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Enhanced the Antioxidant Activity of 1-Amino-2-naphthol-4-Sulfonic acid by Complexation with Organotin(IV) Compounds

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Abstract:

This study focuses on the measure the antioxidant activity by two methods: Free radical scavenging activity (DPPH) andCUPRAC Method fordi and tri- organotin(IV) compounds and contrasts whether the antioxidant activity of 1-Amino-2-naphthol-4-Sulfonicacid (L)and it's organotin complexes have increased.Four organotin complexes (**1-4**)were successfully prepared by the condensations reactions of 1-Amino-2-naphthol-4-Sulfonicacid as aligandwih di and tri-organotin(IV)compounds.These prepared complexes were characterized by deferential techniques, infrared spectroscopy (FTIR), ^{119}Sn-nuclear magnetic resonance (NMR) and ^{1}H-NMR techniques. Organotin(IV) complexes showed higher antioxidant activity than aligand, due the metal moiety, while complex **3** showed higher antioxidant activity than other complexes.

Keywords: Antioxidant Activity , Complexation , Organotin(IV) Compounds , 1-Amino-2-naphthol-4-Sulfonic acid.

Introduction

The Sn element is classified in group fourteen in the periodic table, with the elements carbon, silicon, germanium, and lead. The two stable oxidation states of tin are Sn (+2) and Sn (+4). The Sn (+2) uses the 5p orbitals primarily for bonding and leaves the singlet unshared pair with a little p-character in the 5s orbital, but the organotin (II) compounds are not very stable due to the fact that [1, 2] .The biological activity of the organotin(IV) compounds stimulates their applications in pharmaceuticals [3] also, The presence, depending of the nature and number of alkyl(R) substituents that attached to the Tin center, of one or more of these

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Covalant C-Sn connections influences the activity of the complete component[1].

The variation in organotin(IV) alkyl and Aryl substituents shows significant achives on the biological activity of these complexes. In some research, organotin compounds have demonstrated high biological activity , toxicity and indeterminate acted. A toxic effects of these compounds is due to a variety of factors: attachment of the Sn atom to SH factions of proteins, activation of oxidative stress in the organism, damage to the cell membrane and others [4, 5]. Simultaneously , both the ability of organotin compounds to accretion in cells and their toxicity offer an incentive to recognize them as potential pharmaceuticals for particular action[6] , such as Cytotoxic antitumor agents for cancer chemotherapy [7].Tin compounds are among the organometallic compounds that are most commonly used. They have been used for a number of industrial and agricultural applications over the last few decades[8], including pesticides, antifouling agents, synthetics, fungicide [9], and biological applications [10] , The main feature among other things is the presence of a metallic moiety that rises the biological activity of these organotin(IV)complexes and makes them good antioxidants compared to the pure organic ligand. Where antioxidants are known as Compounds are capable of either delaying or inhibiting the oxidation of organisms under ambient oxygen and atmospheric oxygen. They are used to stabilize polymeric and petrochemical materials, foodstuffs, and cosmetics. About pharmaceuticals, antioxidants are part of the organism's defense mechanism[11-13].

The chemistry Organotin compounds remains of interest due to their remarkable structural [14] properties and also because of their potential as agricultural biocides,and polypropylene antitumor agents [15].This research aims to study the antioxidantactivity for Sn(IV)complex ,and compare the values if there is an increase or decrease in antioxidant activity with 1-Amino-2-naphthol-4-Sulfonicacid and with organotin (IV) complexes that derived from 1-Amino-2-naphthol-4-Sulfonicacid .

Materials and Methods

2.1 General

On the FTIR 8300 Shimadzu spectrophotometre, FTIR spectra (400–4000 cm^{-1}) were registered with KBr disks (Tokyo, Japan). Mitamura Riken Kogyo (MPD) apparatus was used to produce melting points (Tokushima, Japan).Bruker DRX300NMRspectrometer, were used to record ^{1}H-(300 MHz), and ^{119}Sn(107 MHz) NMR- spectra (Zurich, Switzerland).

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*2.2 preparation of Triorganotin(IV) Complexes(**1-2**)*

(1.19g , 5mmol) of the ligand was dissolved in 50 ml of methanol then the solution was added to (5mmol) of (1.92g or1.62g) from tri-phenyltinchloride or tri-butyltinchloride was dissolved in 30 ml of methanol [16], then the mixture was left to reflux for 4 hours. The solid cooling precipitate was collected and recrystallized to provide **1** and **2**complex[17].

*2.3 Preparation of di- organotin(IV) Complexes (**3-4**)*

(1.4g , 6mmol) of the ligand was dissolved in 50 ml of methanol was added to thesolution of (3mmolof 0.66g or 0.74g) ofdimethy or dibutyltinin 30 ml of methanol [16], then they were mixed together and left to reflux for 4 hours. The solid cooling precipitate was collected and recrystallized to provide **3** and **4**complex [17].

2.4 Antioxidant activity:

Two methods were employed to measure antioxidant activity;(DPPH) and Cuprac Method

2.4.1 Free radical scavenging activity (DPPH method)

An electron providing ability of samples and standards - gallic acid and Vit-C were controlled from decolorizing of purple colored ethanol solution of DPPH. This spectrophotometric testemploys the stable radical 2, 2-diphenyl-1-picrylhydrazyl as a reagent. A 0.002% of DPPH was prepared then several concentrations of samples were used in a separate test tubes and volumes were compeleted by ethanol to 2 mL.A 2 mL of the prepared DPPH solution (2.0 to 0.001 mg/mL) was added to the test tubeseparetly.For 30 minutes, these solutions were kept in dark. The similar technique was repeted for Vit-C and gallic acid. A triplicate tested were applied for all the samples.By using soectrophotometer the optical density was recorded at 517 nm. The control used was (Ethanol with DPPH)[18-19],as in equation bellow:

$$\textit{\% Inhibition of DPPH activity} = (A\text{-}B/A) \times 100 \qquad (1)$$

Where A = control optical density and B = sample optical density.

2.4.2 Cuprac Method

0.01M of Copper(II) chloride solution was prepared by dissolving 0.4262g in 250mL of H_2O.

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Buffer solution (pH =7) was prepared by dissolving 19.27 g of Ammonium acetate (NH_4Ac) in 250 mL water. 0.0075M of Neocuproine (Nc){2,9-dimethyl-1,10-phenanthroline} solution was prepared by dissolving 0.039 g Nc in 96% EtOH, the volume was completed to 25 mL with ethanol. The standard solutions of sample antioxidants were prepared at 1.0 * 10^{-3}M Torolox[20].

Total antioxidants levals =(A_{test} / A_{STD})× Conc. of STD (mmole/L) (2)

3. Results and Discussion:

*3.1 preparation of Organotin(IV) Complexes **1**–**4***

Four organotin(IV) complexes were prepared through interaction of di- andtri-organotinchloride with1-Amino-2-naphthol-4-Sulfonic Acid as aligand (L) in the presence of methanol as solvent under reflux for 4hours to give the corresponding tri-organotin(IV)complexes**1** and**2** about65% and 70% yield, respectively, as inFigure1 and gave the corresponding di-organotin(IV)complexes **3**and**4**with89% and 95% yield percentagefor 3 and 4 complexes as in (Figure2) [13, 21]. Table 1 presents the color, melting points, and yields of complexes **1**–**4**.

Figure 1. Synthesis of Tri-Ph or Bu-Tin(IV) Complexes **1** and **2**.

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Figure 2. Synthesis of Di-Me or Bu-Tin(IV) Complex **3**and **4.**

Table 3.1 Physical Properties of **1**–**4** Complexes.

Tin-Complex	R-group	color	Yield(%)	MP(°C)
1	Ph_3	Pale pink	65%	213-215
2	Bu_3	Pale purple	70%	150-152
3	Me_2	Pale purple	89%	243-245
4	Bu_2	Dark gray	95%	166-167

*3.2 FTIR Spectroscopy of Prepared Complexes **1–4***

The infrared spectrum for the ligand hasdistinguish band at 1606-1656 cm^{-1},related to υ(C-N) group,this band showed ashift in wave length in it's complexes, this refers to the particiption of nitrogen of amino group in coordination of the metal ion [22-23].The stretching vibration ofυ(O-H) band of the ligand is dis appeared due to comlexation and deprotonation -OH group and coordination with oxygen atom with metal ion (Sn). The stretching vibration of υ(C-O) of phenolic group at 1531 cm^{-1} in ligand,this band is shifted to lower wave numbers after complexation of the participation of phenolic group (oxygen atom) in the coordination by Sn-O bond [24]. The symmetric and asymetric vibrations of SO_3 group of sulfonic acid are assignable at 1354-1043 cm^{-1} in ligand , this group are not participate in the complexation. New bands are appeared at 455-432 cm^{-1} and at 552 cm^{-1} as aresult of Sn-N and Sn-O bond respectively.

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Table 3.2 , Lists the frequencies for stretching (**υ**)Some of the distinctive groups in the Complexes.

Table 3.2 FTIR Spectral Data (υ, cm^{-1}) of Complexes **1–4**.

Sn (IV)Complex	C-N	C-O	Sn-N	Sn-O
1	1608	1527	455	515
2	1608	1525	457	518
3	1629	1527	457	515
4	1602	1527	457	515

3.3 ^{1}H NMR Spectroscopy of Prepared Complexes 1–4

The ^{1}H chemical shift values were reported on the d scale in ppm, relative to TMS (d – 0.00 ppm) and chemical shift values were reported relative to DMSO (d = 77.00 ppm), as internal standards respectively**.** ^{1}H-NMR spectral data (δ,ppm) of the ligand and complexes were showed in table 3.3. The presence of singlet signals at the (–174 towards –283) ppm was indicated by ^{119}Sn-NMR spectra for thecomplexes **1-4**, which is poitedlylesser than related organotin(IV) salts. Also, the geometry of the complex was affected to the chemical shift of the complex [25,26], the chemical shifts are increase with the tin atom coordination number [27].

Table 3.3. ^{1}H and ^{119}Sn -NMR Spectral data(DMSO-*d6*) of ligandand **1**–**4**Complexes.

Sn(IV) Complex	^{1}H-NMR	^{119}Sn-NMR
L	6.47(d,2H, NH_2), 5.45(s,1H,OH), 7.47-8.80(m, 5H, Ar),2.2(s, 1H, SO_3H)	--
1	6.36(d,2H, NH_2), 7.47-8.80(m, 5H, Ar),2.2(s, 1H, SO_3H)7.86-7.89(m, 12H, Ph).	-174
2	6.37(d,2H, NH_2), 7.31-8.73(m, 5H, Ar), 2.2(s, 1H, SO_3H)2.04(s, 3H, CH_3), 1.86(s, 2H, CH_2), 1.46-1.70(m, 5H, CH_2)0.8-0.87(m, 2H, CH_3).	-167
3	6.35(d,2H, NH_2), 7.36-8.69(m, 5H, Ar), 2.2(s, 1H, SO_3H), 0.56(t, 3H, CH_3).	-274

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4	6.35(d,2H, NH_2), 7.33-8.73(m, 5H, Ar), 2.2(s, 1H, SO_3H), 2.07(s, 3H, CH_3), 1.88(s, 2H, CH_2), 1.44-1.68(m, 5H, CH_2), 0.81-0.86(m, 2H, CH_3).	-283

3.4 Antioxidant Activity:

The antioxidant activity of ligand and its prepared organotin(IV)complexes were measured by two methods of Free radical scavenging activity (DPPH) and glutathione-S-transferase (GST) activity. It was noted that the results of antioxidant activity by the DPPH method were more excellent than by the GST method, also the results were close to the standard substance used (ascorbic acid), Figures (3, 4).

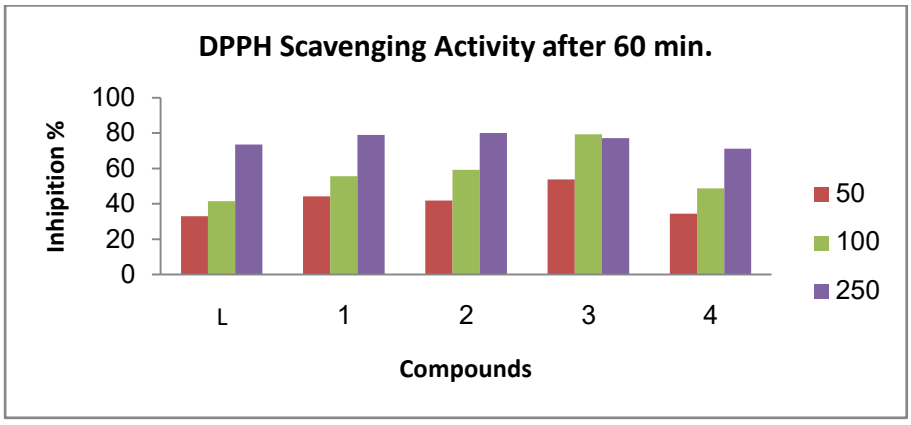

Figure 3. DPPH scavenging activity of (L) and its complexes at 250 µg/mL DMSO solutions at T = 60 min.

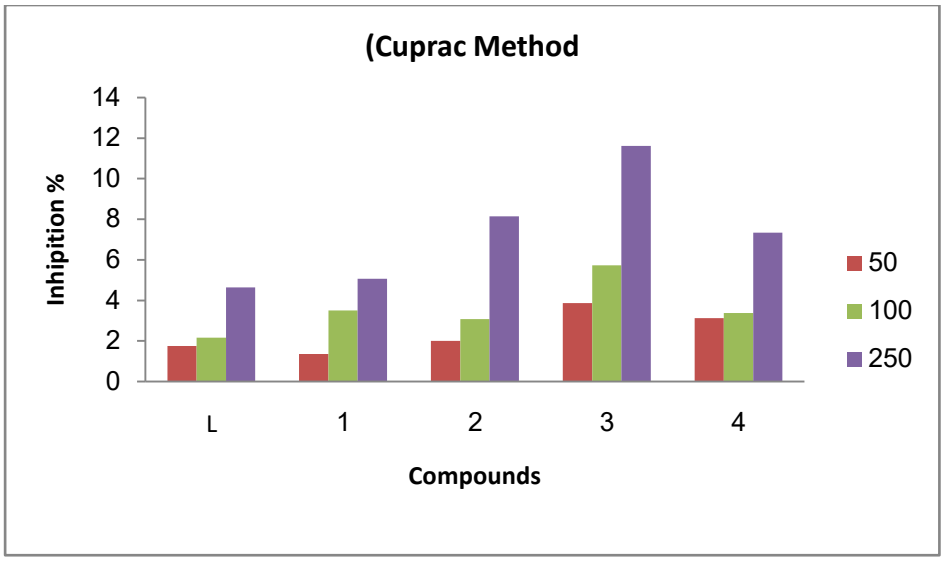

Figure 4. Cuprac Method activity(L) and its complexes at T = 60 min.

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In some studies, metalic complexes have antioxidant activity due to the presence of the metal moiety, which will increase their activity, so it is expected that organotin(IV)complexes have antioxidant activity due the metal moiety [28, 29].

Organotin(IV) complexes showed a higher antioxidant activity than aligand against the stable free radical of DPPH. This is a significant consequence of the broad biological activity of organotine(IV) compounds since, despite their implicit toxicity, this category of compounds may also have an antioxidants impact[30-33].

The complex **2 (**Bu_3SnCl)showed a higher percentage of scavenging behavior than other complexes , while complex **3** (Me_2SnCl_2) givs higher scavenging at low concentration (50 and 100 µg/mL) this is related to the stability of the symmetric complex besides, this complex has more tin content as compared with others, that lead to increase antioxidant ability [34].

In both of the mentioned methodsCuprac Method and DPPH , the application took place at two times 20 and 60min. , the results remained the same for both times, so time was not influential factor.

Conclusions

Fourorganotin(IV)complexes containing 1-Amino-2-naphthol-4-Sulfonicacid were synthesized here in suitable yields using a simple and usual procedure. DPPH andGSH were used as methods to determined the antioxidant activity of ligand and the prepared complexes. The results of the antioxidant activity by two methodsshowed the organotin(IV) complexes had a better antioxidant activity than the ligand that used in their preparation, and compounds 2 and 3 were the best.

Financial disclosure

There is no financial disclosure.

Conflict of interest

None to declare.

Ethical Clearance

"All experimental protocols were approved under the College of Science and carried out in

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accordance with approved guidelines".

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