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SYNTHESIS, EVALUATION, AND STRUCTURAL CHARACTERIZATION OF ANTIOXIDANT DIORGANOTIN(IV) COMPLEXES DERIVED FROM AMPICILLIN: A COMPREHENSIVE STUDY

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ABSTRACT. This study offerings the preparation, structural analysis, and estimation of novel diorganotin(IV) complexes derived from an ampicillin as a ligand in terms of their antioxidant activity. The diorganotin complexes were yielded by a direct reaction between ampicillin and a different number of diorganotin(IV) chloride precursors. Various spectroscopic techniques, including CHNS, FTIR and nuclear magnetic resonance (^{1}H, ^{13}C, ^{119}Sn NMR), were used to explain the molecular structures of the produced complexes. Through in vitro experiments such as the CUPRAC and DPPH (2,2-diphenyl-1-picrylhydrazyl) free radical scavenging technique, the novel diorganotin complexes' antioxidant activity were assessed. The results were compared to that of ligand antioxidants to evaluate the effectiveness of the complexes that were produced. The structural properties of the complexes were linked to their antioxidant capacity to identify the connection between molecular structure and biological function.

KEY WORDS: Ampicillin, DPPH method, Diorganotin(IV) complexes, Antioxidants

INTRODUCTION

Antioxidants are important for inhibiting damage from free radicals and oxidative stress in biological systems [1]. Organotin complexes have been investigated in the quest for new antioxidant molecules and have demonstrated encouraging antioxidant qualities [2]. The ampicillin ligand, which has distinct structural characteristics that make it a useful ligand to produce organotin complexes, is the source of the novel organotin(IV) complexes that are the subject of this study's evaluation of antioxidant activity [3, 4].

Because of their complementary properties, ampicillin and organotin(IV) moieties together may create molecules with improved antioxidant capacity. Various investigations have highlighted the numerous biological functions of organotin(IV) complexes, such as their antitumor, antibacterial, and anti-inflammatory characteristics [5]. But little is known about their structural makeup and antioxidant capacity, particularly when it comes to ampicillin-based ligands. The coordination geometry, molecular structure and bonding interactions with the complexes will be better understood thanks to these approaches [6]. The assessment of antioxidant activity will be carried out using validated assays, including total antioxidant capacity (TAC), ferric reducing antioxidant power (FRAP) tests and 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging [7]. One stimulating option for the creation of new compounds with improved biological activity in the field of organotin(IV) complexes is the addition of ligands from popular antibiotics, such ampicillin. One beta-lactam antibiotic that is well-known for its antibacterial qualities is ampicillin [8]. But the investigation of its potential as an organotin(IV) complex ligand offers up new therapeutic uses beyond its traditional use [9]. Numerous scholarly investigations have emphasized the importance of organotin(IV) complexes in demonstrating antioxidant characteristics [10, 11]. These complexes have the capacity to reduce oxidative stress and

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scavenge free radicals, which may be advantageous in the setting of a number of disorders [12]. Determining the medicinal potential of organotin(IV) complexes generated from ampicillin ligands requires an understanding of their antioxidant activities [13]. The results of these tests will be used to assess the overall antioxidant capacity and free radical-neutralizing potential of the organotin complexes. By shedding light on the antioxidant potential of organotin(IV) complexes formed from the ampicillin ligand, this study seeks to advance knowledge of these compounds' possible uses in the pharmaceutical and medical industries. A thorough understanding of the characteristics and possible medical advantages of these novel compounds will be possible through the combination of structural characterization and antioxidant assessment [14, 15]. In this work, novel complexes of diphenyl, dibutyl, and dimethyl-tin were created by using ampicillin as a ligand in a condensation process with the respective organotin chloride ions. The diorganotin(IV) complexes demonstrated a greater percentage inhibition in both DPPH and cuprac techniques compared to the ligand, suggesting the important significance of the tin moiety in boosting the complexes' antioxidant activity. In addition, out of all the complexes, the diphenyl tin carboxylate complex exhibited the highest level of antioxidant activity. These findings imply that the produced complexes may be used to create novel antioxidant-active medicinal medicines.

EXPERIMENTAL

Synthesis of diorganotin(IV)-ampicillin complexes [16]

High yields were obtained when diorganotin(IV)-ampicillin complexes were synthesized at a molar ratio of 1:2. To make the complexes, excess ampicillin was reacted in methanol with trisubstituted tin chloride (diphenyl, dibutyl, and dimethyl tin dichloride) for five hours under reflux. The resultant solution was filtered, dried, and recrystallized to create a precipitate. Table 1 illustrates the weights and molar ratios of the diorganotin(IV)-ampicillin complex. Scheme 1 shows the synthesis of diorganotin complexes.

Table 1. The weights and molar ratios of diorganotin(IV) complexes and ligands.

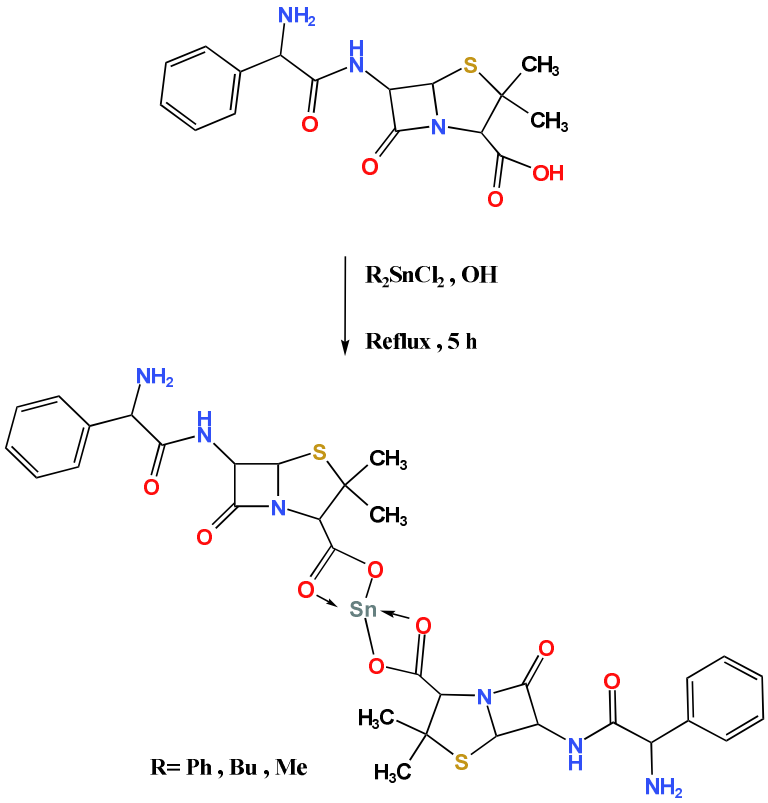
No. of compd.	Weights (g) of diorganotin(IV) dichloride			Ligand	Weights (g) of ligand	No. of molar ratios
	Ph_2SnCl_2	Bu_2SnCl_2	Me_2SnCl_2			
1	0.8595	0.7596	0.5492	Ampicillin	1.7470	1: 2

Assay for scavenging free radicals with DPPH

Antioxidants were determined according to their capacity to neutralize free radicals. The activity of radical scavenging was evaluated using the radical 2,2-diphenyl-1-picrylhydrazyl by microplate reader spectrophotometry at λ_{max}= 490 nm, as per the usual procedure. The reaction mixture contained DPPH (200 µg/mL) and test complexes in methanol (50 µg/mL). The reaction was tested for five, ten, and fifteen minutes. The data was calculated using Microsoft Excel 2010 [17, 18]. The % inhibition was calculated using the procedure below (Equation 1).

$$I\% = \frac{A\ blank - A\ sample}{A\ blank} \times 100 \quad (1)$$

where A_{blank} is the absorbance of the control reaction (all reagents except the test complex), and A_{sample} is the absorbance of the test complex [19].



Scheme 1. Synthesis of the ampicillin complex using diorganotin(IV).

Free radical scavenging using CUPRAC assay

Using microplate reader spectrophotometry at λ_{max} = 450 nm, the capacity of the complexes to undergo one electron transition was measured using neocuproine (Sigma-Aldrich, 98%) and 2,9-dimethyl-1,10-phenanthroline. The reaction mixture contained the following components: ammonium acetate buffer (100 µg/mL, pH 7.0), neocuproine solution in methanol (50 µg/mL), and $CuCl_2$ solution in methanol (50 µg/mL). Each complex solution (dissolved in methanol) received 20 µg/mL of this reagent and tannic acid (dissolved in water) [20, 21].

RESULTS AND DISCUSSION

Identification of diorganotin(IV)-ampicillin complexes

The elemental composition of the diorganotin(IV)-ampicillin complexes were determined using CHNS analysis. The results agree with the calculated values of the ligand (ampicillin) and its complexes in general (Ph_2SnL_2, Bu_2SnL_2 and Me_2SnL_2). Table 1 shows the elemental analysis data of (C, H, N, S and Sn %) colors, melting points and yields of diorganotin(IV)-ampicillin complexes along the ligand. Table 2 illustrates the physical data of the diorganotin(IV)-ampicillin complex.

Table 2. Physical data for ligand (ampicillin) and diorganotin(IV) complexes.

Compounds	Color	Melting points °C	Yields %	Calculated % (Measured %) C	H	N	S	Sn
Ampicillin (L)	White	199-201	--	55.00 (54.93)	5.48 (5.74)	12.03 (12.18)	9.18 (8.57)	--
Ph_2SnL_2	Yellowish orange	96-98	92	54.50 (54.08)	4.78 (5.04)	8.67 (8.13)	6.61 (6.31)	12.24 (12.05)
Bu_2SnL_2	Yellow	101-103	86	51.67 (50.93)	5.85 (5.74)	9.04 (9.35)	6.90 (6.53)	12.77 (12.54)
Me_2SnL_2	Brown	120-122	97	48.30 (49.03)	5.01 (5.24)	9.94 (9.33)	7.58 (7.15)	14.03 (13.93)

FTIR spectrum

The carboxylic group Figure 1 in ampicillin causes it to show a significant absorption peak in the ligand spectrum at 1775 cm^{-1} when the principal FTIR frequencies of ampicillin and its diorganotin(IV) complexes are compared. Additionally, a stretching band in the 3600-2400 cm^{-1} region is associated with the stretching vibration of carboxylic acid's hydroxyl group $^{-}$OH [22]. On the other hand, after complexation between the ligand and organotin was evident from the significant shift in wavelength of these groups' vibrations in comparison to the ligand's [23]. These bands are attributed to Sn–O and Sn–C resonances, which are found in the 572-530 and 464-422 cm^{-1} areas, respectively. Such bands confirm that the ligand and metal ion are coordinated [24, 25].

Table 3. The ^{1}H-NMR spectra of ampicillin and its complexes.

No.	Compounds	^{1}H-NMR
1	Ampicillin (A)	δ 12.89 (s, 1H, COOH), 10.21 (s, 1H, NH), 8.90 (d, J = 9.5 Hz, 2H, Ar), 8.60-7.28 (m, 2H, Ar), 7.23 (t, J = 8.6 Hz, 1H, Ar), 5.41 (d, J = 10.1 Hz, 1H, N-CH), 5.24 (d, J = 9.1 Hz, 1H, CO-CH), 5.03 (s, 1H, PhCH-), 4.54-4.04 (br, 2H, NH_2), 3.53 (d, J =13.7 Hz,1H, S-CH), 2.52 (s, 6H, 2Me).
2	Ph_2SnL_2-A	δ 9.38 (s, 2H, 2NH), 8.65 (d, J = 26.5, Hz, 2H, Ar), 8.09-7.20 (m, 14H, Ar), 6.55 (t, J = 11 Hz, 1H, Ar), 6.46 (t, J = 10.0 Hz, 3H, Ar), 6.03 (d, J = 10.2 Hz, 2H, 2N-CH), 5.24 (d, J = 8.8 Hz, 2H, 2CO-CH), 4.45 (s, 2H, 2PhCH-), 3.38-3.22 (br, 4H, $2NH_2$), 3.11 (d, J = 14.0 Hz, 2H, 2S-CH), 1.12 (s, 12H, 4Me).
3	Bu_2SnL_2-A	δ 8.23 (s, 2H, NH), 8.18 (d, J = 8.3 Hz, 4H, Ar), 8.05 (t, J = 6.1Hz, 2H, Ar), 7.27-6.24 (m, 4H, Ar), 5.05 (d, J = 12.5 Hz, 2H, N-CH), 4.44 (d, J = 13.5 Hz, 2H, CO-CH), 3.54 (s, 2H, PhCH-), 3.43 (d, J = 9.1 Hz, 2H, S-CH), 3.22-3.14 (br, 4H, NH_2), 1.58 (s, 12H, 2Me), 1.31 (qut, J = 7.5 Hz, 4H, $2CH_2$), 1.15 (sex, J = 7.5 Hz, 4H, $2CH_2$), 1.17 (t, J = 8.5 Hz, 6H, 2Me), 1.06 (t, J = 7.9 Hz, 4H, $2CH_2$).
4	Me_2SnL_2-A	δ 8.44 (s, 2H, NH), 8.75(d, J = 19.4, Hz, 4H, Ar), 8.54-7.35 (m, 4H, Ar), 6.67 (t , J = 10.3 Hz, 2H, Ar), 6.29 (d, J = 10.9 Hz, 2H, N-CH), 5.56 (d, J = 8.5 Hz, 2H, CO-CH), 5.43 (s, 2H, Ph CH-), 3.47-3.27 (br, 4H, NH_2), 3.16 (d, J = 9.3 Hz, 2H, S-CH), 1.12 (s, 12H, 4Me), 0.95 (s, 6H, 2Me).

Nuclear magnetic resonance spectroscopy

Diorganotin(IV) moiety in complexes has a smaller up-field shift. As the tin atom's coordination number rises, the chemical shift also rises [26]. All complexes revealed the ligand's N-H proton as a singlet, indicating that the N atom does not coordinate with the tin center. In terms of synthesizing compounds, the ^{1}H-NMR data matched the ^{13}C-NMR data of the ligand and their

complexes. Because oxygen is connected to an electropositive tin atom, the complexes' C_3-carboxyl was pushed downfield relative to the ligand site. It is demonstrated by this data that complexation took place through the oxygen atoms in the carboxylic group. When analyzing the ^{119}Sn-NMR spectra of Ph_2SnL_2, Bu_2SnL_2, and Me_2SnL_2 complexes, which resonant at -298.52, -262.50, and -211.20 ppm, respectively, it falls within the range of hexa-coordinated diorganotin(IV)-ampicillin [27, 28].

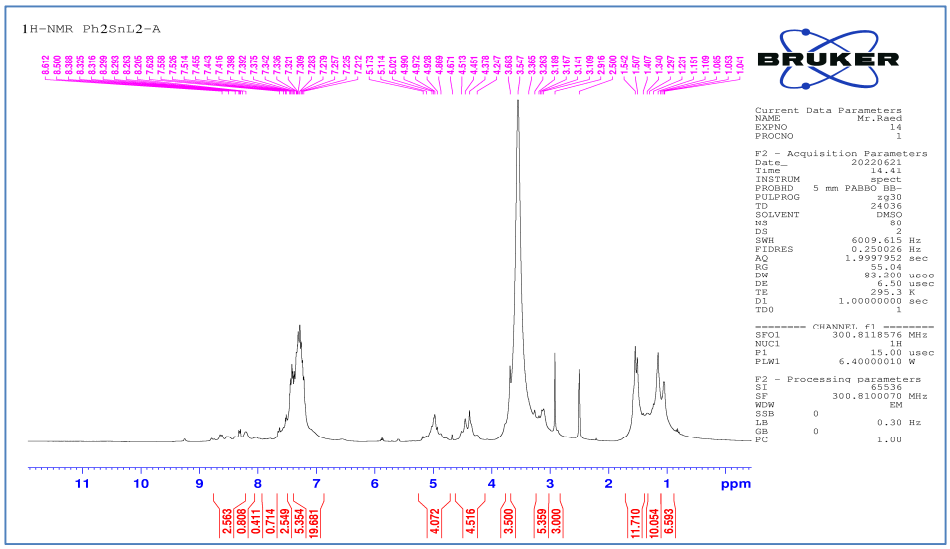


Figure 1.[1]H-NMR spectrum of Ph_2SnL_2-A complex.

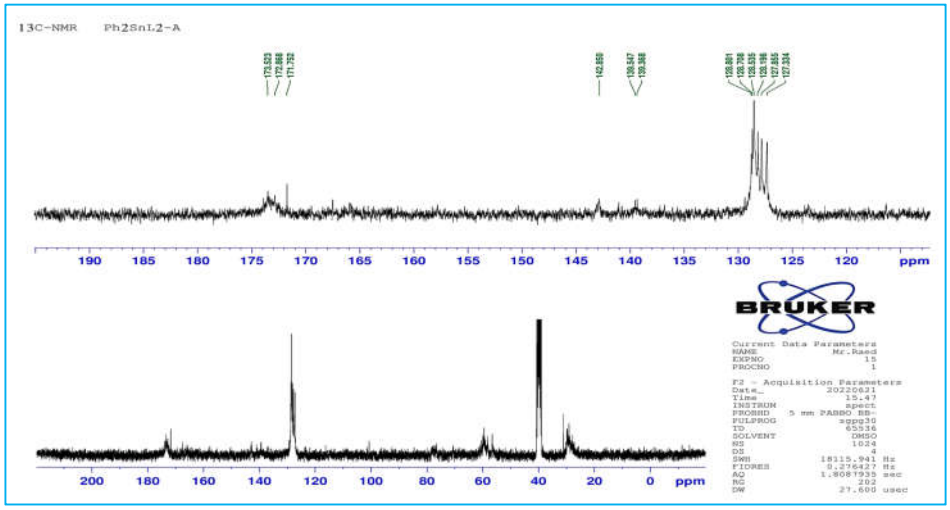
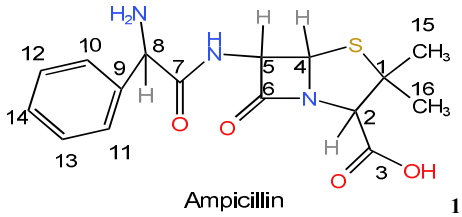
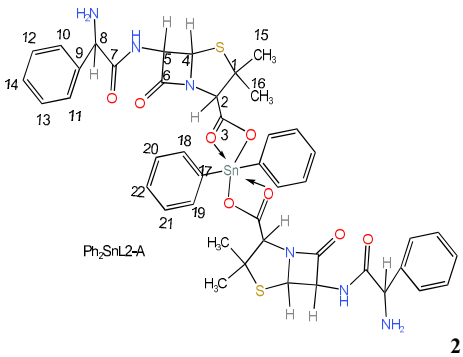
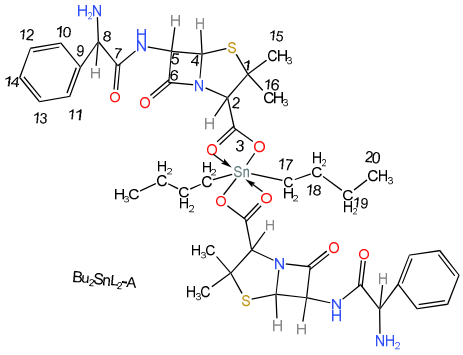
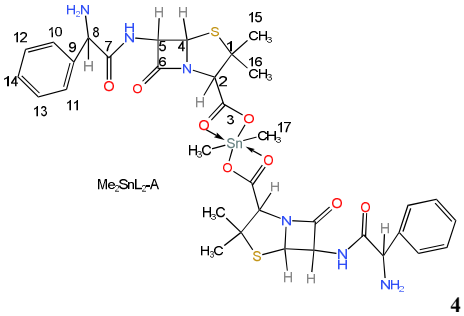


Figure 2. [13]C-NMR spectrum of Ph_2SnL_2-A complex.

Table 4. ^{13}C-NMR spectra (DMSO-d$_6$; ppm) of ampicillin and its complexes.

Compounds	^{13}C-NMR
 Ampicillin **1**	(C_6, 1C, 173.5), (C_3, 1C, 172.1), (C_7, 1C, 169.4), (C_{12}, C_{13}, 2C, 128.5), (C_{10},C_{11}, 2C, 127.9), (C_{14}, 1C, 127.1), (C_9, 1C, 125.7), (C_2, 1C, 72.9), (C_4, 1C, 66.7), (C_1, 1C, 65), (C_5, 1C, 58.5), (C_8, 1C, 55.9), (C_{16}, 1C, 31), (C_{15}, 1C, 27).
 Ph_2SnL2-A **2**	(C_6, 2C, 178.9), (C3, 2C, 175.4), (C_7, 2C, 173.2), (C_{12}, C_{13}, 4C, 131.6), (C_{14}, C_{17}, 4C, 130, 9), (C_{18}, C_{19}, C_{20}, C_{21}, C_{22}, 10C, 129.5), (C_{10}, C_{11}, 4C, 129.05), (C_9, 2C, 128.1), (C_2, 2C, 78.3), (C_4, 2C, 69.5), (C_1, 2C, 68.3), (C_5, 2C, 61.8), (C_8, 2C, 59.5), (C_{16}, 2C, 36.1), (C_{15}, 2C, 29.5).
 Bu_2SnL_2-A **3**	(C_6, 2C, 179.3), (C_3, 2C, 174.5), (C_7, 2C, 171.5), (C_{12}, C_{13}, 4C, 132.5), (C_{10}, C_{11}, 4C, 130.3), (C_{14}, 2C, 129.4), (C_9, 2C, 128.4), (C_2, 2C, 85.1), (C_{17}, C_{18}, 4C, 75.5), (C_4, 2C, 69.3), (C_1, 2C, 66.5), (C_5, 2C, 59.6), (C_8, 2C, 57.5), (C_{16}, 2C, 35.4), (C_{15}, 2C, 29.7), (C_{20}, 2C, 26.2), (C_{19}, 2C, 15.08).
 Me_2SnL_2-A **4**	(C_6, 2C, 178.5), (C_3, 2C, 176.1), (C_7, 2C, 172.6), (C_{12}, C_{13}, 4C, 132.2), (C_{10}, C_{11}, 4C, 128.5), (C_{14}, 2C, 127.9), (C_9, 2C, 127.8), (C_2, 2C, 78.4), (C_{17}, 2C, 75.8), (C_4, 2C, 69.1), (C_1, 2C, 67.3), (C_5, 2C, 63.5), (C_8, 2C, 58.2), (C_{16}, 2C, 36.5), (C_{15}, 2C, 28.7).

Diorganotin(IV) ampicillin complexes' antioxidant activity

Scavenging technique of DPPH radicals

The antioxidant capability of diorganotin(IV)-ampicillin complexes was assessed by dissolving them in methanol at a fifty-µg/mL concentration for every test solution. Following 5, 10, and 15 min, the absorbance of the solutions was measured using a microplate reader set to an optimal wavelength of 490 nm. Based on the data acquired, Equation 1 was used to calculate the percentage of inhibition against DPPH. Plotting the relationship between the percentage of inhibition and time allowed for the identification of the complexes with the highest inhibition. There will be a decrease in the DPPH radical (light yellow solution). Diorganotin compounds are expected to be antioxidants because of the presence of the metal moiety [29, 30].

Table 5. Data for evaluating the antioxidant activity of ampicillin and its complexes at different times.

Controlled absorbance = 0.378 λ = 490 nm						
Compounds	After Time 5 min		After Time 10 min		After Time 15 min	
	Sample Abs.	% Inhibition	Sample Abs.	% Inhibition	Sample Abs.	% Inhibition
Ampicillin	0.278	26.455	0.262	30.687	0.261	30.952
Ph_2SnL_2-A	0.175	53.703	0.179	52.645	0.181	52.116
Bu_2SnL_2-A	0.198	47.619	0.201	46.825	0.205	45.767
Me_2SnL_2-A	0.183	51.587	0.188	50.264	0.191	49.470

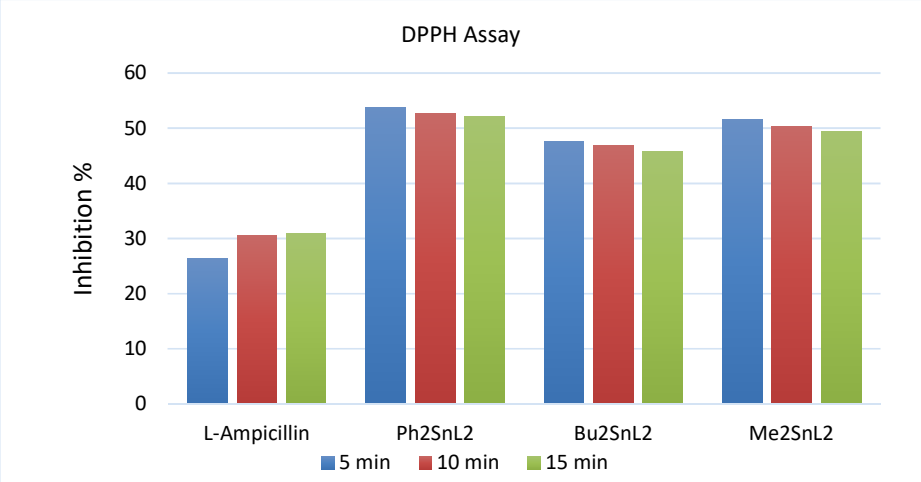


Figure 3. DPPH Assay: ampicillin and its complexes at times 5, 10, and 15 min.

The complex Ph_2SnL_2-A exhibited higher percentages of scavenging than the ligand ampicillin. This is due to the presence of the two phenyl groups in addition to the increase in aromatization. The complexes' percentage of dose-dependent inhibition was determined by employing a concentration range of 25-75 µg/mL. That the complex's ideal concentration for high inhibition was 50 µg/mL. Tannic acid was selected as the typical antioxidant component; nevertheless, its scavenging percentage was higher than that of the organotin(IV)-ampicillin complexes [31-33].

Assay for CUPRAC activity

The cuprac test evaluates antioxidant activity by measuring the decrease of Cu^{2+} in an excess of neocuproine using a reducing agent. This leads to the production of a Cu^{+} blend with an optimal wavelength of 450 nm [34, 35]. At a concentration of 20 µg/mL, the absorbance and percentage inhibition were determined for every complex, ligand, ampicillin, standard reference, and tannic acid. The reference antioxidant, had consistently higher antioxidant activity when compared to these substances. Tannic acid is the effective natural antioxidant component that can be used as food preservative agents or nutraceuticals. [36, 37]. However, as Table 6 and Figure 4 demonstrate, Ph_2SnL_2-A complexes have more antioxidant activity than their ligand.

Table 6. Displays the absorbance and percentage inhibition of Ampicillin, Complexes, and Tannic Acid at a concentration of 20 µg/mL.

Control Absorbance = 0.238 λ = 450 nm		
Complexes	Absorbance at concentration 20 µg/mL	% Inhibition
Ampicillin	0.193	18.917
Ph_2SnL_2-A	0.123	48.32
Bu_2SnL_2-A	0.163	31.51
Me_2SnL_2-A	0.139	41.60
Tannic acid	0.121	49.16

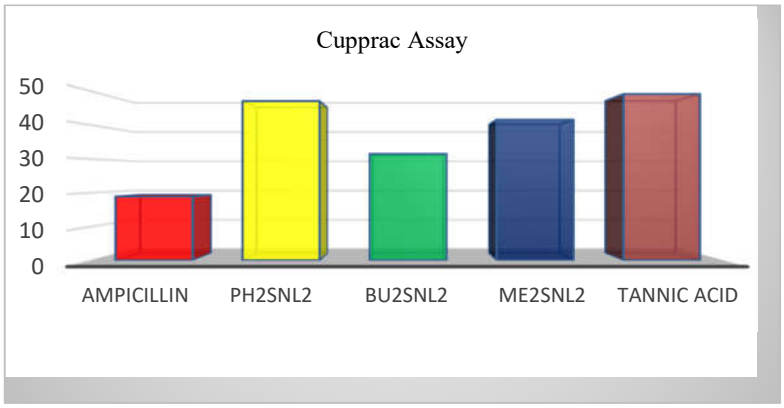


Figure 4. CUPRAC assay: 20 µg/mL for ampicillin, complexes, and tannic acid.

The study evaluated the antioxidant activity of the diphenyltin(IV)-ampicillin complex at varying doses (20, 40, and 60 µg/mL). To maximize antioxidant activity, the best dose was found to be 40 µg/mL based on absorbance and inhibition ratio.

CONCLUSION

Diorganotin(IV) complexes were created via condensation reactions with ampicillin. Antioxidants were utilized throughout both the DPPH and CUPRAC procedures. All synthesized complexes have higher antioxidant activity than ligand-derived complexes. The findings show that the Ph_2SnL_2-A complex performed better in both operations.

REFERENCES

1. Sultan, S. Reviewing the protective role of antioxidants in oxidative stress caused by free radicals. *Asian Pac. J. Health Sci.* **2014**, 1, 401-406.
2. Antonenko, T. Biological activity of novel organotin compounds with a Schiff base containing an antioxidant fragment. *Int. J. Mol. Sci.* **2023**, 24, 2024.
3. Kalsoom, A. Synthesis, characterization and biological activity of organotin derivatives of 2-thionaphthalene, including the crystal structures of (naphthalenethiolato-S) triphenyltin(IV) and bis (naphthalenethiolato-S) dimethyltin(IV). *Appl. Organomet. Chem.* **1997**, 11, 47-55.
4. Smolyaninov, I.; Poddel'sky, A.; Burmistrova, D.; Voronina, Y.; Pomortseva, P.; Polovinkina, M.; Eremenko, I. The synthesis and biological activity of organotin complexes with thio-Schiff bases bearing phenol fragments. *Int. J. Mol. Sci.* **2023**, 24, 8319.
5. Curfs, J.; Chwalibog, A.; Savenije, B.; Ritskes-Hoitinga, M. 11 Chapter: *Nutrient Requirements, Experimental Design, and Feeding Schedules in Animal Experimentation*. *Handbook of Laboratory Animal Science*, Vol. I: *Essential Principles and Practices*, **2010**, 1, 307.
6. Refat, M.; Al-Maydama, H.; Al-Azab, F.; Amin, R.; Jamil, Y. Synthesis, thermal and spectroscopic behaviors of metal–drug complexes: La(III), Ce(III), Sm(III) and Y(III) amoxicillin trihydrate antibiotic drug complexes. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **2014**, 128, 427-446.
7. Hussien, M.; Samy, M.; Moamen, S. Spectroscopic and molecular structure characterization of Cu(II), Co(II), Ni(II) and Fe(III) amoxicillin antibiotic drug complexes in alcoholic media. *J. Mol. Liq.* **2016,** 221, 61-71.
8. Arraq, R.; Hadi, A. Synthesis, identification, and antioxidant activity of di-organotin(IV)-cephalexin complexes. *J. Med. Chem. Sci.* **2023**, 6, 392-401.
9. Arraq, R.; Hadi, A. Enhanced the antioxidant activity of tri organotin(IV) complexes derived from cephalexin. *AMJ* **2022**, 62, 2197-2209.
10. Hadi, A.; Hassen, T.; Mahdi, I. Synthesis, characterization, and antioxidant material activities of organotin(IV) carboxylates with tin-para methoxy benzoic acid. *Mater. Today: Proc.* **2022**, 49, 2797-2801.
11. Saddam, N.; Hadi, A.; Mohammed, A. Enhanced antioxidant activity of chitosan extracted from fish shells materials. *Mater. Today: Proc*. **2022**, 49, 2793-2796.
12. Jomova, K.; Valko, M. Importance of iron chelation in free radical-induced oxidative stress and human disease. *Curr. Pharm. Design* **2011**, 17, 3460-3473.
13. Adeyemi, J.; Onwudiwe, D. Organotin(IV) dithiocarbamate complexes: Chemical and biological activity. *Molecules* **2018**, 23, 2571.
14. Schlesier, K.; Harwat, M.; Böhm, V.; Bitsch, R. Assessment of antioxidant activity by using different in vitro methods. *Free Radical Res.***2002**, 36, 177-187.
15. Arraq, R.; Angham, G. Synthesis and identification of triorganotin(IV)-tyrosine complexes and study their applications as antioxidant by DPPH and CUPRAC methods. *Bagh. Sci. J.* **2024**. https://orcid.org/0000-0002-5396-7560
16. Hadi, A.; Jawad, K.; Ahmed, D.; Yousif, E. Synthesis and biological activities of organotin(IV) carboxylates: A review. *Sys. Rev. Pharm*. **2019**, 10, 26-31.
17. Hadi, A.; Yousif, E.; El-Hiti, G.; Ahmed, S.; Jawad, K.; Alotaibi, M.; Hashim, H. Long-term effect of ultraviolet irradiation on poly(vinyl chloride) films containing naproxen diorganotin(IV) complexes, *Molecules* **2019**, 24, 1-17.
18. Hadi, A.; Zaooli, R.; Ahmed, S.; Yousif, E. Antioxidant activity of naproxen and its diorganotin complexes. *Int. J. Drug Del*. **2021**, 11, 383-385.
19. Brand-Williams, W.; Cuvelier, E.; Berset, C. Use of a free radical method to evaluate antioxidant activity. *LWT Food Sci. Technol.* **1995**, 28, 25-30.

20. Bektaşoğlu, B.; Celik, E.; Özyürek, M.; Güçlü, K.; Apak, R.; Novel hydroxyl radical scavenging antioxidant activity assay for water-soluble antioxidants using a modified CUPRAC method. *Biochem. Biophys. Res. Commun*. **2006**, 345, 1194-1200.
21. Arraq, R.; Salih, H. Synthesis and identification of $Co_3O_4 \cdot Fe_3O_4$/CaO spinel supported catalyst. *Asian J. Chem.* **2018**, 30, 2502-2508.
22. Ghazi, D.; Emad, Y. Design of organotin(IV) complexes derived from ciprofloxacin. *Int. J. Res. Eng. Innov. (IJREI)* **2017**, 1624-1627, 1628.
23. Arraq, R.; Hadi, A.; Ahmed, S.; Zainulabdeen, K.; Hashim, H.; Ahmed, A.; Yousif, E.; Reducing environmental pollutants by using triorganotin(IV)-tyrosine complexes that prolong the life of the polymers used in outdoor patios. *Pollut*. **2023**, 9, 1501-1514.
24. Hadi, A.; Jawad, K.; Yousif, E.; El-Hiti, A.; Alotaibi, H.; Ahmed, S. Synthesis of telmisartan organotin(IV) complexes and their use as carbon dioxide capture media. *Molecules* **2019**, 24, 1631.
25. Jasem, H.; Hadi, A.; El-Hiti, G.; Baashen, M.; Hashim, H.; Ahmed, A.; Yousif, E.; Tin-naphthalene sulfonic acid complexes as photostabilizers for poly (vinyl chloride). *Molecules* **2021**, 26, 3629.
26. Arraq, R.; Hadi, G.; Ahmed,S.; Al-Mashhadani, H.; Hashim, H.; Ahmed, A.; Yousif, E. Color changes, AFM and SEM study of PVC/triorganotin (IV)-cephalexin complexes samples via UV radiation. *PCCC* **2023**, 16, 283-294.
27. Pejchal, V.; Holeˇcek, J.; Nádvorník, M.; Lyˇcka, A. ^{13}C and ^{119}Sn NMR spectra of some mono-n-butyltin(IV) compounds. *Collect. Czech. Chem. Commun*. **1995**, 60, 1492-1501.
28. Shahid, K.; Ali, S.; Shahzadi, S.; Badshah, A.; Khan, K.; Maharvi, G. Organotin(IV) complexes of aniline derivatives. I. Synthesis, spectral and antibacterial studies of di- and triorganotin(IV) derivatives of4-bromomaleanilic acid. Synth. React. *Inorg. Met. Org. Chem*. **2003**, 33, 1221-1235.
29. Rehman, W.; Baloch, M.K.; Badshah, A.; Ali, S. Synthesis and characterization of biologically potent di-organotin(IV) complexes of mono-methyl glutarate. *J. Chin. Chem. Soc.* **2005**, 52, 231-236.
30. Corona, B. Antioxidant activity of butyl-and phenylstannoxanes derived from 2-, 3-and 4-pyridinecarboxylic acids. *Molecules* **2010**, 15, 5445-5459.
31. Avelelas, F. Antifungal and antioxidant properties of chitosan polymers obtained from nontraditional *Polybius henslowii* sources. *Marine Drugs* **2019**, 17, 239.
32. Al-Shemary, R.S.; Jasem, H.; Hadi, A. G.; Baqir, S.J. Boosted antibacterial efficacy: Di and triorganotin complexes via 2-[(2,3-dimethylphenyl) amino] benzoic acid. *Bull. Chem. Soc. Ethiop*. **2024**, 38, 647-655.
33. Hashim, D.J.; Al-Rikabi, E.H.; Hadi, A.G.; Baqir, S.J. 4-Aminoantipyrine - new organotin complexes, synthesis, structure and antioxidant activity. *Bull. Chem. Soc. Ethiop.* **2023**, 37, 1163-1170.
34. Dawidowicz, A.; Wianowska, D.; Olszowy, M. On practical problems in estimation of antioxidant activity of compounds by DPPH method (problems in estimation of antioxidant activity). *Food Chem*. **2012**, 131, 1037-1043.
35. Munteanu, I.; Apetrei, C. Analytical methods used in determining antioxidant activity: A review. *Int. J. Mol. Sci.* **2021**, 22, 3380.
36. Özyürek, M.; Güçlü, K.; Bektaşoğlu, B.; Apak, R. Spectrophotometric determination of ascorbic acid by the modified CUPRAC method with extractive separation of flavonoids–La(III) complexes. *Anal. Chim. Acta* **2007**, 588, 88-95.
37. Hashim, D.; Waheed, E.; Hadi, A.; Baqir, J. Exploring the biological activity of organotin carboxylate complexes with 4-sulfosalicylic acid. *Bull. Chem. Soc. Ethiop.* **2023**, 37, 1435-1442.