Synthesis and Characterization of Sodium Diphenylcarbamodithioate Ligand [L] and its Cobalt, Nickel, and Copper Complexes

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***Abstract*—A correlation of the infrared (IR) spectra of thiocarbonyl derivatives based on the literature data has been carried out. Assignments have also been made in some new systems. Sodium diphenylcarbamodithioate ligand and its monomeric complexes were synthesized at room temperature and stirring condition. The ligand and its complexes of the general formula $[M(L)_2]$ (where M=Co^{II}, Ni^{II}, and Cu^{II}) were characterized by spectroscopic methods (IR and ultraviolet-visible), elemental analysis (CHN and S) metal content, magnetic susceptibility measurement, and biological activity (an antibacterial activity of the complex was studied by agar disc diffusion method and minimum inhibitory concentration strain against *Staphylococcus aureus* and *Bacillus subtilis*). The complex exhibited significant activities against *S. aureus and B. subtilis*, thin-layer chromatography, mass spectrometry, X-ray powder diffraction, and molar conductance. Our study revealed the formation of four-coordinate square planar complexes around Co^{II}, Ni^{II}, and Cu^{II} metal ions.**

***Index Terms*—Diphenylcarbamodithioate complexes, Four-coordinate square planar complexes, Sodium diphenylcarbamodithioate ligand, Structural study.**

I. Introduction

Diphenylamine is an organic compound with the formula $(C_6H_5)_2$.NH. The compound is a derivative of aniline, consisting of an amine group bounded with two phenyl groups. The compound is a colorless solid, but commercial samples are often yellow due to oxidized impurities (Vogt and Gerulis, 2005). Diphenylamine dissolves well in many common organic solvents and is moderately soluble in water (Canady, et al., 2013). It is used mainly for its antioxidant properties. It is used as scald inhibitor for apples applied as an indoor drench treatment. Its anti-scald activity is the result of its antioxidant properties, which protect the apple skin from the oxidation products during storage scald (or “apple scald”) as physical injury that manifests in brown spots after fruit is removed from cold storage (Ingle and D’Souza, 1989). Carbon disulfide (CS_2), also called carbon bisulfide, a colourless, toxic, highly volatile and flammable liquid chemical compound, large amounts of which are used in the manufacture of viscose rayon, cellophane, and carbon tetrachloride; smaller quantities are employed in solvent extraction processes or converted into other chemical products, particularly accelerators of the vulcanization of rubber or agents used in flotation processes for concentrating ores (Holleman and Wiberg, 2001). Copper$^{(II)}$ complexes have been described as a plastic metal ion because the chemistry of its complexes exhibits different coordination numbers with many kinds of irregular coordination geometries, such as tetrahedral or square planar four-coordinate, octahedral six coordinate, and square pyramidal or trigonal–bipyramidal five coordinate (Saadeh, 2013).

In this manuscript, we describe the synthesis and physical characterization of sodium diphenylcarbamodithioate ligand and its new monomeric metal complexes with a range of divalent transition metal ions (Co^{II}, Ni^{II}, and Cu^{II}), in the ratio of 1:2 metal ligands, forming new compounds of C-S and S-M new bands by condensation reaction, and it has been supported by the most important techniques.

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II. Materials and Measurements

A. Materials

Chemical reagents were commercially available and used without purification. Solvents were distilled from appropriate drying agents immediately before to use.

B. Physical Measurements

Reagents were purchased from Fluka and Redial–Dehenge Chemical Co. Melting points were obtained on a

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Buchi SMP-20 capillary melting point apparatus and are uncorrected. Fourier transform IR (FTIR) spectra were recorded as FTIR spectrophotometer in the range 4000-400 cm^{-1}. Electronic spectra of the prepared compounds were measured in the region 200-900 nm for 10^{-3} M solutions in dimethyl sulfoxide (DMSO) and distilled water at 25°C using a Shimadzu160 spectrophotometer with 1.000±0.001 cm matched quartz cell. Elemental microanalyses were performed on a CHN analyzer. While metal contents of the complexes were determined by atomic absorption (AA) technique using a Shimadzu AA 680G AA spectrophotometer. Electrical conductivity measurements of the complexes were recorded at 25°C for 10^{-3} M solutions of the samples in DMSO and distilled water using a PW 9526 digital conductivity meter. Magnetic measurements were recorded on a Bruker BM6 instrument at 298°K following the Faraday's method.

III. Synthesis

A. Preparation of Sodium Diphenylcarbamodithioate Ligand

A suspension of finely powdered sodium hydroxide (0.15 g, 3.75 mmol) in (10 ml) absolute methanol was added dropwise with continues stirring for 24 h to a solution of diphenylamine (0.5 g, 2.95 mmol) and CS_2 (0.22 ml). The solvent was removed under reduced pressure, and the residue was dried from methanol to form a white precipitate. Yield: (74%), m.p. (66°C).

B. General Synthesis of the Complexes

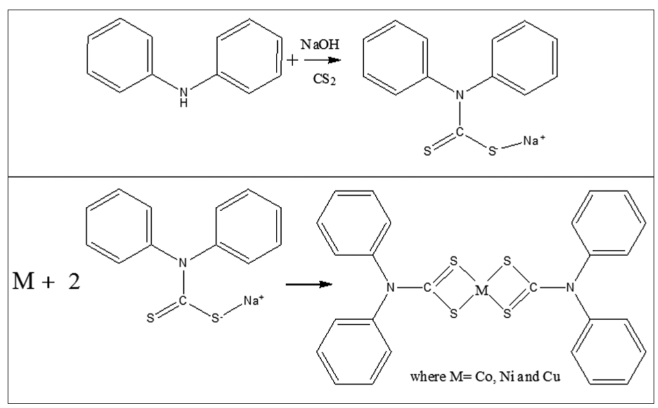
Diphenylcarbamodithioate complexes were prepared by the general methods and as follows: A solution of methanol (10 ml) and nickel chloride salt (0.177 g, 0.75 mmole) was added with stirring into methanolic solution of the sodium diphenylcarbamodithioate ligand (0.2 g, 1.49 mmol) in methanol (15 ml). The mixture was allowed to stir for 2 h, and then distilled water was added, the resulted solid was filtered off, and washed with methanol and dried at room temperature to give the required diphenylcarbamodithioate complex. All the other complexes have been prepared in the ratio of 1:2 metal-ligand. Elemental analysis data, colors, and yields for the complexes are given in Table I.

IV. Results and Discussion

Sodium diphenylcarbamodithioate ligand was achieved from the reaction of diphenylamine with CS_2 in the ratio of 1:1 in alkaline medium. The general synthetic method for the preparation of the ligand and its complexes involves the reaction of the metal chloride salts with exothermic behavior according to Scheme 1. The ligand was obtained in almost a quantitative yield, and the metal complexes of the ligand with Co^{II}, Ni^{II}, and Cu^{II} metal ions were obtained in moderate yields. The compounds were characterized by elemental analysis, IR, ultraviolet-visible (UV-Vis), magnetic susceptibility, melting point, thin-layer chromatography (TLC), and conductivity measurements.

A. The IR Spectrum of the Ligand

The band at 3210 cm^{-1} due to the υ(N–H) amine group (Semalty, et al., 2010) of diphenylamine has been disappeared in the spectrum of the sodium diphenylcarbamodithioate ligand as a result of the replacement the hydrogen atom by CS_2 and forming strong vibrational coupling is operative in the case of the nitrogen containing thiocarbonyl derivatives and three bands seem to consistently appear in the regions 1386-1566 cm^{-1}, 1250-1411 cm^{-1}, and 955-1110 cm^{-1} due to the mixed vibrations, these bands, which may be tentatively designated as the Ph_2N-CS_2 ~ (Venkataraghavana and Raoa, 2005). On the other hand, a new bands have been formed at 1500 cm^{-1}, 1070 cm^{-1}, and 1300 cm^{-1} due to aliphatic υ(C-N)



Scheme 1: Synthetic route for ligand, and general structure for suggested Co^{II}, Cu^{II}, and Ni^{II} metal ion complexes

TABLE I
The Physical Properties of the Ligand and its Metal Complexes

Molecular formula	Molecular weight	Yield%	Color	M.P.°C	Found (calc%)					ƐM(Ω^{-1} cm^2mol^{-1})
					M	C	H	S	N	
[L] $C_{13}H_{10}NNaS_2$	267.35	74	White	66	8.6	58.4	3.77	23.99	5.24	-
					7.33	54.12	3.02	22.43	5.01	
$C_{26}H_{20}CoN_2S_4$	547.64	66	Yellow	170	10.76	57.02	3.68	23.42	5.12	10.6
					9.55	54.87	3	20.02	4.23	
$C_{26}H_{20}N_2NiS_4$	547.4	56	Pal yellow	103	10.72	57.05	3.68	23.43	5.12	12.9
					9.99	55.65	2.39	22.89	4.69	
$C_{26}H_{20}CuN_2S_4$	552.26	78	Orange	90	11.51	56.55	3.65	23.22	5.07	11.2
					10.79	54.12	3.03	22.23	4.77	

(Bailey, et al., 1991), υ(C-S) (Roeges, 1994), and υ(C=S) (El-Shazly, et al., 2005). Moreover, the band at 1610 cm^{-1} of υ(C=C) is still presented of the aromatic ring (Seleem, et al., 2011) (Table II).

B. The UV-Vis Spectrum of the Ligand

The UV-Vis spectra of the ligand exhibit a high intense absorption peak at 253 nm (39,525 cm^{-1}) (∈max=1420 $molar^{-1}$. cm^{-1}), assigned for ($\pi \rightarrow \pi^*$), with a shoulder peak at 302 nm (33112 cm^{-1}) (∈max=54 $molar^{-1}$.cm^{-1}) were assigned to ($n \rightarrow \pi^*$) transitions (Anuradha and Rajarel, 2011) (Table III).

C. The IR Spectrum of the Complexes

An important bands of all the formed complexes at 1110 cm^{-1}, 1131 cm^{-1}, and 1120 cm^{-1} attributed to υ(C-S), and the bands at 1210 cm^{-1}, 1231 cm^{-1}, and 1220 cm^{-1} assigned to υ(C=S) for (Co^{II}, Ni^{II} and Cu^{II}) ion complexes, respectively (Al-Fahdawi and Al-Salihi, 2015), which are shifted to lower frequency as a result of the coordination with metal ions. Moreover, the new bands at 440 cm^{-1}, 450 cm^{-1}, and 477 cm^{-1} have been formed are attributed to υ(M-S) of (Co^{II}, Ni^{II}, and Cu^{II}) ion complexes, respectively (Al-Fahdawi, et al., 2014; Beer et al. 2003; and Bensebaa, et al., 1999) (Table II).

D. The UV-Vis Spectra of the Complexes

The UV-Vis spectra of Co^{II}, Ni^{II}, and Cu^{II} complexes showed two intense peaks in the range 243 nm (41,152 cm^{-1}) (∈max=1243 $molar^{-1}$. cm^{-1}), 222 nm (45,045 cm^{-1}) (∈max=765 $molar^{-1}$. cm^{-1}), and 249 nm (40,160 cm^{-1}) (∈max=1567 $molar^{-1}$. cm^{-1}) range assigned to the ligand field for Co^{II}, Ni^{II}, and Cu^{II} metal ions, respectively (Griffith, et al., 2011). Other peaks at 366 nm (27,322 cm^{-1}) (∈max=65 $molar^{-1}$. cm^{-1}), 310 nm (32,258 cm^{-1}) (∈max=100 $molar^{-1}$.cm^{-1}), and 300 nm (33,333 cm^{-1}) (∈max=81 $molar^{-1}$. cm^{-1}) range assigned to the charge transfer transition for Co^{II}, Ni^{II}, and Cu^{II}, respectively (Amy, et al., 2011). The third peak detected in the visible region for same complexes at 560 nm (17,857 cm^{-1}) (∈max=50 $molar^{-1}$. cm^{-1}), 534 nm (18,726 cm^{-1}) (∈max=90 $molar^{-1}$. cm^{-1}), and 555 nm (18,018 cm^{-1}) (∈max=204 $molar^{-1}$.cm^{-1}) is due to $^4T_1g_{(F)} \rightarrow {}^4A_2g_{(p)}$, $^1A_2g \rightarrow {}^1A_1g$, and $^2A_1g \rightarrow {}^2B_1g$ transitions indicating square planar structure (Manishankar, et al., 2001) around Co^{II}, Ni^{II}, and Cu^{II} metal complexes (Table III).

E. Molar Conductance

The molar conductance of the Co^{II}, Ni^{II}, and Cu^{II} metal ion complexes indicates non-electrolytic nature in DMSO solutions (Kai, et al., 2009) (Table I).

F. Magnetic Moment

The magnetic moment (2.2, 1.9, and 2.1 B.M) value of the Co^{II}, Ni^{II}, and Cu^{II} ion complexes, respectively, as well as the other analytical data Table III is in agreement with suggested structure of square planar geometry for the three complexes in the solid state (Uppadin, et al., 2001; Al-Jeboori, et al., 2010). TLC measurement for the derivative ligands [L] and

TABLE II
FTIR Spectra for the Ligand and its Complexes

Compound	ν(N-H)	ν(X-N)	ν(X=Σ)	ν(X-Σ)	ν(M-Σ)
Diphenylamine	3210	1550	-	-	-
[L] $C_{13}H_{10}NNaS_2$	-	1500	1300	1170	-
$C_{26}H_{20}CoN_2S_4$	-	1355	1220	1110	440
$C_{26}H_{20}N_2NiS_4$	-	1362	1231	1131	450
$C_{26}H_{20}CuN_2S_4$	-	1359	1220	1120	477

FTIR: Fourier transform infrared

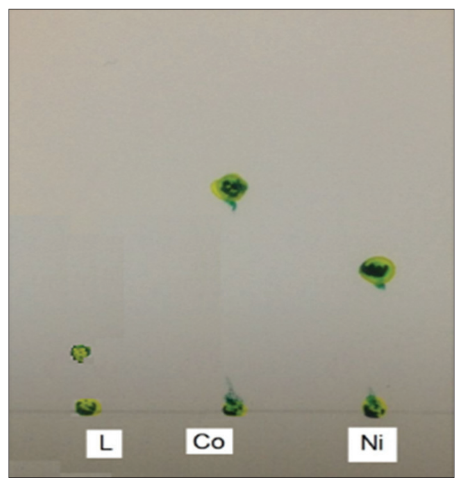


Fig. 1. The thin-layer chromatography measurements for the [L] ligand and its Co^{II} and Ni^{II} metal ion complexes

TABLE III
The Electronic Spectral Data for the Ligand and its Complexes

Compound	Band position λ_{nm}	Wave number (cm^{-1})	ε_{max} (dm^3 mol^{-1} cm^{-1})	Assignment	Magnetic Moment (B.M)	Suggested Configuration
[L]	253	39525	1420	$\pi \rightarrow \pi^*$	-	-
$C_{13}H_{10}NNaS_2$	302	33112	54	$n \rightarrow \pi^*$		
$C_{26}H_{20}CoN_2S_4$	243	41152	1234	$\pi \rightarrow \pi^*$	2.2 paramagnetic	Square planar
	366	27322	65	Ch.T		
	560	17857	50	$^4T_{1g}$ (F)$\rightarrow {}^4A_{2g\,(p)}$		
$C_{26}H_{20}N_2NiS_4$	222	45045	765	$\pi \rightarrow \pi^*$	1.9 diamagnetic	Square planar
	310	32258	100	Ch.T		
	534	18726	90	$^1A_{2g} \rightarrow {}^1A_{1g}$		
$C_{26}H_{20}CuN_2S_4$	249	40160	1567	$\pi \rightarrow \pi^*$	2.1 diamagnetic	Square planar
	300	33333	81	Ch.T		
	555	18018	204	$^2A_{1g} \rightarrow {}^2B_{1g}$		

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TABLE IV
THE TLC MEASUREMENTS FOR THE [L] LIGAND AND ITS Co^{II} AND Ni^{II} COMPLEXES

Compound	Range of R_f (mm)
[L] $C_{13}H_{10}NNaS_2$	0.4
$C_{26}H_{20}CoN_2S_4$	3.5
$C_{26}H_{20}N_2NiS_4$	2.5

TLC: Thin-layer chromatography

its complexes were performed with Co^{II} and Ni^{II} are showed in Fig. 1. The appearance of new spots with different Rf compared with the Rf of the ligand Table IV for Co^{II} and Ni^{II} indicated the formation of the complexes. Since the spots positions belong to Co^{II} and Ni^{II} ion complexes are differ from the positions of the ligands spot. The biological activity of the [L] ligand and its Co^{II}, Cu^{II}, and Ni^{II} complexes was tested on two types of pathogenic bacteria using inhibition method (Anacona, 2006; Tauber and Nau, 2008; Petra, et al., 2005; Sultana and Arayne, 2007). The two types of bacteria were Gram-positive *Staphylococcus aureus* and *Bacillus subtilis*. The ligand [L] showed inhibition diameter against the two types of bacterial after 24 h, and this inhibition diameter was increased after 48 h (Fig. 2). Furthermore, experimental results indicated that the complexes show more activity than the ligand under similar experimental conditions with the same kinds of bacteria. The X-ray powder diffraction (XRD) pattern of Co^{II} complex shows well-defined crystalline peaks indicating that the sample is 25% crystalline in nature (Dokken, et al., 2009). An XRD powder diffraction pattern of copper complex has been given in Fig. 3 of different scale particles are well coincident with each other, and it means that different forms of complexes have the same structure (Guillemet-Fritsch, et al., 2006). The sample has been dried and then scanned in the 2θ range of 10-80° confirming square planar geometry around Co ion complex (Kavitha and Lakshm, 2017; Zheng, et al., 2017). The mass spectrum shows the base peak at 267 related to the molecular weight of the ligand. Moreover, all the other fragmentations are compatible with the value of the fragments of the ligand as shown in Fig. 4. The proposed molecular structure of the [L] ligand and its Ni^{II} complex according to Chemoffice program displays geometrical shape of the complexes is square planer (Fig. 5a and b).

V. CONCLUSION

The reaction of diphenylamine with CS_2 in alkaline solution gives the required sodium diphenylcarbamodithioate ligand. The reaction of this ligand with metal chloride salts resulted in the formation of the required diphenylcarbamodithioate complexes with the square planar geometry around Co^{II}, Cu^{II}, and Ni^{II} ion complexes. Physical, chemical, and spectroscopic methods were used to investigate the mode of bonding and overall structure of the complexes. Co^{II}, Cu^{II}, and Ni^{II} complexes of sodium diphenylcarbamodithioate ligand have been synthesized and characterized by elemental analyses and spectroscopic techniques. The XRD of the (Co^{II}, Ni^{II}, and Cu^{II}) ion complex revealed that the complexes are 25% crystalline. The FTIR measurements, UV-Vis and mass spectrum for the

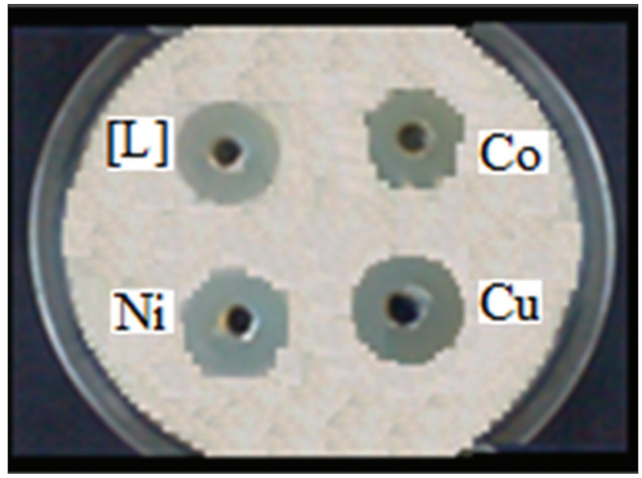

Fig. 2. The biological activity of the [L] ligand and its Co^{II}, Cu^{II}, and Ni^{II} metal ion complexes after 48 h

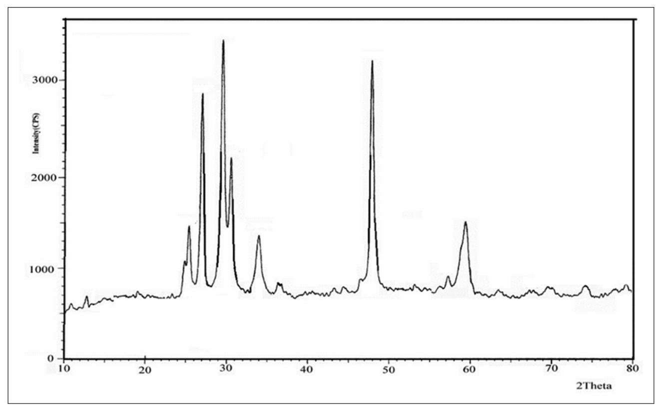

Fig. 3. The X-ray powder diffraction pattern for Co^{II} complex

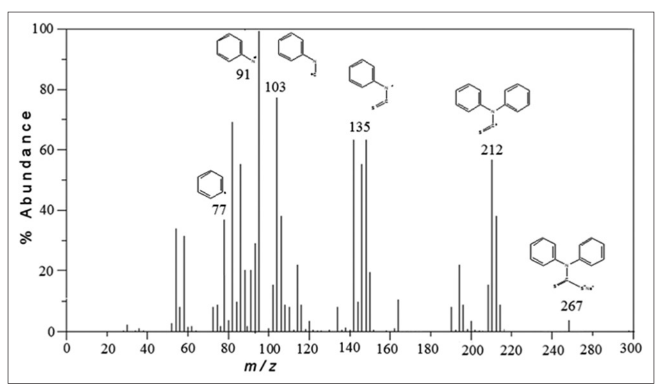

Fig. 4. The mass spectrum for the ligand

ligand and its complexes reveal the exact peak for each of the compounds functional groups. Moreover, the aims of this study are to:

1. The formation of new complexes by the reaction between diphenylamine and CS_2 with Co^{II}, Ni^{II}, and Cu^{II} metal ions
2. Determine the best some metal complexes for activating the multiple bonds in C-S_2, C-S, and S-M
3. Syntheses of new ligand with CS_2
4. Studding the characteristic properties of the sodium diphenylcarbamodithioate ligand and its complexes.

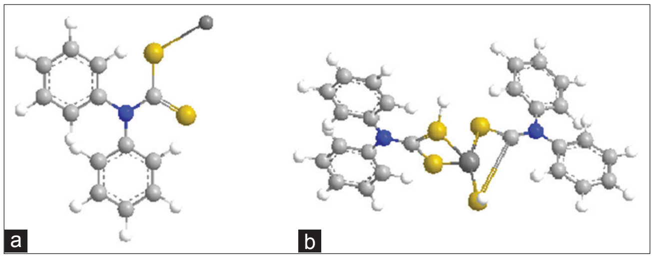

Fig. 5. (a and b) The proposed molecular structure of [L] and Ni^{II} complex according to Chemoffice program

A. Prospective Studies

1. Preparing new complexes with other transition elements
2. Modern industries rely heavily on sulfuric materials because of their real effectiveness in many fields, so it can be used in industry and health field as well.

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