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Chemistry

SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF SN(II) AND SN(IV) IONS COMPLEXES CONTAINING *N*-ALKYL-*N*-PHENYL DITHIOCARBAMATE LIGANDS

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Abstract. In the current study, ligands S2 donor atoms, sodium *N*-methyl-*N*-phenyldithiocarbamate [L1], and sodium *N*-ethyl-*N*-phenyldithiocarbamate [L2] are prepared from carbon disulfide with *N*-methyl aniline and *N*-ethyl aniline, respectively. Sn(II) and Sn(IV) ions complexes containing *N*-alkyl-*N*-Phenyl dithiocarbamate are prepared and characterized by CHNS elemental analysis, infrared spectroscopy (FT-IR), ^{1}H NMR-spectroscopy, mass spectroscopy, UV-visible spectroscopy, magnetic susceptibility and conductivity measurements. The analytical and spectral data show that the stoichiometry for all complexes is 1 : 2 metal to ligand. The spectral data confirm good coordination of dithiocarbamate ligand with the metal through sulfur atoms of dithiocarbamate moiety. Molar conductivity of complexes are measured using DMF as a solvent and indicated that the complexes of Sn(II) are non-ionic whereas Sn(IV) complexes are ionic. The ligands L1 and L2 and their complexes are examined against *Staphylococcus aureus* bacteria and *Escherichia coli* bacteria.

Keywords: antibacterial activity, N-alkyl-N-phenyl dithiocarbamate, tin complexes, spectral data.

1. Introduction

Carbamate DTCs analogs and amide of dithiocarbamic acid (DTCs) are described as "versatile ligands"; however, this is considered as an understatement because of their ability to form stable complexes with a wide range of primary and transition metals.[1] They can be used for various types of chemicals and situations. Also, their attachment to other molecules is possible with dithiocarbamates,[2] because they have two sulfur atoms, which are continually ready to contribute their electrons to the metal atom centers in at least nine distinct coordination modes. As a result, a wide range of binding characteristics can be obtained. Dithiocarbamates are used to bond together almost identical metallic-sulfur linkages. DTC derivatives are widely used as herbicides, pesticides, antibacterial, antifungal, and anticancer medicines.[3,4] Bacterial growth can be slowed by interfering with the metabolic functions of the bacterium. For food and turf disease prevention (thiram),[5,6] and for alcoholism treatment (disulfiram), several DTC derivatives are currently in use. In addition, dithiocarbamate metal complexes have been found to be useful precursors for metal sulfide nanoparticles.[7,8]

These metalloids include the tin(II), and tin(IV) isomers. Moreover, structural diversity, catalytic and redox capacity, ability to interchange ligands, and a wide spectrum of interactions with therapeutic effects[9] are some of the unique chemical aspects of these compounds. At least one carbon-tin bond has been identified to have an impact on the overall activity of the molecule. Sn atom activity is also affected by the amount and type of alkyl/aryl (R) substituents attached to it. Tin(II), (IV) different properties have been shown to be significantly influenced by variations in the alkyl or aryl group substituents.[10,11] Yet, the mechanism by which tin(II) and tin(IV) compounds exert their therapeutic actions on tumor cells has not been established. Antibacterial, anticancer, schizonticidal, antimalarial, and biocidal properties have been demonstrated in agriculture.[12,13] Complexes of tin(II), and tin(IV) cations may be formed by the ligands containing the donor atoms S, N, O, and P. Dithiocarbamate is one of these ligands.[12]

Tin (II),(IV) dithiocarbamate complexes have been used as anti-cancer drugs,[13] antibacterial agents, catalysts for the synthesis of other compounds,[14] SnS nanoparticles, or a single-source precursor.[15] Researchers found that the complexes either evaporate, leaving behind a little quantity of residue, or decompose and produce the equivalent metal sulfide.[16] When compared to other structurally related compounds, tin dithiocarbamates show complex thermochemistry and an unusual

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pattern of heat breakdown. Consequently, certain tin(II),(IV) complexes of *N*-methyl or *N*-ethyl -*N*-phenyl dithiocarbamates are produced and described in this study.

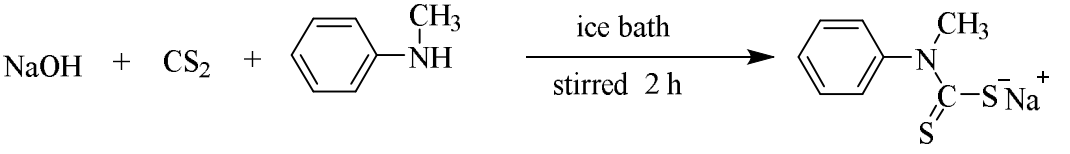
2. Experimental

2.1. Chemicals and Instrument

In the current study, sodium hydroxide 97% (GCC, England), carbon disulfide 99.8 (LOBA. Chem), *N*-methyl aniline 89% (GCC, England), *N*-ethyl aniline 99% (Merk, KGaA, Germany), Diethyl ether 95% (Scharlau), Ethanol 99% (Sigma-Aldrich, Germany), Tin(II) chloride dihydrate 99% (BDH, England), Tin(IV) chloride pentahydrate 98% (BDH, England) were used. On the other hand, the methods utilized in this project are innovative. FT-IR spectra of the ligands L1 and L2 and their complexes were characterized using the FTIR 8400s (Shimadzu). The spectra were recorded in the range of 4000-400 cm-1. NMR spectra were obtained by a BAMX400 MHZ Spectrophotometer in DMSO-d6 as a solvent. UV-visible spectra were reordered using Shimadzu double beam 1800 UV spectrophotometer in dimethylformamide (DMF) as a solvent at $1x10^{-3}$ M. Elemental analyses were performed by using a EuroEA Elemental Analyzer. The melting point of compounds produced was measured by using the Gallen Kamp melting point. The molar conductivity for complexes was measured using Digital Conductivity Series. The magnetic susceptibility of prepared complexes was measured by using a magnetic susceptibility balance, Johnson Mattey.

2.2. Synthesis of Sodium N-methyl-N-phenyldithiocarbamate [L1]

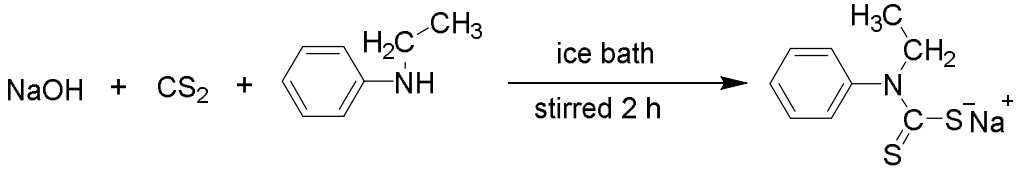
Sodium hydroxide (2 g, 0.05 mol) was dissolved in a small amount (approximately 3 mL) of distilled water and allowed to cool. To this cold solution, a carbon disulfide (3.8 g, 0.05 mol) was added. *N*-methyl aniline was then added (5.44 mL, 0.05 mol). The mixture was swirled for 2 hours at a temperature below 4 degrees Celsius. The result was a yellowish-white solid product that was separated, filtered, washed with ether, and then recrystallized with warm acetone. The white solid product was dried under vacuum over $CaCl_2$ at room temperature giving 1.633 g (yield = 82%) of the product with mp>300 °C.[17] Elemental analysis CHNS: Found (%): C; 46.80 ; H; 3.91 ;N; 6.80 ; S; 31.22. Calc. C; 46.82; H; 3.92; N; 6.82; S; 31.24. The general steps of preparation are shown in Scheme 1.



Scheme 1. Schematic representation for the preparation of Sodium N-methyl- N-phenyldithiocarbamate [L1]

2.3. Synthesis of Sodium N-ethyl-N-phenyldithiocarbamate [L2]

Sodium hydroxide (2 g, 0.05 mol) was dissolved in a minimum amount (about 3 mL) of distilled water and allowed to attain an ice temperature. To this cold solution a carbon disulfide (3.8, 0.05 mol) was added. This was followed by the addition of *N*-ethyl aniline (6.05 mL, 0.05 mol). The mixture was stirred for 2 hrs while keeping the temperature below 4 °C. A yellowish-white solid product was formed, separated, filtered, washed with ether, and finally recrystallized with warm acetone. The white solid product was dried under vacuum over $CaCl_2$ at room temperature giving 0.42 g (yield = 51%) of the product with a melting point of 215 °C.[17] The elemental analysis CHNS: Found (calc.) %: C; 49.27 (49.29); H; 4.56 (4.59);N; 6.37 (6.38); S; 29.20 (29.23) . The general steps of preparation are shown in Scheme 2.



Scheme 2. Schematic representation for the preparation of Sodium *N*-ethyl- *N*-phenyldithiocarbamate [L2]

Table 1. Physical properties of tin complexes

Complex	Metal ion	Yield%	Color	Melting point °C (de)
C1L1	Sn(II)	75	Yellowish-white	350
C2L1	Sn(IV)	76	Yellowish-white	350
C3L2	Sn(II)	78	Yellowish-white	330
C4L2	Sn(IV)	70	Greenish-yellow	265

2.4. Synthesis of the Tin Complexes with L1 and L2 Ligands

To a stirred solution of appropriate ligand (2 mol) in ethanol (5 mL), a solution of tin chloride (1 mole) in 5 mL of ethanol was added. The mixture was refluxed for about 1 hr. The colored precipitate was filtered, washed with ethanol and dried under vacuum. The physical properties of the synthesis complexes are shown in Table 1.

3. Results and Discussion

3.1. Infrared Spectroscopy

Figs. (1-2) and Table 2 show FT-IR peaks of ligands L1 and L2. They are 3367, 3351 cm^{-1}, and 1633, 1627 cm^{-1}, respectively, characterized by O–H stretching and vibrational bands of water. This indicates that the compounds are hydrated. Some alkali salts of dithiocarbamate are known to be crystallized with lattice water molecules.[17,18] The "thioureide" bands(-N-C(=S)) of ligands L1 and L2 were observed as sharp peaks at 1442 and 1438 cm^{-1}, respectively.[19] The stretching frequencies of $\nu(C_2–N)$ groups were observed within the range of 1250–1350 cm^{-1}.[20] The emergence of a new peak ν_{asym}(C=S) of sodium salts of dithiocarbamates was observed for ligands L1 and L2, which occurred at 962 cm^{-1} and 987 cm^{-1}, respectively, with disappearance of the stretching vibrations N-H for the *N*-methyl aniline molecule.[21] The FT-IR spectra of tin (II) complexes (C1L1) and (C3L2), are shown in Figs. (3-4) and Table 2. In the FT-IR spectra of the complexes, a strong thioureide ν(C–N) band of (C1L1) and (C3L2) complexes was found in the region of 1491 cm^{-1} and 1485 cm^{-1} respectively.[22] The high stretching vibration can be ascribed to an increase in the carbon-nitrogen double bond character due to the delocalization of electrons toward the metal atom in each complex. Split absorption bands of ν(C-S) stretching vibrations in (C1L1) and (C3L2) complexes were observed in the range of 1070–1068 cm^{-1}, which indicated a bidentate mode of coordination through the sulfur atom of the dithiocarbamate moiety.[22] The ν(Sn–S) bands (found in the far-infrared region) were observed around 411–450 cm^{-1}. This band indicates coordination between the tin ion and the ligand moiety. Tin (IV) complexes (C2L1) and (C4L2) spectra are shown in Figs. (5-6) and Table 2. In the FT-IR spectra of these complexes, a strong thioureide ν(C–N) band was found in the region of 1489 cm^{-1}, 1485 cm^{-1} , respectively.[23] A sharp band assigned to the ν_{asym} (C-S) stretching is observed at 1097 and 1093 cm^{-1} for (C2L1) and (C4L2), respectively. The ν(Sn–S) bands (found in the far-infrared region) were observed around 411–459 cm^{-1}. This band indicates coordination between the tin compounds and the ligand moiety.

Table 2. FT-IR Spectra data for ligands and Complexes

Compound	C-H (Methyl or ethyl)	C-N thioureide	C=S	C-S	M-S
L1	2825, 2937	1442	960	1158	_
(C1L1)	2850, 2920	1491	1016	1070	445
(C2L1)	2833, 2933	1489	1014	1097	437
L2	2982	1438	987	1158	_
(C3L2)	2980	1485	1001	1068	435
(C4L2)	2983	1485	1031	1093	459

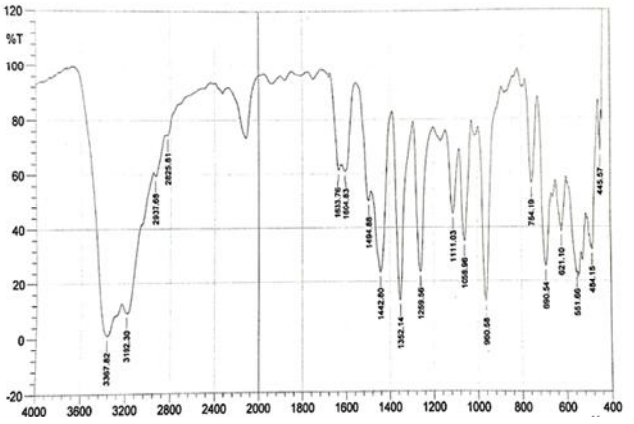


Fig. 1. FT-IR spectrum of Ligand L1

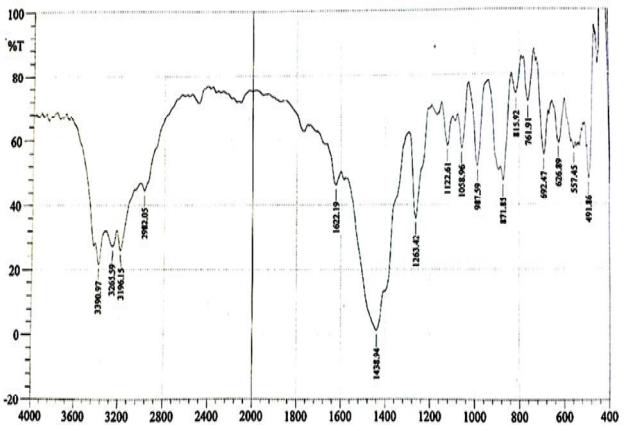


Fig. 2. FT-IR spectrum of Ligand L2

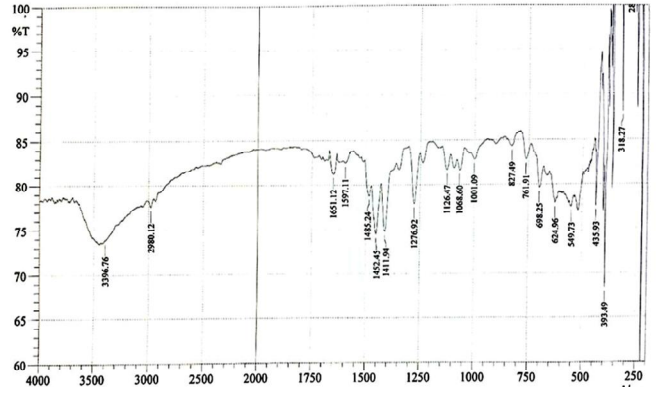


Fig. 4. FT-IR spectrum of Complex (C3L2)

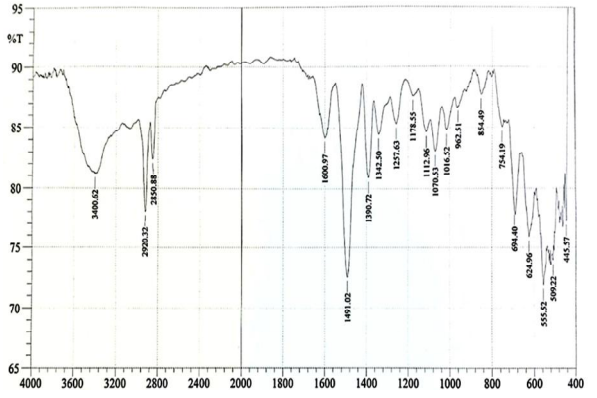


Fig. 3. FT-IR spectrum of Complex (C1L1)

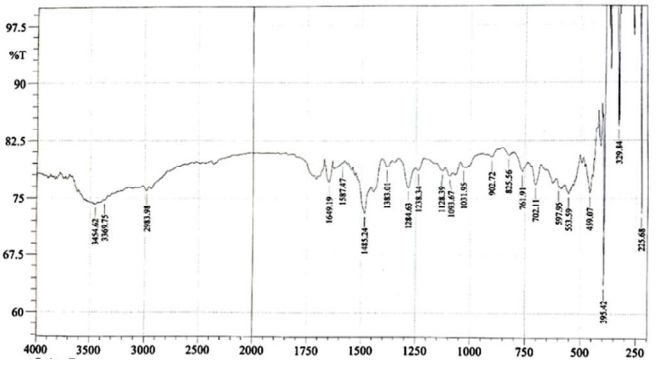


Fig. 6. FT-IR spectrum of Complex (C4L2)

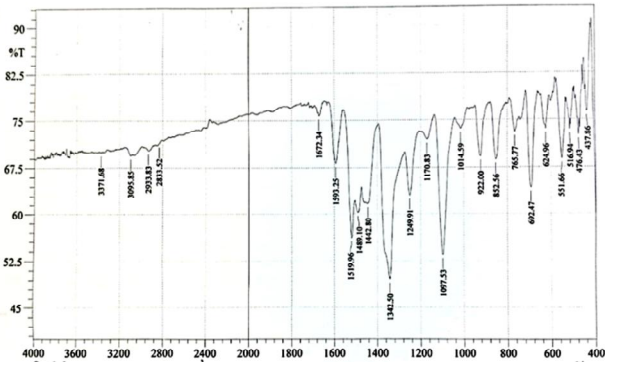


Fig. 5. FT-IR spectrum of Complex (C2L1)

3.2. ^{1}H NMR and mass Spectroscopy of Complexes

In ^{1}H NMR spectra of (C1L1) and (C2L1) complexes (Figs. 7-8) a singlet peak at δ=3.25 ppm is observed, equivalent to three protons of the methyl group in N–CH_3, as well as at δ=(7.20-7.60) ppm, attributed to the aromatic protons. ^{1}H NMR spectra of (C3L2) and (C4L2) complexes are shown in Figs. 9-10. The methyl group and the methylene group of the ethyl substituents appear between 1.25–1.30 ppm as a triplet, and between 3.05–3.15 ppm as a quartet, respectively, and at δ=(7.20-7.57) ppm, attributed to the aromatic protons.[12, 24-26]

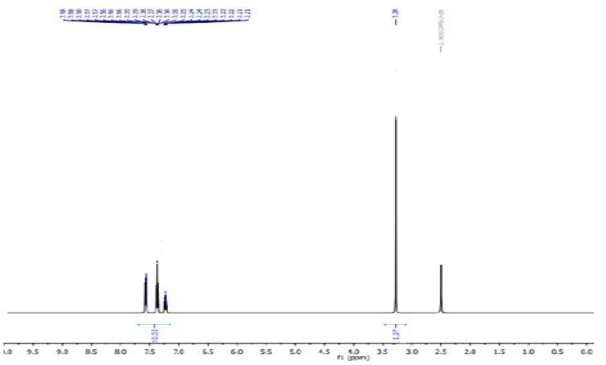


Fig. 7. ^{1}H NMR Spectrum of Tin(II) Complex (C1L1)

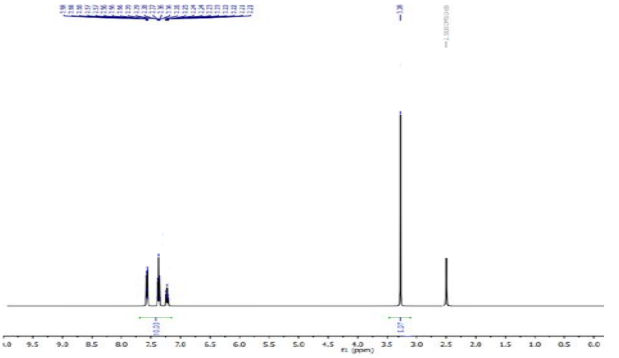


Fig. 8. ^{1}H NMR Spectrum of Tin(IV)Complex (C2L1)

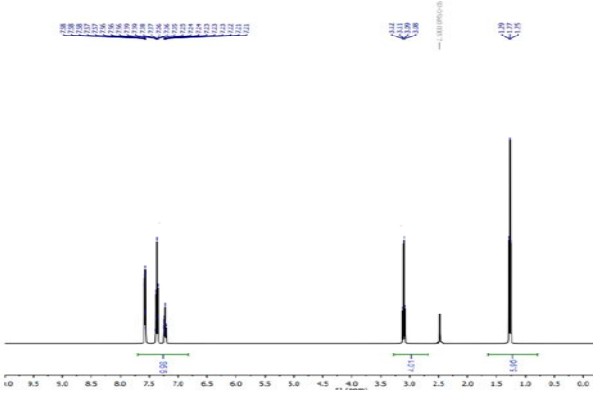


Fig. 9. ^{1}H NMR Spectrum of Tin (II) Complex (C3L2)

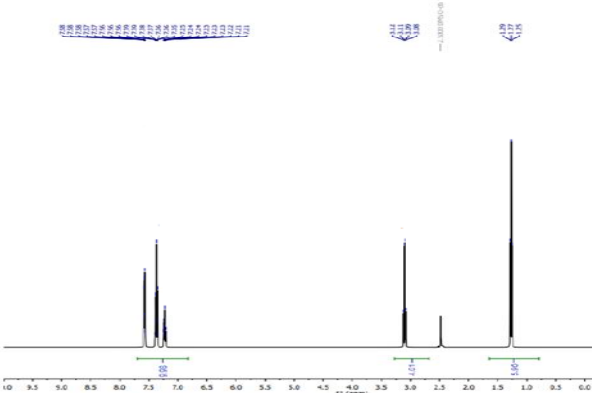


Fig. 10. ^{1}H NMR Spectrum of Tin (IV) Complex (C4L2)

The mass spectra of the complexes (C1L1), (C2L1),(C3L2), and (C4L2) were recorded to establish their structural formula, as illustrated in Figs. 11-14. The experimental parent molecular ion peaks of prepared complexes were at (483.20), (554.10), (511.90), and (581.70) (m/z), whereas the theoretical ones were (483.27), (554.17), (511.95) and (581.67), respectively. The results are consistent with the proposed molecular formula of each compound. The most significant ligands are thioureide and thiocarbonyl coupled with the production of positive molecular ions and other positively charged fractions.

3.3. Electronic Spectra and Magnetic Properties

Two kinds of transitions may be seen in the electronic spectrum of the ligand (L1), ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) Fig. 15. The transitions with a ($\pi \rightarrow \pi^*$) are more powerful than those with ($n \rightarrow \pi^*$). The peaks were observed at 251 nm, which corresponds to the electronic transmission ($\pi \rightarrow \pi^*$) in pi system in a benzene ring and N–C=S systems, and at 321 nm, which corresponds to the electronic transmission ($n \rightarrow \pi^*$) in nitrogen and sulfur systems ($n \rightarrow \pi^*$).[27-30] The electronic spectra of complexes (C1L1) and (C2L1), showed the same bands at 294 nm, 364 nm, 492 nm (Figs. 16-17), but the difference is in the strength of the bands. The bands around 294 nm are intra-ligand bands due to ($\pi - \pi^*$) transition and those bands around 364 nm are also intra-ligand bands due to ($n \rightarrow \pi^*$) transitions. For Sn(II) complexes with electronic configuration d^{10}, no d-d transitions were expected; however, the bands observed in the visible region at 492 nm of the complexes were metal to ligand charge transfer (MLCT) bands, consistent with a d^{10} system that tailed into the visible region. This confirms the existence of the tetrahedral geometry in the (C1L1) and (C2L1) complexes.[31] The electronic spectrum of the ligand L2 (Fig. 18), shows two electronic bands, which are assigned to the ($\pi \rightarrow \pi^*$) transitions in pi system in the benzene ring and N–C=S system, and ($n \rightarrow \pi^*$) transition located on the nitrogen and sulfur atoms. The peaks were observed at 254 nm, which corresponds to the pi system in the benzene ring and N–C=S system's ($\pi \rightarrow \pi^*$) electronic transmission, and at 317 nm, which corresponds to the nitrogen and sulfur system's ($n \rightarrow \pi^*$) electronic transmission.[32,33]

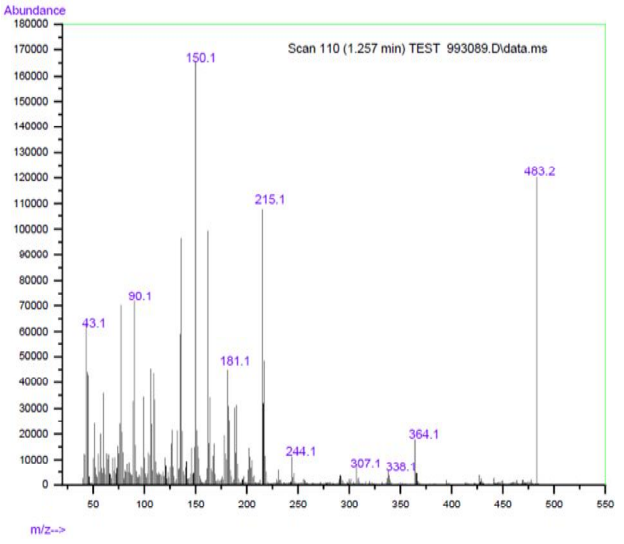


Fig. 11. Mass spectrum of Tin(II) complex (C1L1)

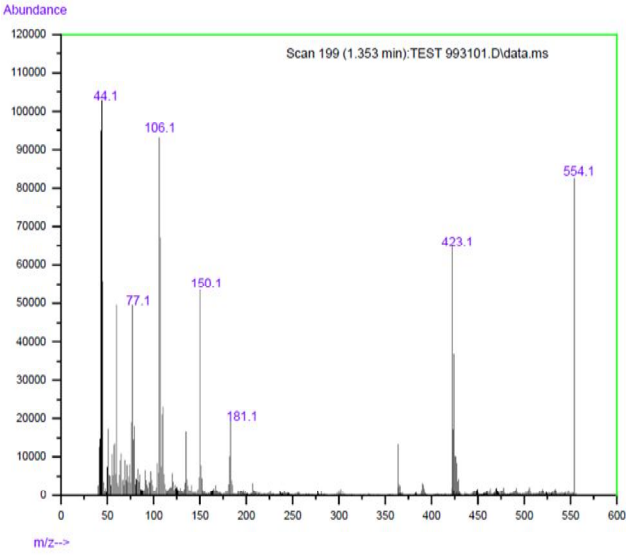


Fig. 12. Mass spectrum of Tin(IV) complex (C2L1)

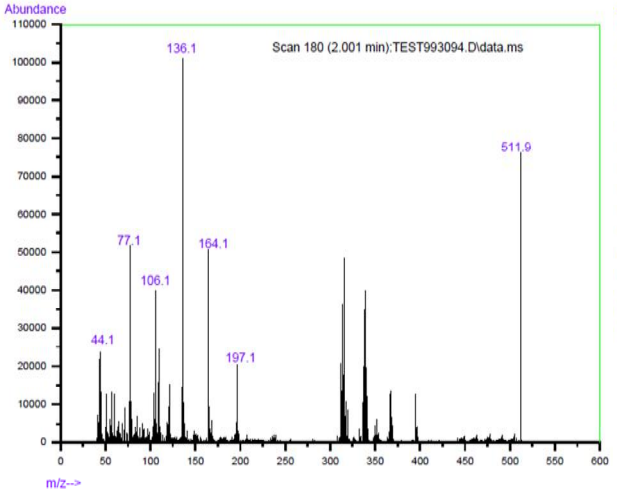


Fig. 13. Mass Spectrum of Tin(II) Complex (C3L2)

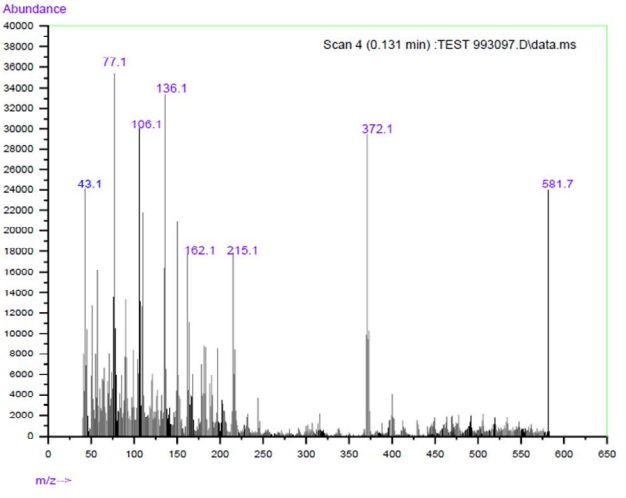


Fig. 14. Mass Spectrum of Tin(IV) Complex (C4L2)

The electronic spectra Figs. (19-20) of complexes (C3L2) and (C4L2) show the absorption peak at 281 nm, due to the ($\pi \rightarrow \pi^*$) electronic transition in the pi system in the benzene ring and N–C=S group, whereas the absorption peak at 345 nm is due to the ($n \rightarrow \pi^*$) electronic transition located on the nitrogen and sulfur atoms. No d-d transitions appeared in (C3L2) and (C4L2) complexes; nevertheless, bands found in the visible area of the complexes at 492 nm were metal to ligand charge transfer (MLCT) bands, consistent with a d^{10} system that tailed into the visible region. The presence of the tetrahedral geometry in the Tin(II)and (IV) complexes was thus established. This is consistent with the spectra of tetrahedral Tin(II)and (IV) complexes.[32,34] The magnetic susceptibility of complexes was equal to (0.0) B.M. The molar conductivity of Tin (II) complexes for the ligands L1 and L2 was measured by DMF. They were non-electrolyte and they were (15, 17, $ohm^{-1} .cm^2 .mol^{-1}$). Tin (IV) complexes for the ligands L1 and L2 were (154, 165 $ohm^{-1} .cm^2 .mole^{-1}$), respectively. These values indicated that the Tin (IV) complexes were electrolytic with 1 : 2 ratio.[35] The proposed structure of Sn(II),(IV) complexes is shown in Figs. 21 and 22.

3.4. The Effect of pH on (L1) and (L2) Ligands, Formation of Tin (II) and (IV) Complexes, and Determination of Complexes Stoichiometry

The effect of pH on L1 and L2 and their complexes were scanned. The results of (Figs. 23-28) show that the pH λ_{max} for the L1 and L2 was at pH=9, whereas the λ_{max} of their complexes was at pH=2 for (C1L1) and (C3L2), and at pH=4 for (C2L1) and (C4L2).

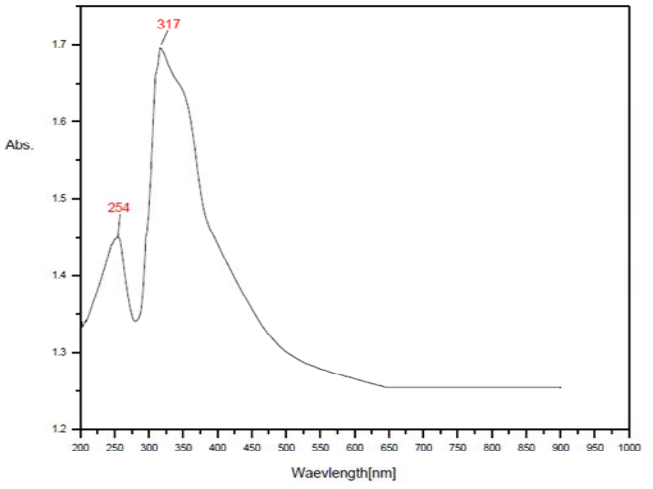


Fig. 18. UV-Vis- spectrum of ligand (L2)

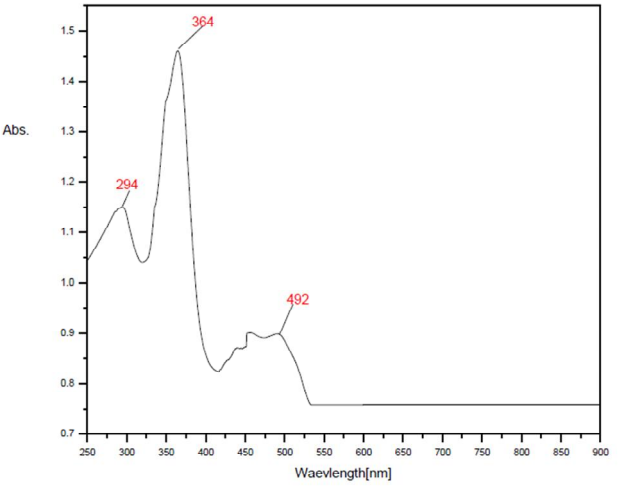


Fig. 17. UV-Vis- spectrum of Complex (C2L1)

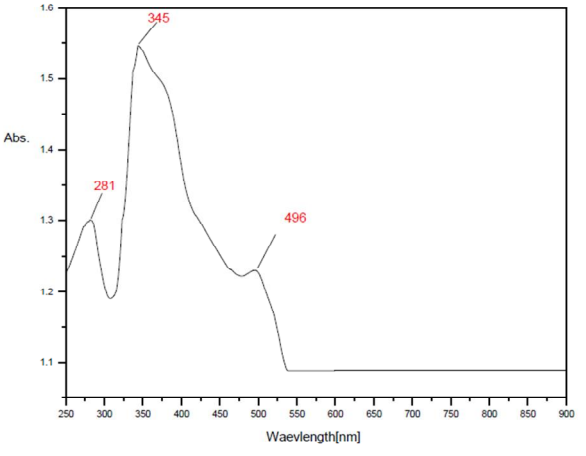


Fig. 19. UV-Vis- spectrum of Complex (C3L2)

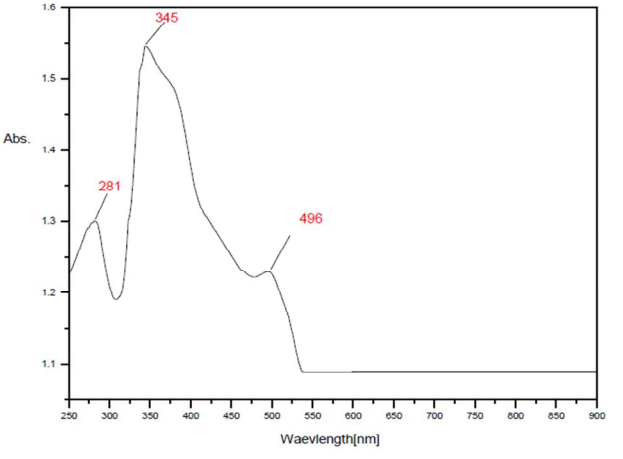
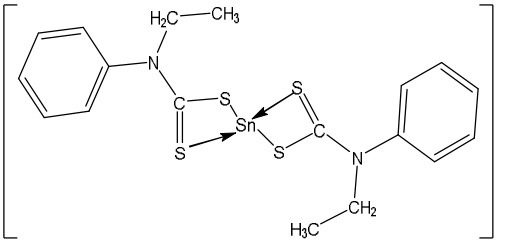
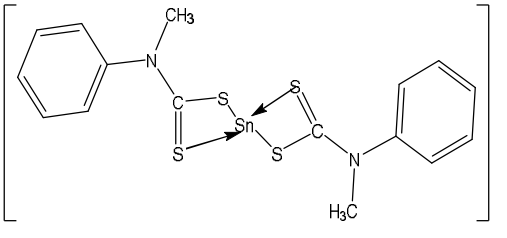


Fig. 20. UV-Vis- spectrum of Complex (C4L2)



n=0 for C3L2, n=2 for C4L2

Fig. 22.The proposed structure of (C3L2) and (C4L2) Complexes with L2 ligand



n=0 for C1L1 ,n=2 for C2L1

Fig. 21. The proposed structure of (C1L1) and (C2L1) Complexes with L2 ligand

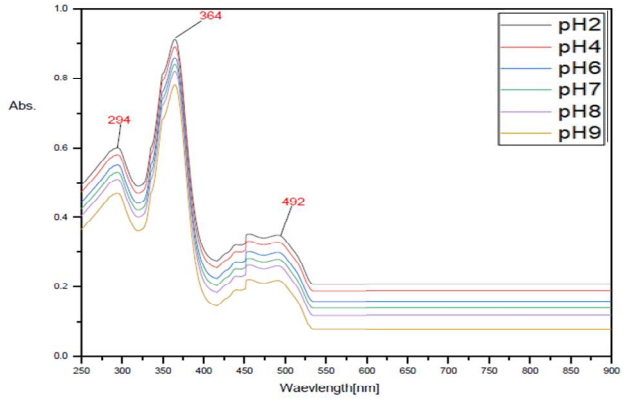


Fig. 24. pH formation of (C1L1)complex

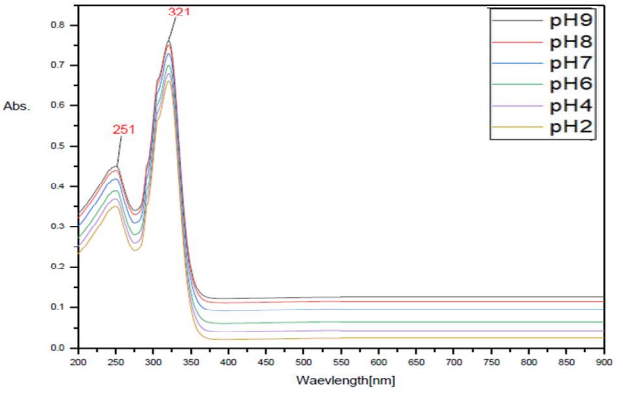


Fig. 23. pH formation of (L1) ligand

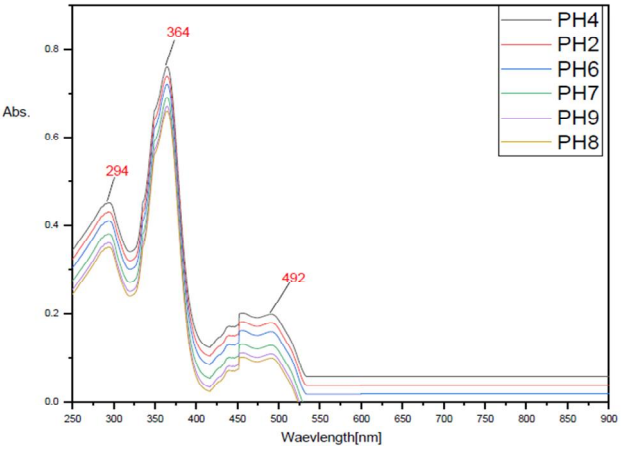


Fig. 25. pH formation of (C2L1) complex

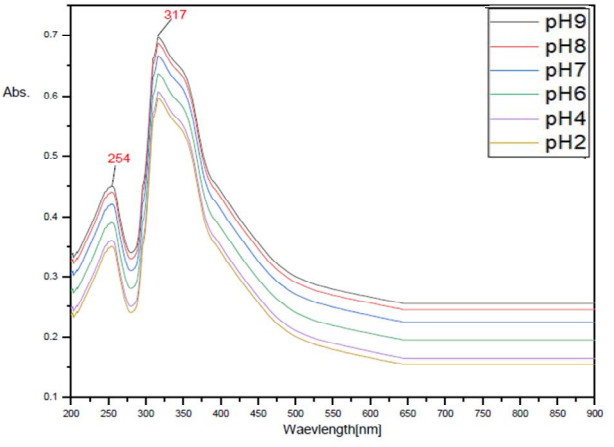


Fig. 26. pH formation of (L2) ligand

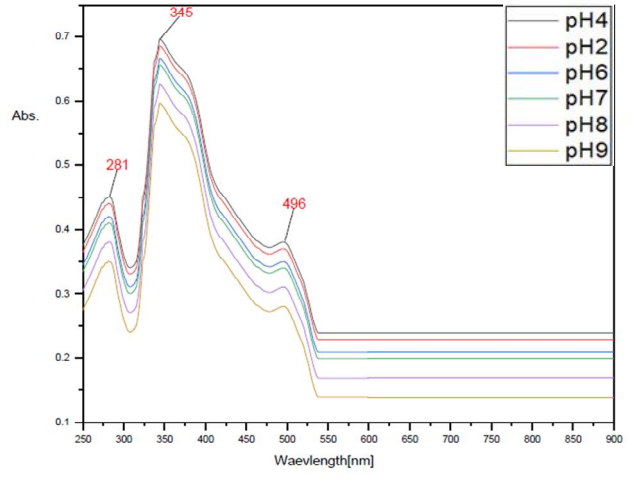


Fig. 28. pH formation of (C4L2) complex

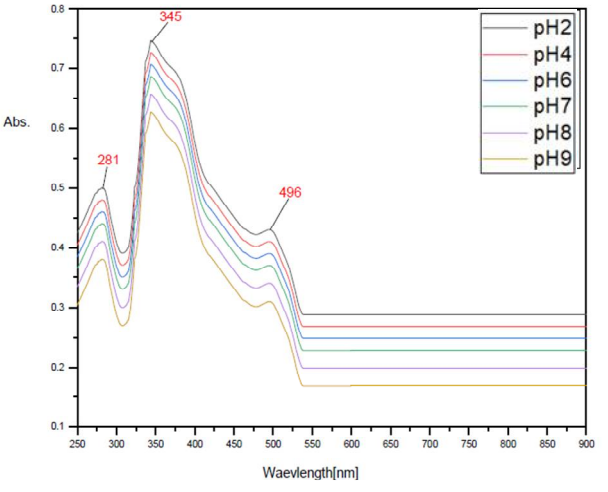


Fig. 27. pH formation of (C2L2) complex

Job's method was adopted for continuous changes in order to determine the positional formula of the complexes. This was conducted by mixing different volumes of solutions with equal concentrations ($2.29x10^{-4}$) of an appropriate metal ion with the L1 and L2 ligands separately to have a final volume of 10 mL. By fixing the optimum conditions reached in this study, the absorption of the complexes was measured at the greatest wavelength λ_{max}. Table 3 illustrated the results of this method. Through these results, the correlation in the complexes between the ion and the ligand ratio was (1 ; 2) mole for each one mole of metal to two moles of the ligand, *i.e.* ML_2.

Table 3. The results of Job's method (Continuous variables) for complexes derivative from L1, and L2 ligands at the greatest wavelength (λ_{max})

$\frac{VM}{VM+VL}$	Absorbance			
	C1L1	C2L1	C3L2	C4L2
0.1	0.115	0.115	0.226	0.332
0.2	0.275	0.284	0.295	0.416
0.3	0.486	0.491	0.478	0.592
0.4	0.490	0.486	0.494	0.595
0.5	0.468	0.471	0.467	0.582
0.6	0.448	0.456	0.456	0.562
0.7	0.437	0.442	0.425	0.541
0.8	0.325	0.430	0.423	0.521
0.9	0.416	0.419	0.420	0.510

3.5. Antibacterial Activity

The antibacterial activity of L1, L2 ligands, C1L1, C2L1, C3L2 and C4L2 complexes are shown in Table 4. All complexes were examined for their antibacterial activity in vitro against one type of Gram-positive bacteria (*Staphylococcus aurous*) and one type of Gram-negative bacteria (*Escherichia coli*). The agar plates were surface- inoculated uniformly from both cultures of the tested bacteria. In the solidified medium, the spaced-apart holes were all made 6 mm in diameter. These holes were filled with 40 µL of the prepared compounds (0.01 and 0.1) g/mL in DMF as a solvent. It is worth noting that the Augmentin was used as a control drug for comparison in the same concentrations as used for the complexes. These plates were incubated at 37 ^{o}C for 24 h. for both bacteria. The zones of bacterial growth inhibition around the discs were measured in (mm). The results indicated an inhibition of antibacterial activity. The L1 and L2 ligands and complexes C1L1, C2L1 and C3L2 showed greater activity against *Staphylococcus aurous* and *Escherichia coli* in high concentration, while C4L2 complex demonstrated higher activity toward *Staphylococcus aurous* and lower activity toward *Escherichia coli* in high concentration. These activities may be explained by Tweedy's chelation theory[36] according to which chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge in the ligand, which favors the permeation of the complexes through the lipid layer of the cell membrane.[37]

Table 4. The antibacterial activity of L1, L2 ligands, C1L1,C2L1,C3L2 and C4L2 complexes and Augmentin as a control drug

Bacteria	*Staphylococcus aurous*		*Escherichia coli*	
Compounds	Diameter of inhibition zone in (mm)			
	1mg	10mg	1mg	10mg
L1	12	16	11	15
L2	11	17	10	16
C1L1	13	18	14	14
C2L1	11	17	12	15
C3L2	11	12	10	14
C4L2	8	19	0	10
DMF	0	0	0	0
Augmentin	15	20	15	20

4. Conclusions

N-Alkyl-*N*-phenyl dithiocarbamate ligands L1 and L2 were used to prepare C1L1, C2L1, C3L2 and C4L2 complexes. According to elemental analyses (CHNS), ^{1}H NMR spectra, mass spectra, FT-IR spectra, UV-Vis spectra, molar conductivity and magnetic susceptibility, the structural formulas of the complexes were proposed. From the ^{1}H NMR and FT-IR spectra, it was clear that the groups of alkyl and thioureide in the ligands changed through coordination process with tin ions. The results of mass spectra showed consistency with the theoretical molecular weights of prepared complexes with the proposed molecular formula. The molar conductance values of the complexes C1L1 and C3L2 indicate the non-electrolyte nature, and of the complexes C2L1 and C4L2

indicate 1 : 2 electrolytic nature. The antibacterial activity of the metal complexes reveals that all the prepared metal complexes have effects on *Staphylococcus aureus* and *Escherichia coli* bacteria.

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СИНТЕЗ, ХАРАКТЕРИСТИКА Й АНТИБАКТЕРІАЛЬНА АКТИВНІСТЬ КОМПЛЕКСІВ ІОНІВ Sn(II) ТА Sn(IV), ЩО МІСТЯТЬ N-АЛКІЛ-N-ФЕНІЛДИТІОКАРБАМАТНІ ЛІГАНДИ

Анотація. *У цій роботі ліганди з донорними атомами S2, N-метил-N-фенілдитіокарбамат натрію [L1] та N-етил-N-фенілдитіокарбамат натрію [L2] одержано з дисульфіду карбону за допомогою N-метиланіліну та N-етиланіліну, відповідно. Комплекси іонів Sn(II) та Sn(IV) з N-алкіл-N-фенілдитіокарбаматом одержано та охарактеризовано за допомогою CHNS елементного аналізу, інфрачервоної спектроскопії (FT-IR), ^{1}H ЯМР-спектроскопії, масспектроскопії, УФ-спектроскопії, вимірювання магнітної сприйнятливості та провідності. Аналітичні та спектральні дані показують, що стехіометрія для всіх комплексів становить 1 : 2 метал до ліганду. Спектральні дані підтверджують добру координацію дитіокарбаматного ліганду з металом через атоми сульфуру в дитіокарбаматному фрагменті. Вимірювання молярної провідності комплексів з використанням ДМФА як розчинника показало, що комплекси Sn(II) є неіонними, тоді як комплекси Sn(IV) є іонними. Ліганди L1 і L2 та їхні комплекси досліджено щодо бактерій Staphylococcus aureus і Escherichia coli.*

Ключові слова: *антибактеріальна активність, N-алкіл-N-фенілдитіокарбамат, комплекси стануму, спектральні дані.*