $\gamma=90$**



**C6 :  $\alpha=92.9810$ ,  $\beta=91.1800$ ,  $\gamma=116.9660$**



**Figure 1.** 3D structures of tested Sn(VI) complexes [36–38].

### 2.11. Oxidation of Catechol in the Presence of Organotin Complexes

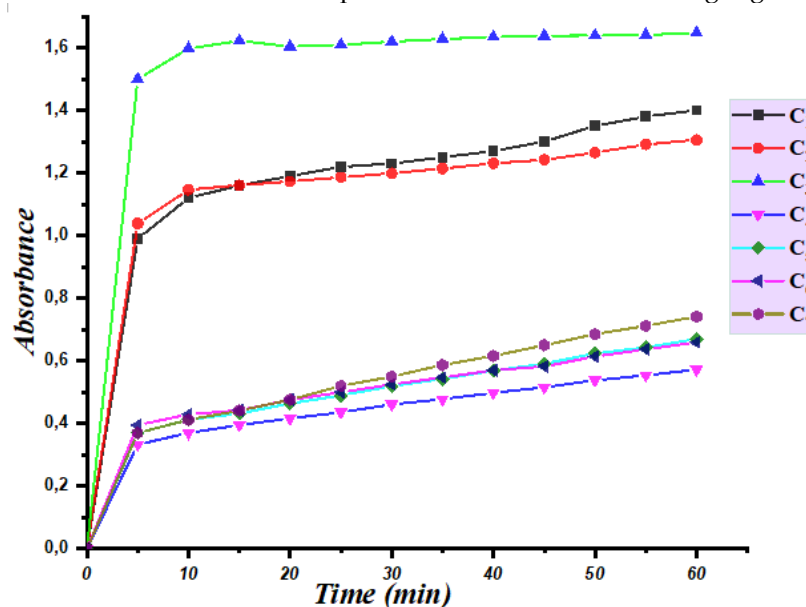
In an quartz tank, add 2 mL of a 3,5-di-tert-butylcatechol solution ( $10^{-1}$  mol. L $^{-1}$ ) to 0.3 mL of the organotin complex ( $2 \cdot 10^{-3}$  mol. L $^{-1}$ ). The evolution of the absorbance of 3,5-di-tert-butyl-o-benzoquinone is monitored for 1 hour. The manipulation was carried out in DMSO.

## 3. Results and Discussion

### 3.1. Catecholase Studies

In this work, we have carried out the study of the oxidation activity of the 3, 5-di-tert-butylcatechol to 3, 5-di-tert-butyl-o-benzoquinone by organotin complexes in the solvent dimethyl sulfoxide (DMSO).

The catalytic activity of tin C<sub>1</sub>-C<sub>7</sub> complexes has been studied in DMSO. The evolution of the absorbance as a function of time for these complexes is shown in the following Figure 2:



**Figure 1.** Absorbance evolution of 3,5-di-tert-butyl-o-benzoquinone in presence of organotin complexes (C<sub>1</sub>-C<sub>7</sub>) in DMSO.

The calculation of the oxidation rates of 3,5-di-tert-butylcatechol in the presence of organotin complexes (C<sub>1</sub>-C<sub>7</sub>), led us to the results gathered in Table 1.

**Table 1.** Oxydation rates of 3,5-di-tert-butylcatechol for organotin complexes (C<sub>1</sub>-C<sub>7</sub>).

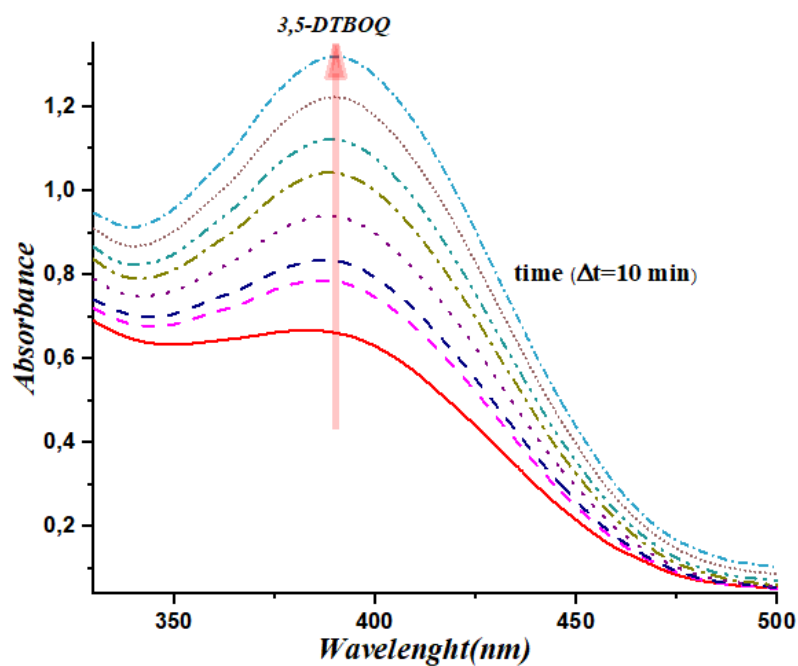
| <i>Organotin complexes</i> | <i>V (μmol. L<sup>-1</sup>. min<sup>-1</sup>)</i> |
|----------------------------|---|
| C <sub>1</sub>             | 7.83  |
| C <sub>2</sub>             | 7.72  |
| C <sub>3</sub>             | 7.26  |
| C <sub>4</sub>             | 5.95  |
| C <sub>5</sub>             | 6.98  |
| C <sub>6</sub>             | 6.86  |
| C <sub>7</sub>             | 6.84  |

The data represents the catalytic activity of twelve different organotin complexes in the oxidation of 3,5-di-tert-butylcatechol, a commonly used substrate in biochemical assays. The measured values are given in μmol. L<sup>-1</sup>. min<sup>-1</sup>, which reflects the rate of reaction of the complexes in the presence of the substrate. The results show that the catalytic activity of the different organotin complexes varies significantly, with values ranging from 5.9 μmol. L<sup>-1</sup>. min<sup>-1</sup> for C<sub>4</sub> to 7.83 μmol. L<sup>-1</sup>. min<sup>-1</sup> for C<sub>1</sub>. This suggests that the structural and chemical properties of the organotin complexes play a critical role in their catalytic activity. Interestingly, the data reveals that the top-performing complexes, C<sub>1</sub> and C<sub>2</sub>, exhibit catalytic activities of 7.83 μmol. L<sup>-1</sup>. min<sup>-1</sup> and 7.72 μmol. L<sup>-1</sup>. min<sup>-1</sup>, respectively, which are significantly higher than the other complexes tested. This suggests that these two compounds possess unique structural features that contribute to their high catalytic activity. Conversely, some of the organotin complexes, such as complexes (C<sub>4</sub> and C<sub>6</sub>), show relatively low catalytic activity with values of 5.9 μmol. L<sup>-1</sup>. min<sup>-1</sup>. These results suggest that the design of organotin complexes with optimized structural and chemical properties is crucial to achieving high catalytic activity. Overall, the data provides valuable insights into the catalytic activity of organotin complexes and highlights the potential for designing novel catalysts with enhanced activity and selectivity. This knowledge can be utilized to develop more efficient and cost-effective catalysts for various applications in industry and biomedicine.

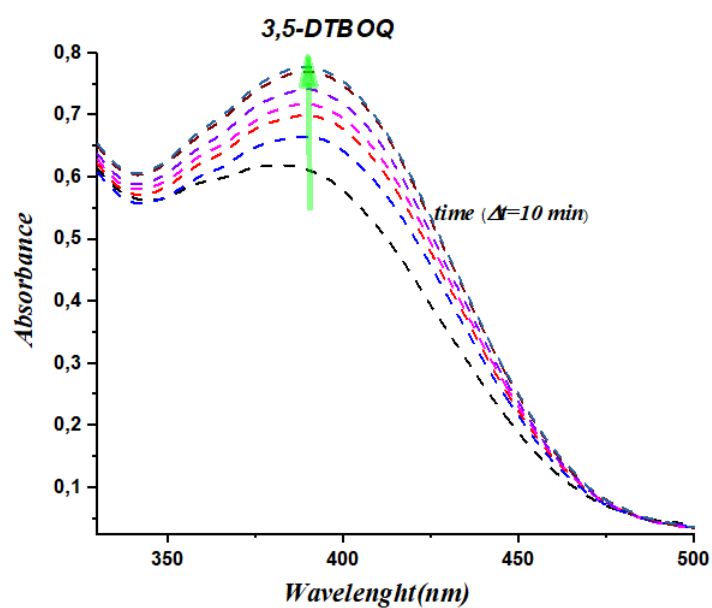
3.2. UV-Vis Spectrophotometric Study

To validate the significant catalytic activity of our synthesized organotin complexes, we conducted kinetic experiments to monitor the formation of 3,5-di-tert-butyl-o-benzoquinone in the presence of the complexes (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>5</sub>). The evolution of absorbance was recorded at λ= 400nm every 10 minutes at room temperature. The results are presented in Figures 3–6. Our results show that the complexes C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>5</sub> exhibit significant catalytic activity in the oxidation of 3,5-di-tert-butylcatechol to 3,5-di-tert-butyl-o-benzoquinone. The appearance of a centered band at 400 nm (Figures 3-4) clearly indicates the formation of the desired product, which is a testament to the catalytic efficiency of the organotin complexes. The kinetic data obtained provides further evidence of the catalytic activity of our complexes, with the absorbance values increasing steadily over time. Specifically, complexes C<sub>8</sub> and C<sub>9</sub> exhibited the highest catalytic activity, with the absorbance values increasing more rapidly than the other complexes tested. Certainly, these results demonstrate the significant catalytic activity of our synthesized organotin complexes and provide insights into their potential application in catalysis. Further studies can be conducted to optimize the structure and chemical properties of these complexes for enhanced catalytic activity and selectivity, opening up exciting possibilities for the development of novel catalysts with broad-ranging applications.

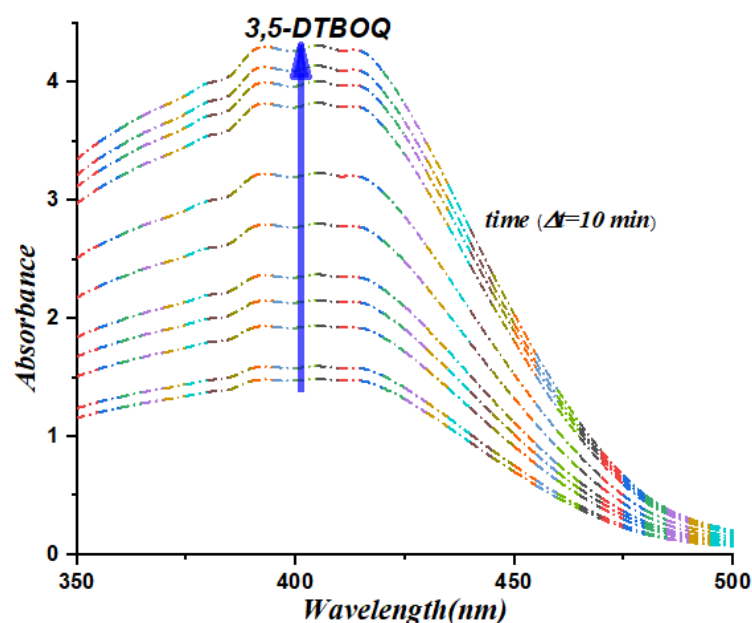




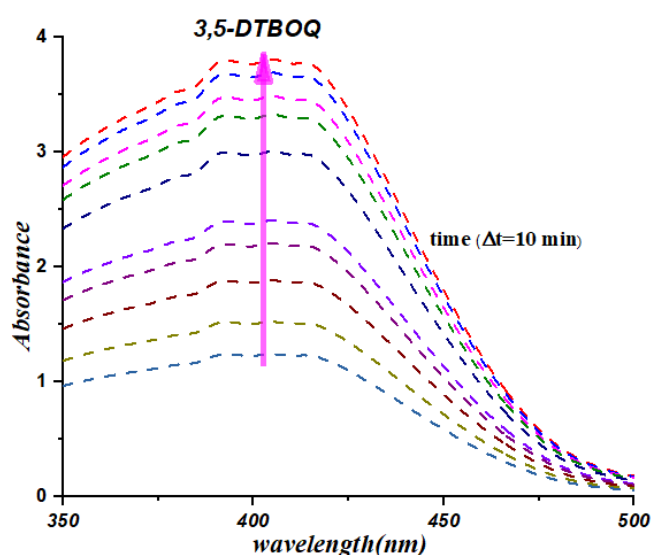
**Figure 3.** Variation in spectral behavior after the addition of complex  $C_1$  to 3,5-di-tert-butylcatechol in DMSO. Spectra are recorded every 10 min.



**Figure 4.** Variation in spectral behavior after the addition of complex  $C_2$  to 3,5-di-tert-butylcatechol in DMSO. Spectra are recorded every 10 min.



**Figure 5.** Variation in spectral behavior after the addition of complex  $C_3$  to 3,5-di-tert-butylcatechol in DMSO. Spectra are recorded every 10 min.



**Figure 6.** Variation in spectral behavior after the addition of complex  $C_5$  to 3,5-di-tert-butylcatechol in DMSO. Spectra are recorded every 10 min.

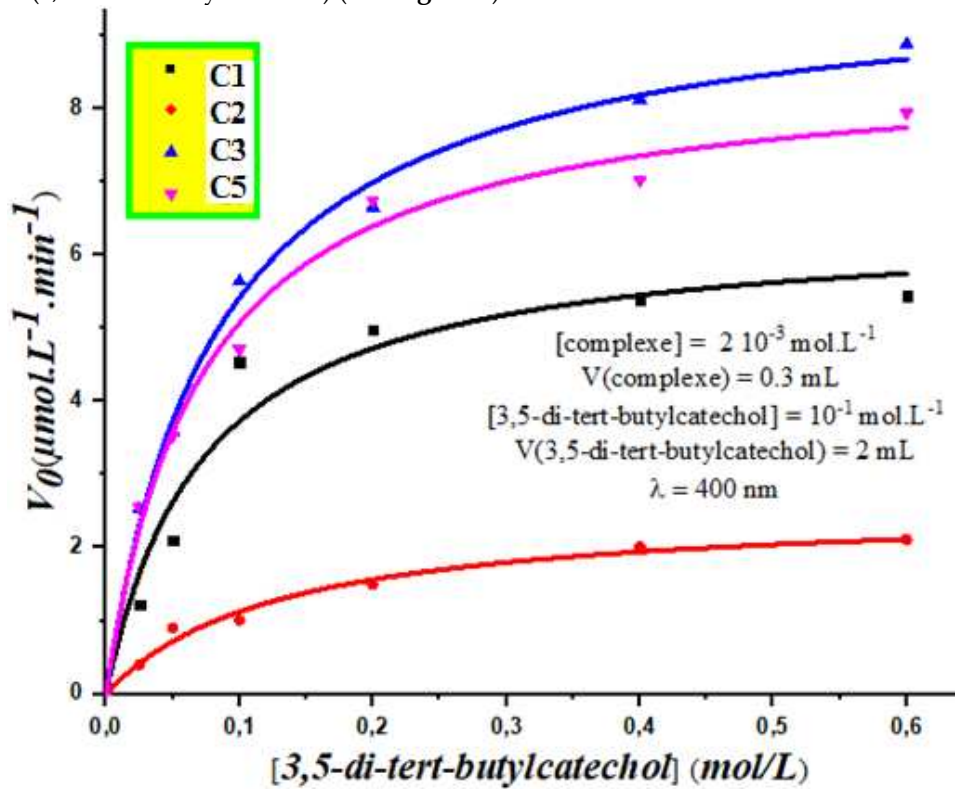
### 3.3. $V_{max}$ and $K_m$ Study

A kinetic study is a critical tool for characterizing the behavior of enzymatic reactions, and in this case, the catalytic activity of our synthesized organotin complexes. By measuring the initial rate ( $V_0$ ) of the reaction at different concentrations of the substrate, we were able to construct a graph of  $V_0$  ( $\mu\text{mol.L}^{-1}.\text{min}^{-1}$ ) versus the substrate concentration ( $\text{mol.L}^{-1}$ ), which provided us with information on the  $K_m$  and  $V_{max}$  constants.

The  $K_m$  value is a measure of the affinity of the enzyme (or in this case, the complex) for the substrate, whereas the  $V_{max}$  value represents the maximum velocity of the reaction. These kinetic constants are crucial in understanding the behavior of the reaction and optimizing its conditions. Our study involved mixing a solution of the organotin complexes with the substrate 3,5-di-tert-butylcatechol (3,5-DTBC) at varying concentrations, and monitoring the rate of the reaction over time. The results indicated that the complexes  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_5$  exhibited significant catalytic activity for the oxidation evaluation of 3,5-di-tert-butylcatechol. By determining the  $K_m$  and  $V_{max}$  constants for

each of the complexes, we were able to gain insights into their catalytic behavior, and evaluate their potential application in various catalytic processes. The obtained results can also help in optimizing reaction conditions and identifying the most effective catalyst for a given substrate. In general, our study demonstrates the power of kinetic studies in characterizing the catalytic, behavior of enzymes and organometallic complexes, and provides valuable insights for developing more efficient catalytic systems in the future.

In order to further investigate the catalytic activity of our complexes, we conducted a kinetic study to determine the  $K_m$  and  $V_{max}$  constants of the catechol oxidation reaction. To achieve this, we mixed 0.3 ml of a solution of Sn (IV) complexes C1, C3, C8, and C9 at a concentration of  $10^{-4}$  mol/L with a solution of 3,5-di-tert-butylcatechol at a concentration varying from  $2.5 \cdot 10^{-2}$  mol/L to 0.6 mol/L under ambient conditions. The initial rate ( $V_0$ ) was then plotted as a function of the substrate concentration (3,5-di-tert-butylcatechol) (see Figure 7).



**Figure 7.** Dependence of the reaction rates on the 3,5-di-tert-butylcatechol concentrations varying from  $2.5 \cdot 10^{-2}$  mol/L to 0.6 mol/L for the oxidation reaction catalyzed by C1, C3, C8 and C9 complexes.

From the results obtained, we observed a linear relationship between the initial velocities and the substrate concentration for complexes C8 and C9. This led us to apply the Michaelis-Menten model to determine the kinetic parameters of the best catalyst. Our findings indicate that the rate  $V_{max}$  for complexes C1 and C3 are  $8.80 \mu\text{mol. L}^{-1}.\text{min}^{-1}$  and  $7.90 \mu\text{mol. L}^{-1}.\text{min}^{-1}$  respectively (see Table 2).

**Table 2.** Maximum rate  $V_{max}$  and rate constants  $K_m$  of C1, C2, C3 and C5 complexes.

| Complexes | $V_{max}$ ( $\mu\text{mol. L}^{-1}.\text{min}^{-1}$ ) | $K_m$ ( $\mu\text{mol. L}^{-1}$ ) |
|-----------|---|-----------------------------------|
| C1        | 8.80  | 0.05                              |
| C2        | 8.80  | 0.05                              |
| C3        | 5.43  | 0.06                              |
| C5        | 2.13  | 0.09                              |

Interestingly, we noted a low  $K_m$  value for complex C1, indicating a strong affinity between the tested catalyst and the substrate (3,5-di-tert-butylcatechol) in DMSO organic solvent. This further confirms that complex C1 demonstrated better performance for the oxidation of the substrate (3,5-di-tert-butylcatechol) in our case. generally, these results validate the significant catalytic activity of our

organotin complexes, and highlight their potential as efficient catalysts for various applications in the future.

#### 4. Conclusion

Our study demonstrates the potential of organotin complexes as effective catalysts for the oxidation of 3,5-di-tert-butylcatechol to 3,5-di-tert-butyl-o-benzoquinone. The kinetic analysis revealed that complexes C<sub>1</sub> and C<sub>2</sub> are the most efficient catalysts, exhibiting high rates of oxidation with low K<sub>m</sub> values, indicating strong affinity between the catalysts and the substrate. The results suggest that the catalytic activity of the complexes is influenced by the concentration of the complex and the coordination environment. Furthermore, the mild reaction conditions used in this study, conducted at room temperature and with oxygen as the oxidant, make these complexes attractive candidates for further exploration in catalysis. This study adds to the growing body of knowledge on the use of organotin complexes in catalysis and provides valuable insights into the design of new and effective catalysts for various chemical reactions.

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