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Wissam Abbas Ali
Chemistry Department, College of Science, Kerbala University, Iraq

Hayder Hamied Mihsen
Chemistry Department, College of Science, Kerbala University, Iraq

Sajid H. Guzar
Chemistry Department, College of Education for Pure Sciences, Kerbala University, Iraq

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ORIGINAL STUDY

Novel Derivative for Dithiocarbamite Containing a New Sulphur-Azo Linkage and Its Complexes with Sn(II), Sn(IV), Co(II), Ni(II) and Cu(II) Ions; Synthesis, Characterization and Antibacterial Activity

Wisam A. Ali [a], Hayder Hamied Mihsen [a,*], Sajid H. Guzar [b]

[a] Chemistry Department, College of Science, Kerbala University, Iraq
[b] Chemistry Department, College of Education for Pure Sciences, Kerbala University, Iraq

Abstract

The new ligand *N*-methyl-*N*-((((4-nitrophenyl)diazenyl)thio) carbonothioyl) aniline (LS2) was prepared by the reaction of 4-nitrobenzenediazonium salts with a (sodium *N*-methyl- *N*-phenyldithiocarbamate), a new ligand containing azo-sulphur linkage. A series of metal ions Sn(II), Sn(IV), Co(II), Ni(II), and Cu(II) were used to prepare metal complexes through reaction of two moles of LS2 ligand with one mole of appropriate metal chloride. The prepared compounds were characterized by CHNS elemental analysis, infrared spectroscopy (FT-IR), ^{1}H NMR-spectroscopy, mass spectroscopy, UV-visible spectroscopy, magnetic susceptibility, and conductivity measurements. Stoichiometry was determined using analytical and spectroscopic information and it was found to be 1:2 (metal to a ligand) for all complexes. The spectral data confirm the coordination of the LS2 ligand with all metal ions through sulfur atoms of dithiocarbamate moiety. Molar conductivity of complexes was measured using DMF as a solvent and it was indicated that all prepared complexes were ionic. According to the results obtained from the elemental analysis and spectral measurements were complexes of Sn(II), Sn(IV) and Co(II) tetrahedral geometry, while the complexes with Ni(II) and Cu(II) had a square planar geometry. The ligand LS2 and its complexes were examined against *Staphylococcus aurous* bacteria and *Escherichia coli* bacteria.

Keywords: Antibacterial activity, *N*-Alkyl-*N*-Phenyl dithiocarbamate, Tin complexes, Transition metal complexes, Spectral data

1. Introduction

Organic dithiocarbamate compounds are of great interest to many researchers because of their potential as useful synthetic intermediates and protecting groups in the synthesis of peptides and bonds in the organic solid phase [1–3]. Moreover, their occurrence in a variety of biologically active compounds, their pivotal roles in agriculture and for their biological properties led to the development of methods for their preparation [3,4]. Dithiocarbamate ligands can form many stable metal complexes via CSS^- with many metal ions (transition or non-transition) [2,4–6]. Dithiocarbamate complexes with tin ions are of great importance in stabilizing the stereochemistry of these complexes and have many applications in the fields of catalysis, agriculture and biology [6,7]. The interaction of thiocarbamate salts with the halides of organic acids and their derivatives is of great importance in preparing new types of dithiocarbamate derivatives. Mishra et al. have reported a series of nickel complexes type $[Ni(L)_2Cl_2]$ and $[Ni(L)_2(OCOCH_3)_2]$, where L = (cyclohexyl-N-thio)-1,2-ethylenediamine (L^1) and (cyclohexyl-N-thio)-1,3-propanediamine (L^2). These complexes were applied as antibacterials to bacteria and fungi [8]. Dialkyl dithiocarbamate salts have been reported to have biological features such as antibacterial, antifungal, antiviral, and antitumor [9,10], cytotoxicity and antitumor [11], and anti-HIV

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* Corresponding author.
E-mail address: hayder.kandoh@uokerbala.edu.iq (H.H. Mihsen).

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[12]. Recent study was conducted to prepare azo-dithiocarbamate heterocyclic compounds as a result of improving their special properties and their important applications in biological aspects such as antimicrobial, antitubercular, anticancer, and molecular docking studies [13]. Here we have reported a synthesis of a new ligand having azo-sulphur linkage, then the new ligand was used to synthesize a series of metal complexes with Sn(II) and Sn(IV), Co(II), Ni(II), and Cu(II) ions, in addition to assessing its bacterial activity.

2. Experimental

2.1. Chemicals and instrument

The chemicals that were used in the current study are Sodium hydroxide 97% (GCC, England), carbon disulfide 99.8 (LOBA. Chem), *N*-methyl aniline 89% (GCC, England), Diethyl ether 95% (Scharlau), *p*-nitroaniline 99% (Sigma–Aldrich, Germany), sodium nitrite 97% (Sigma–Aldrich, Germany), Ethanol 99% (Sigma–Aldrich, Germany), Tin chloride dihydrate 99% (BDH, England), Tin chloride pentahydrate 98% (BDH, England), Nickel chloride hex hydrate 96% (BDH, England), Cobalt chloride hex hydrate 97% (BDH, England), Copper chloride dihydrate 96% (BDH, England). The methods utilized in this project are innovative. FT-IR spectra of the ligands LS2 and its complexes were characterized using the FTIR 8400s (Shimadzu). The spectra were recorded at the range of 4000–400 cm^{-1}, ^{1}H NMR was measured by BAMX400 MHZ Spectrophotometer in d6-DMSO as a solvent, mass spectra were characterized using the mass Spectrophotometer (Agilent Technologies 5975C), UV-visible spectra were reordered using Shimadzu double beam 1800 UV spectrophotometer in dimethylformamide (DMF) as a solvent at 1×10^{-3} M, The elemental analysis (CHNS) was conducted on an Eager 300 for EA1112. The melting point of compounds produced was measured by using Gallen Kamp melting point, the molar conductivity for a digital Conductivity Series was used to measure complexes. The magnetic susceptibility of prepared complexes was measured by using Balance Magnetic Susceptibility Model-M.S.B Auto.

2.2. Synthesis

2.2.1. Synthesis of sodium N-methyl- N-phenyldithiocarbamate(L) [4]

The carbon disulfide (3.8 g, 0.05 mol) was added to an ice-cold solution of sodium hydroxide (0.02 g, 0.05 mol) in distilled water (about 3 mL). *N*-methyl aniline was then added to the mixture (5.44 mL, 0.05 mol). For 2 h, the mixture was stirred at a temperature of 4 °C. Through the process of recrystallization using hot acetone, a yellowish-white solid was produced and then separated, filtered, washed with ether, and lastly recrystallized therefrom. The white solid product was dried under vacuum over $CaCl_2$ at room temperature giving 1.633 g (yield = 82%), mp > 300 °C . Elemental analysis CHNS: Found (calc.) %: C; 46.80 (46.82); H; 3.91 (3.92); N; 6.80 (6.82); S; 31.22 (31.24).

2.2.2. Synthesis of N-methyl-N-((((4-nitrophenyl) diazenyl)thio) carbonothioyl) aniline [LS2]

The 4-nitroaniline (1 g, 0.0072 mol) was dissolved in a 5 mL 1:1 ratio of HCl to water and the solution was cooled down quickly to a temperature below 0–5 °C with vigorous stirring to obtain a cooling solution. To this solution, a sodium nitrite (0.5 g, 0.0072 mol) in (3 mL) of cold water was added dropwise. After stirring at 0–5 °C for 30 min a white solution was obtained. To this white solution, a sodium N-methyl-N-phenyldithiocarbamate (1.5 g, 0.0072 mol) dissolved in (6.6 mL) of water was added dropwise, the reaction mixture was left with a stirrer for 1 h. at 0–5 °C . The produced precipitate was filtered and washed with cold water to give new ligand LS2, Red product, yield 80% (1.9 g, 0.0057moL), mp 140 °C Elemental analysis CHNS: Found (calc.) %: C; 50.64 (50.67); H; 3.63 (3.64); N; 16.56 (16.78); S; 19.10 (19.31). Scheme 1: show the preparation of Ligand [LS2].

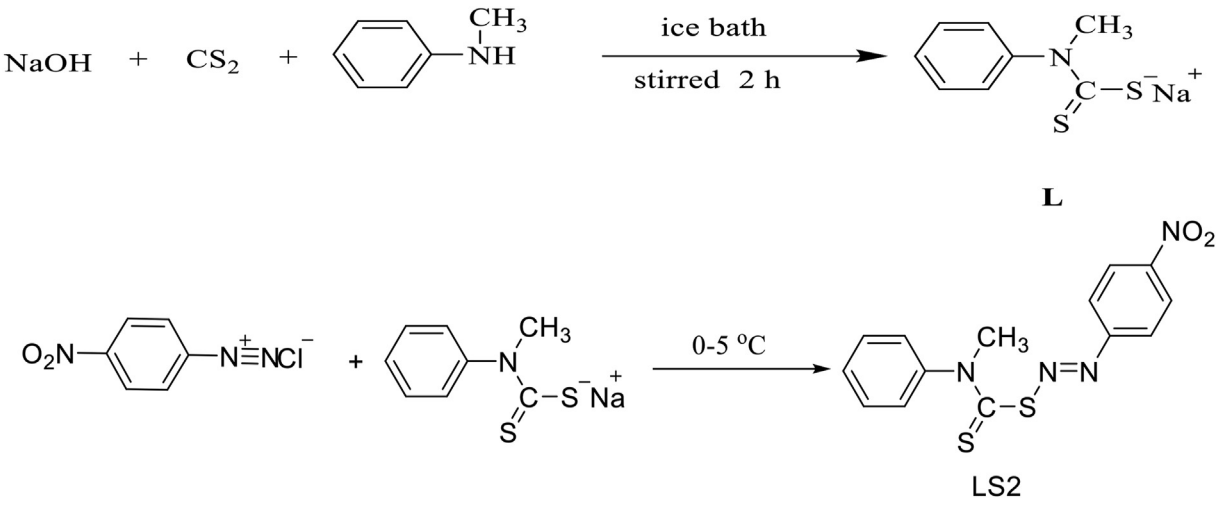
2.2.3. Synthesis of Tin(II), Tin(IV),Cobalt (II), Nickel (II), and Copper (II) complexes with LS2 ligand

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

3. Results and Discussion

3.1. Infrared spectroscopy

The IR spectrum of the ligand LS2 Table 2 exhibit distinct bands between 1450 and 1550 cm^{-1} belonging to the C–N of NCS_2 [14]. The ($CS_{2asym.}$) was observed at 1004 cm^{-1} [15], while the ($CS_{2\ sym.}$) was observed at 1099 cm^{-1}. Further, the peaks appeared at 1597 cm^{-1} and 1518 cm^{-1} assigned to the ν(-N=N-) and ν_{asym} (NO_2) stretching vibrations, respectively [16,17] The IR spectra of (C1LS2) and



Scheme 1. Schematic representation for the preparation of Ligand [LS2].

(C2LS2) complexes showed the thioureide ν(C−N) band to be at around 1492 cm^{-1} [18], while the (C−S) stretching appeared at 1168 cm^{-1} and shifted to a higher energy than the ligand because of the coordination. Azo (-N=N-) functional group stretched at 1599 cm^{-1} for (C1LS2) and 1593 cm^{-1} for (C2LS2) complexes. The C=S characteristic stretching frequency vibrated between 1097 and 1111 cm^{-1} [14,15] .The *υ* (Sn−S) bands (found in the far-infrared region) appeared around 411−472 cm^{-1} [19]. In the IR spectra of transition metal complexes (C3LS2), (C4LS2), and (C5LS2), the peaks in the range 1597−1593 cm^{-1} corresponded to υ (-N=N-) azo stretching band. This confirms that it did not change a lot during the coordination of the ligand with the metal ions. The C=S characteristic stretching frequency was observed at 1111 cm^{-1}, 1101 cm^{-1}, and 1107 cm^{-1}. The asymmetric (C−S) stretching was observed at 1168 cm^{-1}, 1170 cm^{-1}, and 1174 cm^{-1} vibrations, respectively, shifting to higher energy because of the coordination, [17,20]. Furthermore, new bands have been observed in the range (441−437) cm^{-1} related to υ (M−S).

3.2. ^1H NMR and Mass Spectroscopy of Complexes.

The ^{1}HNMR spectrum of LS2 ligand Fig. 1 showed a singlet peak at $\delta = 3.70$ ppm equivalent to three protons of the methyl group in N−CH_3. The multiple signals observed in the region $\delta = 7.20–7.58$ ppm are attributed to the protons of *N*-phenyl rings as follows: at the site δ= (7.20−7.25) ppm, a triplet peak is attributed to the aromatic proton in the site (*b*), at the site δ= (7.25−7.30) ppm, a triplet peak is attributed to the aromatic proton in the two locations (*c*) and at the site δ= (7.55−7.58) ppm, a duplet peak is attributed to the aromatic proton in the two locations (*d*) [21]. This means that the substitution occurred on the sulfur anion of dithiocarbamate (in the reaction between diazonium salt and sodium *N*-methyl- *N*-phenyl-dithiocarbamate), and not the reaction of azo-coupling on the benzene ring in the (*para*) site on sodium *N*-methyl- *N*-phenyldithiocarbamate). The multiple signals observed in the region $\delta = 7.88–8.17$ ppm are attributed to the protons of *Azo*-phenyl rings [22]. In the ^{1}H NMR spectra of the (C1LS2), and (C2LS2) complexes, the most proton signals changed and shifted on complexation due to coordination of the ligand to the metal ion. A singlet peak at $\delta = 3.25$ ppm is equivalent to three protons of the methyl group N−CH_3. A high field by $\delta = 0.45$ ppm as compared to the chemical shifts of *N*-methyl dithiocarbamate (observed at the $\delta = 3.70$) was observed. The difference could be due to the

Table 1. Physical properties of prepared complexes.

Complex	Metal ion	Yield%	Color	Melting point °C (de)
C1LS2	Sn(II)	69	Yellow	164
C2LS2	Sn(IV)	72	Orange	161
C3LS2	Co(II)	65	Black	175
C4LS2	Ni(II)	74	Black	170
C5LS2	Cu(II)	68	Brown	162

Table 2. Frequencies of FT-IR Spectra of LS2 Ligand and its complexes.

Compound	C−H (Methyl)	C−N	C=S	NO_2	N=N	C−S	M-S
LS2	2848	1494	1099	1518	1597	1004	_
(C1LS2)	2850,2926	1492	1097	1519	1599	1168	470
(C2LS2)	2848,2926	1492	1097	1519	1593	1168	472
(C3LS2)	2847,2922	1464	1111	1519	1593	1168	439
(C4LS2)	2926	1484	1101	1519	1593	1173	441
(C5LS2)	2845,2937	1464	1107	1516	1597	1174	437

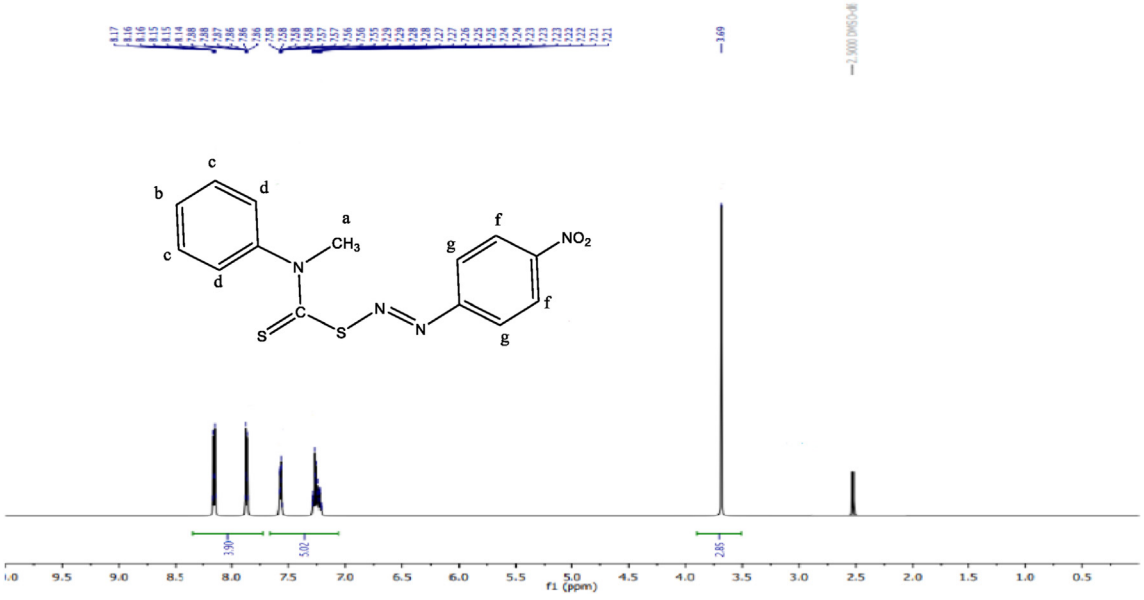


Fig. 1. ^{1}H NMR Spectrum of Ligand LS2.

effect of the electron density of nitrogen atoms compared to alkyl carbon. It is shown that the coordinated dithiocarbamate group had less electron density than in the case where there is no coordination. The multiple signals observed in the region δ = 7.20–7.60 ppm are attributed to the protons of *N*-phenyl rings [21]. The protons of the Azo-nitro benzene showed a sign at the site δ= (8.10–8.33) ppm, [22,23]. The ^{1}H NMR chemical shifts of the (C3LS2), (C4LS2), and (C5LS2) complexes showed a singlet peak at 3.28 attributed to methyl protons. The site δ= (7.20–7.60) ppm had a triplet peak attributed to the aromatic proton in *N*-phenyl rings. The protons of the Azo-nitro benzene showed a sign at the site δ= (7.55–8.20) ppm [22,24].

The mass spectrum of (LS2) ligand Fig. 2 and its complexes (C1LS2), (C2LS2), (C3LS2), (C4LS2) and (C5LS2) were recorded to establish their structural formula. The experimental parent molecular ion peaks of prepared complexes were at (332.1), (853.6),

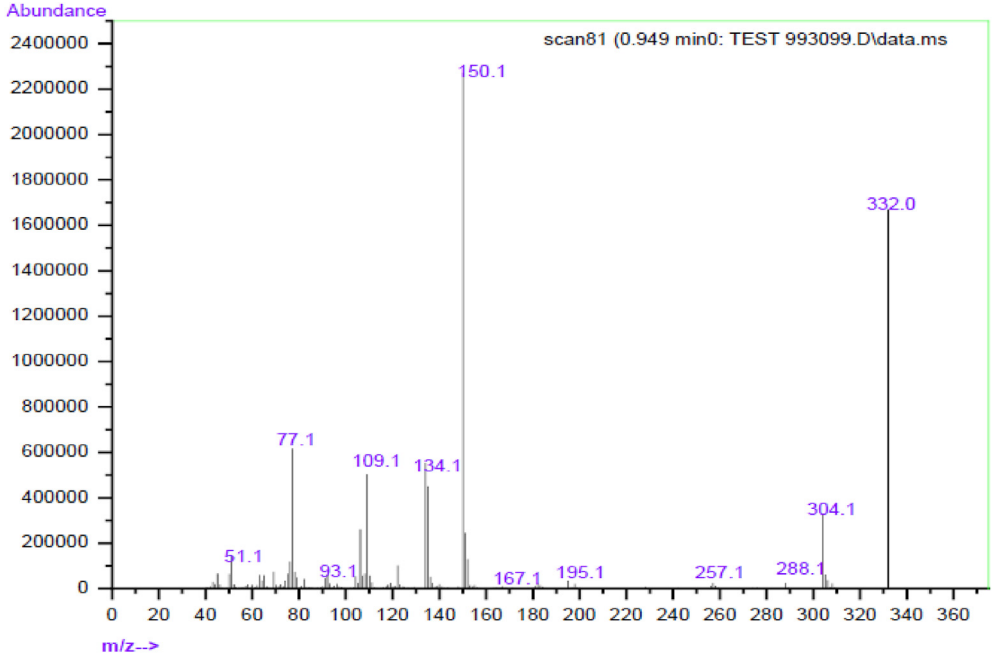


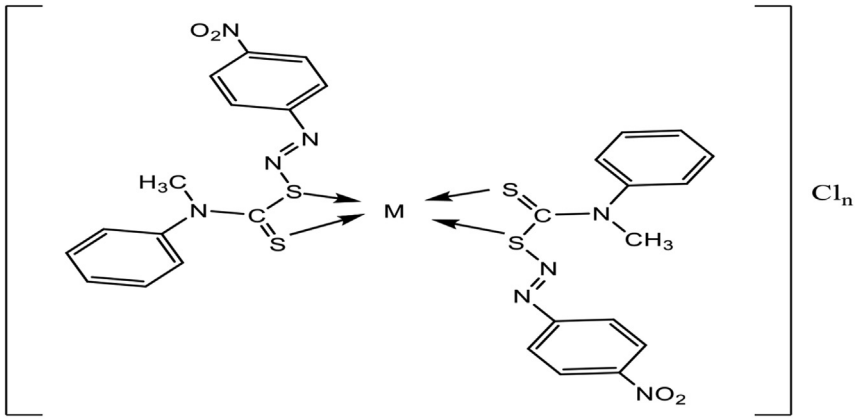
Fig. 2. Mass Spectrum of ligand (LS2).

(924.9), (793.9), (793.6) and (798.5) (m/z). The molecular structures of ligand and its complexes were shown to be accurate. As the most significant ligand are azo, thioureido, and thiocarbonyl coupled with the production of positive molecular ions and other positively charged fractions, ligand and its complexes adopted numerous fractionation pathways due to their large relative abundance [25].

3.3. Electronic spectra and magnetic properties

In the electronic spectrum of the ligand (LS2), a peak was observed at 225 nm and 319 nm, which corresponds to the electronic transition ($\pi \rightarrow \pi^*$) of the C=C in benzene, N−C=S and −N=N− systems [26]. A peak was observed between 400 and 440 nm due to the ($n \rightarrow \pi^*$) electronic transition located on the nitrogen and sulfur atoms in N−C=S and −N=N−systems [27–29] . The electronic spectra of tin complexes (C1LS2) and (C2LS2) showed four peaks, at 248 and 339 nm assigned to electronic transmission ($\pi \rightarrow \pi^*$) of the benzene, N−C=S and *Azo*-phenyl systems. A peak at 464 nm was due to the ($n \rightarrow \pi^*$) electronic transition located on the nitrogen and sulfur atom. No d−d transitions were anticipated for d^{10} complexes, which is consistent with the spectra of tetrahedral tin (II)and (IV) complexes. The fourth absorption band at (584) nm belongs to metal to ligand charge transfer (MLCT), corresponding with a d^{10} system that tailed into the visible range, indicating redshift due to the coordination process. The magnetic susceptibility of tin complexes (C1LS2) and (C2LS2), equal to (0.0)B.M and molar conductivity measurement in DMF was 162 and 165 (μs/cm), respectively. This indicates that the complexes were diamagnetic and electrolytic in 1:2 ratio, [30,31]. The proposed structure of (C1LS2) and (C2LS2) complexes can be suggested as illustrated in Fig. 3.

The UV-Vis spectrum of cobalt (II) complex (C3LS2) showed the bands at 601 nm and 531 nm which are expected to belong to the $^4A_2(F) \rightarrow {}^4T_2(F)$, and the $^4A_2\ (F) \rightarrow {}^4T_1(F)$ transitions in tetrahedral environmental for cobalt (II) complexes [32]. Metal to ligand charge transfer (MLCT) transitions were observed at 446 nm and intra-ligand transitions at approximately 348 and 339 nm [33,34]. The magnetic susceptibility (μ = 4.2 B.M) and conductivity measurement in DMF were 167 (μs/cm) which indicate that the complex had tetrahedral structure and electrolyte [35,36]. The electronic spectrum of nickel complex (C4LS2) showed four peaks as follows: three bands attributed to intra-ligand transitions at approximately 257 nm, 350 nm, and 467 nm. The fourth band around 538 nm can be attributed to $\upsilon_2\ {}^1A_1g \rightarrow {}^1B_1g$ in square planar nickel (II) complexes [37–39]. The electronic spectrum of the Cu(II) complex (C5LS2) exhibits that the absorption band at 472 nm is assigned to metal to ligand charge transfer (MLCT)). The broad band between 601 and 675 nm can be attributed to $^2B_1g \rightarrow {}^2A_1g$, $^2B_1g \rightarrow {}^2B_2g$, $^2B_1g \rightarrow {}^2Eg$ transitions. These transitions belong to the square planar environment in the Cu(II) ion [40,41]. The molar conductivity of the (C4LS2) and (C5LS2) were 152 and 159 (μs/cm). This verifies that the electrolyte solutions had a molar ratio of 1:2. The



C1LS2 ; M=Sn(II) , n=2
C2LS2; M= Sn(IV), n=4
C3LS2; M= Co(II), n=2
C4LS2; M= Ni(II), n=2
C5LS2; M= Cu(II), n=2

Fig. 3. Coordination of metal ions with ligand LS2 via dithiocarbamate moiety.

magnetic moment of nickel complex C4LS2 was 0.0 B.M, which indicates that it has square planar geometry and this complex can have diamagnetic properties because it has no individual electrons in d^8 configuration. The magnetic moment value for copper complex C5LS2 was 2.0 B.M, which is within the range of square planar shape [36,42,43] Fig. 3.

3.4. The effect of pH on the formation of (LS2 ligand and its complexes) and stoichiometry determination of complexes

The effect of pH on formation LS2 ligand and tin (II), (IV),Co(II),Ni(II), and Cu(II) complexes is shown in Table 3. The results show that the pH at λ_{max} of the ligand pH = 8 and complexes is pH = 2,pH = 4, pH = 7, pH = 8 and pH = 9, respectively.

Mole ratio method was used to determine the stoichiometry of complexes. Briefly, this method is conducted by measuring the absorbance of a series of solutions of complexes containing large amounts of ligand concentration with the concentration of the metal ion stable at the previously specified maximum wavelength (λ_{max}) and absence of any absorption of both components in that region. The relationship between the molar absorbance represented by the y-axis and the concentration ratio of Metal: ligand of the mixing solutions represented by the x-axis and then the straight lines were drawn until they intersect and become the point of intersection. This is the molar ratio to be determined for each metal ion in its complex. It is worth noting that the solutions of the complexes in preparation and the intensity of its colors increase when approaching the points of intersection indicating the ratio of (metal: ligand), and the color continues constantly when passing this point, which indicates that the complex formed is stable in its solution [44,45].

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

$\frac{VM}{VM+VL}$	Absorbance				
	C1LS2	C2LS2	C3LS2	C4LS2	C5LS2
1:0.25	0.122	0.138	0.094	0.048	0.068
1:0.50	0.146	0.165	0.116	0.067	0.077
1:0.75	0.162	0.179	0.134	0.078	0.099
1:1.00	0.185	0.203	0.146	0.097	0.116
1:1.25	0.202	0.216	0.163	0.107	0.137
1:1.50	0.229	0.232	0.173	0.119	0.145
1:1.75	0.248	0.251	0.182	0.138	0.157
1:2.00	0.267	0.263	0.204	0.153	0.171
1:2.25	0.274	0.271	0.216	0.157	0.178
1:2.50	0.283	0.278	0.218	0.159	0.185
1:2.75	0.289	0.286	0.219	0.167	0.193
1:3.00	0.296	0.295	0.228	0.173	0.198

Table 4. The antibacterial activity of LS2L Ligand and its complexes.

Bacteria	*Staphylococcus aurous*		*Escherichia coli*	
Compounds	Diameter of inhibition zone in (mm)			
	1 mg	10 mg	1 mg	10 mg
LS2	8	11	7	18
C1LS2	6	7	9	21
C2LS2	13	8	16	20
C3LS2	4	5	6	10
C4LS2	7	18	3	17
C5LS2	0	8	4	13
DMF	0	0	0	0
Augmentin	15	20	15	20

3.5. Antibacterial activity

The antibacterial activity of LS2 ligand and its complexes C1LS2, C2LS2, C3LS2, C4LS2, and C5LS2 complexes are shown in Table 4. All complexes were tested in vitro against one Gram-positive bacteria (*Staphylococcus aureus*) and one Gram-negative bacteria (*Escherichia coli*). Two strains of the bacteria tested were evenly distributed on the agar plates. All holes were 6 mm in diameter and were drilled into the solidified material at intervals of 6 mm. In order to plug these holes, 40 L of the produced compounds were used (0.01 and 0.1) g/mL in DMF as a solvent. It is worth noting that the Augmentin was used as a controlled drug for comparison as an antibacterial in the same concentrations as used for the complexes. Each of these plates was incubated for 24 h with both bacteria at 37 °C. The zones of bacterial growth inhibition around the discs were measured in (mm). The LS2 ligand and C4LS2 complex indicate greater activity against *S. aureus* in increased concentration, but the C1LS2, C2LS2, C3LS2, and C5LS2 complexes gave less efficacy. However, LS2 and C1LS2, C2LS2, C3LS2, C4LS2, and C5LS2 complexes gave higher activity toward *E. coli* in increasing concentration, but among those complexes, complex C1LS2 has the highest activity against *E. coli* bacteria, even more than the Augmentin.

4. Conclusion

N-methyl-*N*-((((4 nitrophenyl)diazenyl)thio) carbonothioyl) aniline Ligand LS2 was used to prepare C1LS2, C2LS2, C3LS2, C4LS2, and C5LS2 complexes. According to elemental analyses (CHNS), FT-IR spectra, UV-Vis spectra, ^{1}H NMR spectra, mass spectra, molar conductivity, and magnetic susceptibility, the structural formulas of the complexes were proposed. From the spectra of ^{1}H NMR and FT-IR, it was clear that the groups of alkyl and

thioureido in the ligands changed through the coordination process with ions tin (II), (IV), cobalt (II), nickel (II), and copper (II). The results of mass spectra were shown consistent with the theoretical molecular weights of prepared complexes with the proposed molecular formula. The molar conductance values of the complexes C1LS2, C2LS2, C3LS2, C4LS2, and C5LS2 indicate a 1:2 electrolytic nature. The antibacterial activity of the metal complexes reveals that all the prepared metal complexes have effect on *S. aureus* and *E. coli* bacteria.

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