

Metal Complexes Derived from Dithiocarbamate Ligand: Formation, Spectral Characterization and Biological activity

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ABSTRACT

The research involves synthesizing and characterizing a new ligand (potassium 5-cyano-3-formyl-1H-indole-1-carbodithioate) containing two atoms of the sulfur donor. The ligand was synthesized for 4 hours in the presence of alkali base (NaOH) through the reaction of one derivative of carbon disulfide and 3-Formyl-1H-indole-5-carbonitrile in ethanol (as a solvent). Dithiocarbamate ligand was characterized along with the melting point using FT-IR, ¹H NMR, ¹³C-NMR, elemental analysis (C.H.N.S), UV-visible, and ESI-mass spectrum. Four metal complexes are prepared under refluxing. The complexes were prepared for 4 hours from the reaction of 2 potassium dithiocarbamate equivalent ligand with 1 equivalent metal salt in refluxing ethanol. For other complexes the complexes were characterized by FT-IR, UV-Visible, molar conductivity, magnetic sensitivity measurements, flammable atomic absorption spectroscopy solubility, melting point,

product microanalysis and mass spectroscopy. The biological function of the synthesized dithiocarbamate ligand and its complexes has been examined using inhibition method for two types of bacteria; one gram positive and one gram negative, and one type of pathogenic fungus. This will assess their possible antimicrobial activity.

Keywords: potassium 5-cyano-3-formyl-1h-indole-1-carbodithioate, metal complexes, synthesis

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INTRODUCTION

Dithiocarbamates (DTCs) are a group of small organic molecules with a good chelate-to-metal ion capability[1]. Numerous studies and reviews have been conducted on transition and non-transition metals, suggesting a broad variety of anion compounds[2]. Dithiocarbamate ligands are more complex compounds consisting of organic sulfur. This may be due to the CSS group's low bite angle, which can interact with most of the metals in the periodic table, and it has the sulfur atoms that can add a single pair of electrons to the central metal atom to form the complexes[3]. DTCs can be stabilized in a variety of metal oxidation states, coordinating geometries and compounds that exhibit broad structural variations ranging from monomeric to polymeric molecular assemblies. Binding properties of dithiocarbamates; monodentate, bidentate chelating and bidentate bridging varieties define the structural structure so that the physical and chemical properties of dithiocarbamates are determined.[4]. There are major uses of dithiocarbamate and dithiophosphinate complexes.[5] Dithiocarbamates are essential materials that have been extensively explored in coordination chemistry, medicine, and radiopharmaceutical chemistry, sensing engineering, materials science, and industry applications. DTCs have shown considerable biological activity, including their antibacterial function [6].

MATERIALS

All needed laboratory chemicals and reagents are available commercially and used with no further purification.

Physical measurements

Elemental analyser (C. H. N. S.) for ligands and their metal complexes (Euro EA 3000) was conducted. Using a Biotic 600 FT-IR spectrophotometer about range 4000-400 cm⁻¹

and Potassium iodide disks about range 400-200 cm⁻¹on Shimadzu 8400s FT-IR, infrared spectra were taken as Potassium bromide Disks. Electronic spectra with (UV-Vis) spectrophotometer were obtained at room temperature Shimadzu 1800 from 200-1000 for 10⁻³ M solutions in dimethyl sulfoxide using by 1.0 cm long quartz cells. Mass spectroscopy of electrospray (ES) on the Shimadzu GC-Mass QPA spectrometer obtained mass spectrum for ligand and mass spectrum LC-MSQP50A Shimadzu (E170Ev) for complex spectrometer. Ligand Nuclear magnetic resonance spectrum was used in Deuterated chloroform using the 400 MHz Ultra Shield configuration Bruker, originating in Germany. Atomic absorption (A.A) technique using a spectrophotometer of Shimadzu (A.A 680 GBC 933 plus) to determine the metal value of complexes. Molecular conductivity calculation is performed at room temperature with DMSO solutions using the Jenway 4071 electronic conductivity meter. Estimated magnetic moments at 303.8 K with a magnetic resistance balance (Sherwood Scientific).

Synthesis the ligand

Ligands are prepared according to the published method [7], with the following minor modifications:

Synthesis of potassium 5-cyano-3-formyl-1H-indole-1-carbodithioate

3-Formyl-1H-indole-5-carbonitrile (0.340g, 0.002 mol) has been dissolved in ethanol (12 ml) Dissolved in double distilled water (1ml) with 30 minutes of stirring at room temperature, potassium hydroxides (0.112 g, 0.002mol) cool solution in the Snow bath. To the commixture, add pure CS₂ (0.152 g, 0.002mol) with daily stirring at temperature (0-4 ° C) for 4 hours. The brown solution was permitted at room temperature, then evaporated until solid brown precipitation was completed. The brown solid was collected

through filtration and then recrystallized from methanol, washed twice with diethylether (10ml), and then dried for 7 hours at temperature (35 °C).

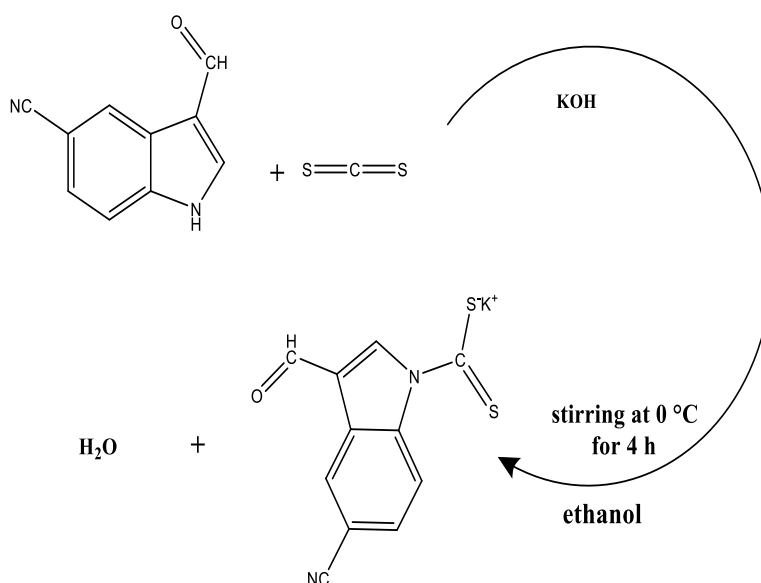
Synthesis of potassium 5-cyano-3-formyl-1H-indole-1-carbodithioate complexes

A general method for achieving dithiocarbamate complexes was used and the following: Complexes were prepared from the reaction of 2 potassium dithiocarbamate salt equivalent (DTC) as ligand in ethanol with 1 metal salt equivalent as the central ion (2:1). In a round bottom bottle, a volume (100) ml containing a dithiocarbamate ligand salt was added metal chloride solution in 10ml of absolute ethanol. The reaction mixture was unstable and warmed under reflux for 4 h. The complex was gathered through filtration, washed

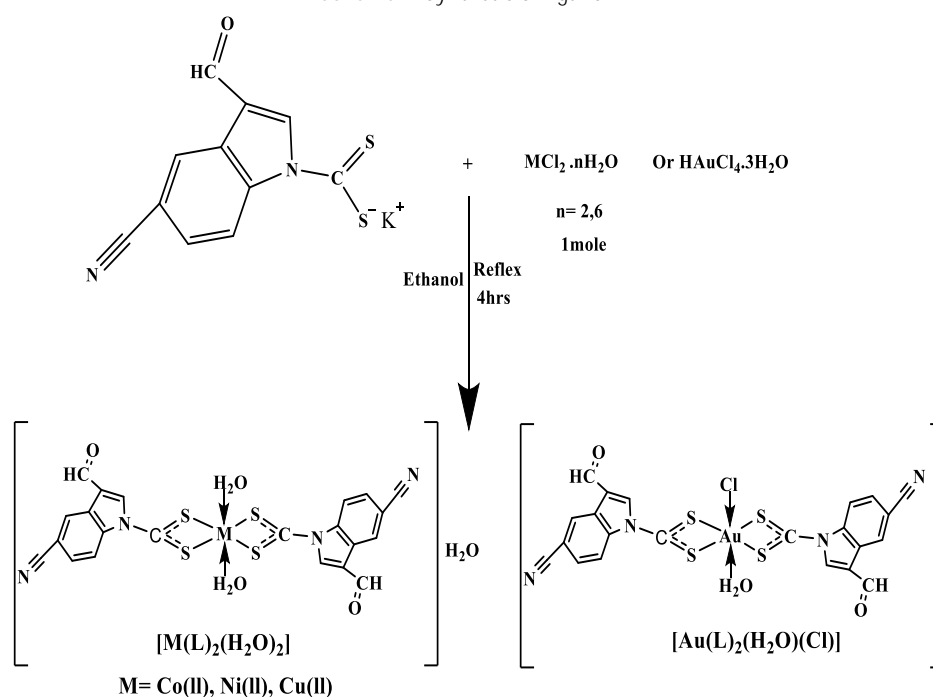
with excess methanol and diethyl ether, dried at room temperature for 48 h [8,9].

RESULTS AND DISCUSSION

This research has identified dithiocarbamate ligand. Synthesis this ligand was based on the reaction with CS₂ that was obtained between NH group. (KL) was synthesized by combining 3-Formyl-1H-indole5-carbonitrile with carbon disulfide in the presence of KOH as a base. The use of ethanol as a solvent scheme (1) indicates that in the mole ratio (1:1). The complexes were prepared from the ligand KL reaction with metal chloride salts in (2:1) mole ratio heated under ethanol reflux to produce pure complexes where isolated at moderate yield, as shown in scheme (2) Where M= Co²⁺, Ni²⁺, Cu²⁺, and Au³⁺.



Scheme 1: Synthetic of ligand KL



Scheme 2: Synthetic of $[M(L)_2(H_2O)_2]H_2O$ and $[Au(L)_2(H_2O)(Cl)]$ complexes

The ligand and complexes were prepared and then characterized by elemental analysis, melting points, spectroscopic methods (FT-IR, UV-Vis, A.A, mass

spectroscopy), molar conductivity, and measurements of magnetic sensitivity. Table (1) explains the physical properties of ligand and complexes.

Table 1: Physical characteristics and elemental analysis of the ligand DTC

The Compounds	Molecular Wt.	Yield (%)	M. P (°C)	Colour	Found (calcd.) (%)				
					C	H	N	S	M
C ₁₁ H ₅ KN ₂ OS ₂	283.95	70.51	213-215	Pale yellow	46.15 (46.46)	1.26 (1.77)	9.53 (9.85)	21.92 (22.55)	
[Co(L) ₂ (H ₂ O) ₂].H ₂ O	603.57	66.2	207-209	Light blue	43.57 (43.78)	2.58 (2.67)	9.18 (9.28)	20.65 (21.25)	9.15 (9.76)
[Cu(L) ₂ (H ₂ O) ₂].H ₂ O	608.18	71.3	190-192	Gray	43.14 (43.45)	2.22 (2.65)	9.39 (9.21)	20.54 (21.09)	9.99 (10.45)
[Ni(L) ₂ (H ₂ O) ₂].H ₂ O	603.33	70.8	204-206	White	43.51 (43.80)	2.52 (2.67)	9.62 (9.29)	20.24 (21.26)	9.42 (9.73)
[Au(L) ₂ (H ₂ O)Cl]	741.02	69.7	211-213	Dark yellow	35.23 (35.66)	1.05 (1.63)	7.76 (7.56)	17.04 (17.31)	26.13 (26.58)

*= decomposed; m.p= melting point; Calc.= Calculated

The ¹H-NMR, ¹³C-NMR and Mass spectra for the ligand KL

The ¹H-NMR spectrums for the ligand KL in (Fig.1). showed the characteristic chemical shift of the solvent DMSO-d₆ at δ=2.51. The spectrum presented singlet signal at δ=9.98 ppm attributed to the one proton for H-C=O group[10]. The singlet signal at δ=8.48 ppm are assigned to protons for CH (benzene ring), The doublet chemical shift at δ=8.40 ppm is assigned to the proton for CH (benzene ring), The doublet chemical shift at δ=7.69 ppm is assigned to the proton for CH (benzene ring) and a chemical shift δ=7.60 ppm is assigned to the proton for CH (indol ring) [11,12]. The ¹³C-NMR spectrum of a ligand KL, (Fig.2). in DMSO-d₆ solvent shows chemical shift at δ=185.62 ppm which can be attributed to carbon atom C1 for HC=O group[13]. The carbon atoms C2, C3 resonated with the chemical shifts at δ= 118.18, 124.81 which can be attributed

to indol ring[14]. The signal at δ=196.03 ppm, which can be attributed to carbon atom C4 for CS₂ group [15]. The carbon atoms C5, C6, C7, C8 resonated with the chemical shifts at δ= 141.34, 114.42, 125.41, 104.42 ppm respectively[16]. These signals are attributed to aromatic carbons. The chemical shift at δ=120.73 ppm attributed to carbon atom C9 for C≡N group[17]. The carbon atoms C10, C11 resonated with the chemical shifts at δ= 126.63, 140.17 ppm respectively[16]. Also these signals are attributed to aromatic carbons. Finally, the chemical shift at δ=40.65 ppm attributed to DMSO solvent. The electrospray (+) mass spectrum of KL is obtainable in (Fig.3). The spectrum exhibits successive fragments related to ligand structure. The parent ion peak for the ligand is observed at m/z = 281 which corresponds to (M+H)⁺ (%) for C₁₁H₅KN₂OS₂; requires = 283.95.

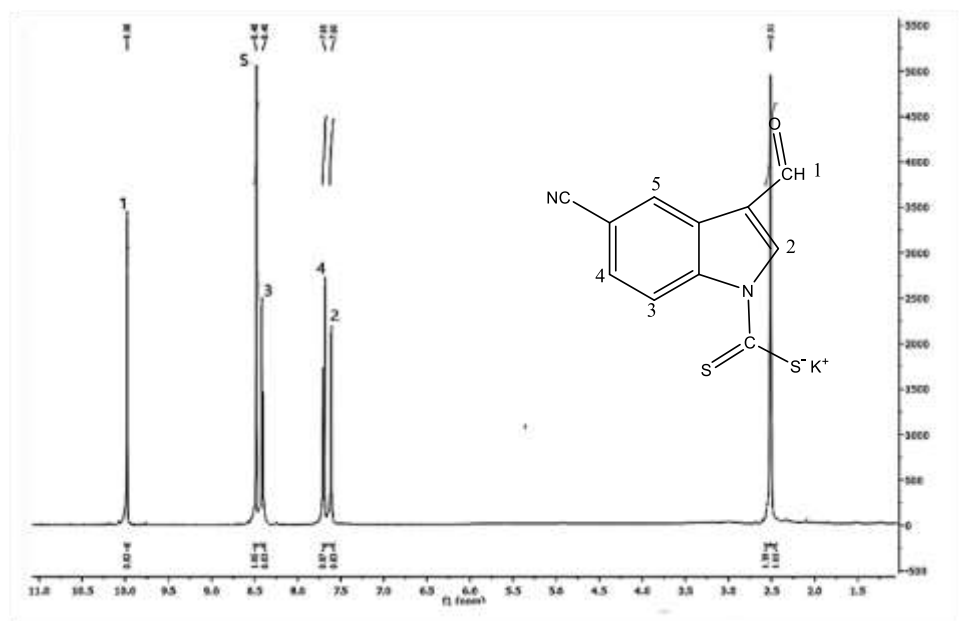


Figure 1: ^1H -NMR spectrum of ligand KL in DMSO-d_6 as solvent.

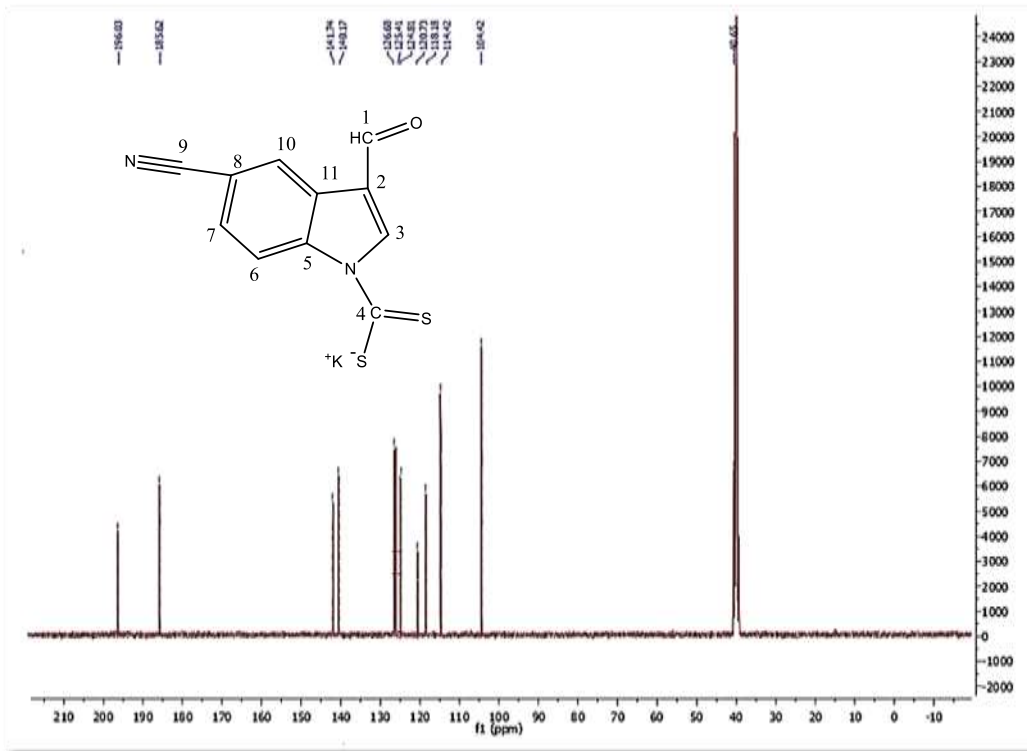


Figure 2: ^{13}C -NMR spectrum of ligand KL in DMSO-d_6 as solvent.

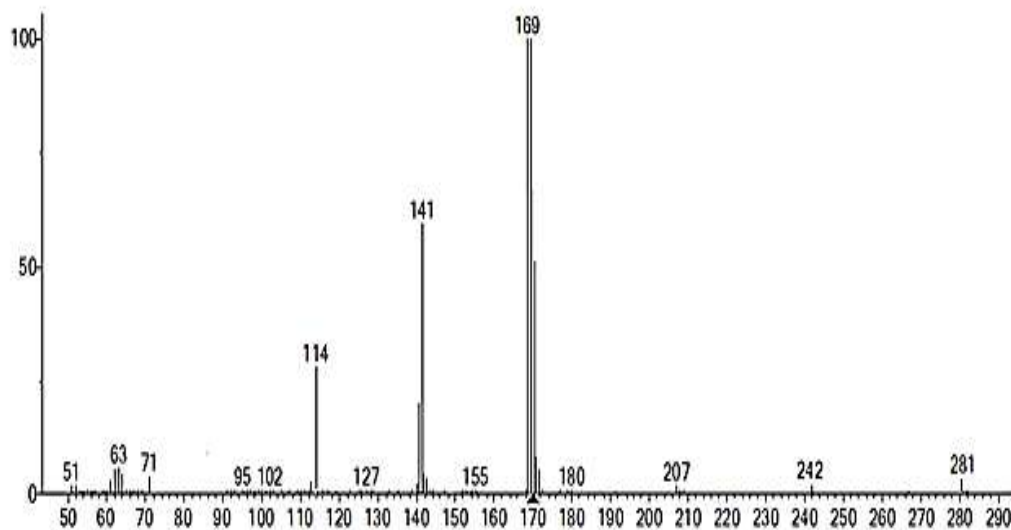


Figure 3: mass spectrum of ligand KL

The Mass Spectra for the complexes

The mass spectra of some complexes is presented in (Fig 4-5).The spectrum exhibits successive fragments related to complexes structure. The parent ion peak are observed at $m/z = 606$ and 744 which corresponds to $(M+H)^+$ (%) for $[\text{Co} (\text{L})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, $[\text{Au} (\text{L})_2(\text{H}_2\text{O})(\text{Cl})]$; requires = 603.57 and 741.02 respectively.

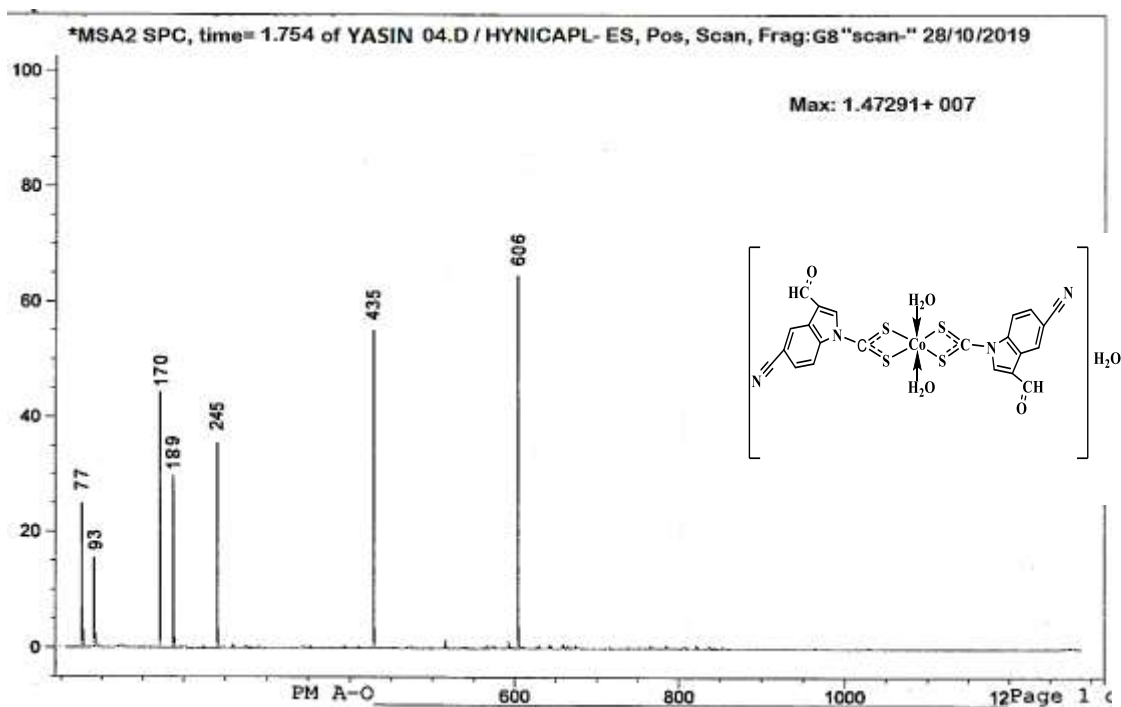


Figure 4: mass spectrum of complex $[Co(L)_2(H_2O)_2] \cdot H_2O$

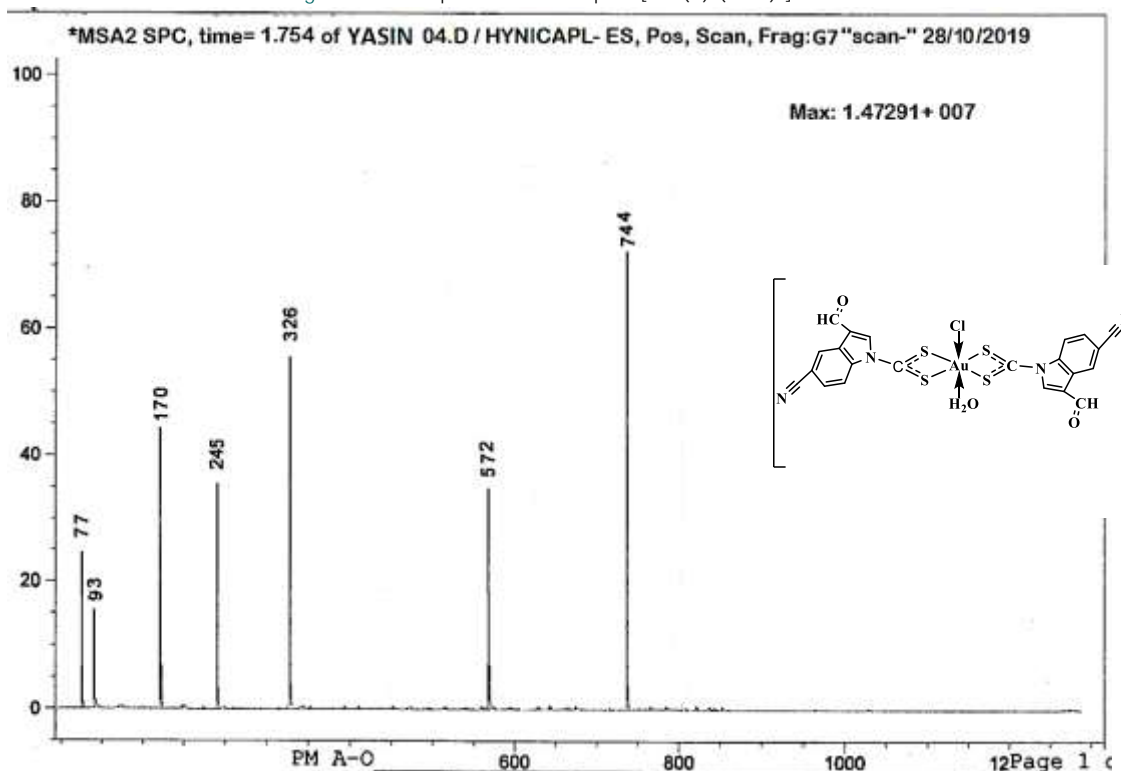


Figure 5: mass spectrum of complex $[Au(L)_2(H_2O)(Cl)]$

The FTIR spectrum for ligand and complexes
The FTIR spectrum of (KL) shows no bands (disappeared) around 3206cm^{-1} which can be assigned to ν (NH) stretching vibration [18]. The FTIR spectrum reveals new bands at 1463cm^{-1} can be attributed to ν (C-N) stretching of (N-CS₂) moiety [19]. Also, two new bands are revealed by the FTIR spectrum at 1002cm^{-1} and 921cm^{-1} attributed to $\nu_{as}(\text{CS}_2)$ and $\nu_{s}(\text{CS}_2)$, respectively [20]. The band at 1652cm^{-1} is assigned to $\nu_{ar}(\text{C}=\text{C})$ for aromatic system [21].

The bands at 2829cm^{-1} and 1735cm^{-1} were assigned to ν (C-H) and ν (C=O) group respectively[22]. The band at 2223cm^{-1} was assigned to ν (C≡N) group[23]. In addition, the spectrum displayed a bands at 1222cm^{-1} and 703cm^{-1} attributed for the ν (C-N)) and ν_{ar} (C-S) respectively[24]. Characteristic bands are summarised in Tables (2). In the continuum of DTC complexes, three essential regions need to be investigated. The first is the band in the range $1421\text{--}1463\text{cm}^{-1}$ corresponding to (NCS₂) stretching vibrations, it

should also be noted that the wave number change because the electron donation character increases [25]. The second is the vibration commitment to the C-S stretching frequency in the finger print area within the range 817–1002 cm^{-1} . The

third important band reveals a distant infrared area of the range 308–325 cm^{-1} it is assigned to the ν (M-S) vibration, where its absent in the ligand but exhibited as a result from coordination.

Table 2: KL ligand's FTIR spectral information and its complexes

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{H})_{\text{arom.}}$	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{C})_{\text{arom.}}$	ν (N- CS_2)	ν_{asCS_2}	$\nu(\text{M}-\text{S})$ $\nu(\text{M}-\text{Cl})$	$\nu(\text{M}-\text{O})$ $\delta(\text{H}_2\text{O})$
(KL ²)	1735	-	3055	2223	1652	1463	1002 921	-	-
[Co(L ²) ₂ (H ₂ O) ₂]H ₂ O	1737	3550	3066	2223	1650	1421	921 887	324 -	555 815
[Cu(L ²) ₂ (H ₂ O) ₂]H ₂ O	1737	3440	3041	2223	1650	1421	958 857	325 -	555 813
[Ni(L ²) ₂ (H ₂ O) ₂]H ₂ O	1737	3550	3097	2223	1650	1421	919 817	312 -	587 817
[Au(L ²) ₂ (H ₂ O)(Cl)]	1737	3552	3065	2223	1660	1423	997 919	308 273	582 815

Uv-Vis spectral data for DTC (KL) and the complexes In DMSO solution, the UV-Vis spectrum of KL. Has two absorption peaks at (266 nm = 37593 cm^{-1} ; $\epsilon_{\text{max}} = 1599$ molar⁻¹ cm^{-1}) and (329 nm = 30395 cm^{-1} ; $\epsilon_{\text{max}} = 1300$ molar⁻¹ cm^{-1}) assigned to " $\pi \rightarrow \pi^*$ " and " $n \rightarrow \pi^*$ " transitions, respectively [26], as shown in Table (3). Most transition

metal complexes are colored. Such colors vary from ligands and transition metal salts, so these colors are considered essential indicators of coordination, so the colored complexes show different bands of absorption in location and strength [27].

Table 3: Uv-Vis spectra of the ligand and complexes in 10⁻³ M DMSO

No	Complexes	Wavenumber		ϵ_{max} molar ⁻¹ cm^{-1}	Assignment	Suggested structure
		nm	Cm^{-1}			
1	(KL ²)	266	37593	1599	$\pi \rightarrow \pi^*$	
		329	30395	1300	$n \rightarrow \pi^*$	
2	[Co(L ²) ₂ (H ₂ O) ₂]H ₂ O	269	37174	2328	L.F	Oh
		327	30581	1693	L.F	
		385	25974	500	C.T	
		615	16260	159	${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{T}_{1g(\text{P})}$	
		679	14727	225	${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{A}_{2g(\text{F})}$	
3	[Ni(L ²) ₂ (H ₂ O) ₂]H ₂ O	270	37037	1655	L.F	Oh
		347	28818	655	L.F	
		489	20449	210	C.T overlap ${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{1g(\text{P})}$	
		540	18518	200	${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{1g(\text{F})}$	
		680	14075	88	${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{2g(\text{F})}$	
4	[Cu(L ²) ₂ (H ₂ O) ₂]H ₂ O	265	37735	1243	L.F	distorted Oh
		319	31347	860	L.F	
		460	21739	99	C.T	
		530	18867	89	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$	
5	[Au(L ²) ₂ (H ₂ O) Cl]	270	37037	1793	L.F	Oh
		327	30581	1092	L.F	
		347	28818	1192	C.T	
		520	19230	95	${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{1g(\text{P})}$	

Molar conductivities and magnetic susceptibility
 The low values of molar conductivities in DMSO of Co II, Ni II, Cu II and Au III complexes are (16.3, 6.7, 19.5, 10.11ohm⁻¹.cm².mol⁻¹) respectively indicate that all the prepared complexes are non - electrolytes [28]. The Co complex magnetic moment measurements show meff value in 4.85 B.M. This value is assigned to Co II complex to octahedral geometries. Ni-complex gave 2.92 B.M. values. The meff value is included in the octahedral array for this complex, suggesting a high geometry spin around the ion of Ni II. The Cu-complex magnetic moment show a value in 1.77B.M, that can be attributed to the octahedral geometry around Cu II ion. Au III is a diamagnetic complex. Two unpaired electrons should be paramagnetic when the complex is in complete octahedral configuration. Nonetheless, the AuIII ion causes extreme ligand field splitting due to the high oxidation state and heavy metal character, and the ideal octahedral structure must be unstable, as two electrons must occupy eg high-energy

orbitals. And the tetragonal distortion must occur in order, making the Au^{III} complex diamagnetic. [29].

The biological activity

Using inhibition method for two types of pathogenic bacteria and one form of pathogenic fungus, the biological function of the synthesized dithiocarbamate ligand and their complexes was studied. One type of bacteria was Staphylococcus aureus, the second was Escherichia coli and the pathogenic fungus was Candida. This is to estimate their possible function as antimicrobials. DMSO's role in the biological activity demonstrated by separate experiments accomplished with DMSO's solutions alone. It did not exhibit any activity against bacterial strains [30]. Tables (4) list inhibition circle diameters in millimeter unit against the growth of various microorganisms. (Figure 5) Screen the synthesized impact dithiocarbamate compounds on bacterial strains and pathogenic fungus.

Table 3: biological activity of KL ligand and its complexes (M(L)₂)

Compounds	<i>Staphylococcus aureus</i> (G+)	<i>Escherichia coli</i> (G-)	<i>Candida</i>
Control (DMSO)	0	0	0
KL	13	14	28
[Co(L) ₂ (H ₂ O) ₂]H ₂ O	15	18	13
[Cu(L) ₂ (H ₂ O) ₂]H ₂ O	20	21	19
[Ni(L) ₂ (H ₂ O) ₂]H ₂ O	15	11	16
[Au(L) ₂ (H ₂ O)Cl]	17	11	19

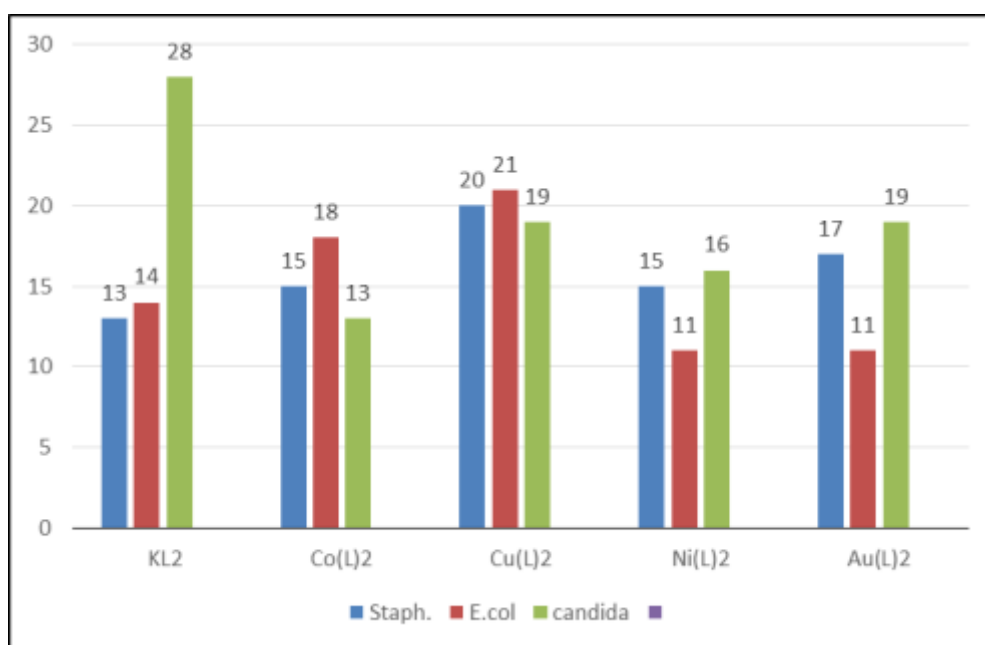


Figure 5: Evolution of the diameter zone (mm) of KL ligand inhibition and its complexes (M(L)₂) against the growth of different bacterial strains and pathogenic fungi.

CONCLUSION

Characterization and ligand preparation, and their complexes. The ligand complexes are prepared from the reaction of 2 equivalent potassium dithiocarbamate salt

(DTC) as ligand in ethanol with 1 equivalent metal salt as central ion. Physicochemical and spectroscopic methods to check bonding mode and over all complex structure have been placed in place. These findings lead to the preparation

of four coordinate complexes and the structure of complexes which is octahedral has been suggested from above discussions. The biological activity of the synthesized dithiocarbamate ligand and its complexes has been examined using inhibition method for two types of bacteria; one gram positive and one gram negative and one type pathogenic fungus. Determining their possible antimicrobial activity. The tests generally show good ligand activity and their complexes against the types of bacteria and pathogenic fungi.

REFERENCES

1. Balakrishnan, S., Duraisamy, S., Kasi, M., Kandasamy, S., Sarkar, R., & Kumarasamy, A. Syntheses, physicochemical characterization, antibacterial studies on potassium morpholine dithiocarbamate nickel (II), copper (II) metal complexes and their ligands. *Heliyon*, 2019. 5(5), 1687.
2. Rathore, H.S.; Varshney, G.; Mojumdar, S.C.; Saleh, M.T., Synthesis, characterization and fungicidal activity of zinc diethyldithiocarbamate and phosphate. *Ther. Anal. Calorim*, 2007, 90 (3), 681–686.
3. Nami S. A., Ullah I., Alam M., Lee D-U., Sarikavakli N., Synthesis, characterization, molecular docking and biological studies of self-assembled transition metal dithiocarbamates of substituted Pyrrole-2-Carboxaldehyde., *J. of Photochemistry and Photobiology B: Biology*, 2016.160: p. 392-399.
4. Baba I., Raya I., Yamin B. M., Synthesis and structural studies of lanthanum (III) Dialkyldithiocarbamates 1,10-phenantroline., *J. Sains Malaysiana.*, 2009. 38(2): p. 185-190.
5. Saad E. Al-Mukhtar, Marwa Th. Aghwan, Synthesis and Characterization of 3-Methoxypropyldithiocarbamate Complexes with Iron(II), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) and Their Adducts with Nitrogen Base Ligands., *Department of Chemistry College of Science University of Mosul, Raf. J. Sci.*, 2013, 24(4), 50-59.
6. Hasan HA, Yousif EI, Al-Jeboori MJ *Global J. Inorg. Chem*, 3. 10. 1-7. 5-Enaam I. Yousif, Synthesis, Characterization and Biological Study of Mixed Ligand Complexes Derived from Dithiocarbamate and Azo, *Journal of Global Pharma Technology*, 2018, 10(03), 875-882.
7. Bala R., P., Venkatesh P., Studies on Diethanolamine dithiocarbamate as Metal Complex, Complexing Agent and Stabilizer in Copper Methanesulphonate Bath., *IJSR*, 2015, 4(2), 919-923.
8. Ingle A. D., Devghare H., Parase K., “Metal complexes of ammonium phenyl dithiocarbamate: Preparation characterization and biological activity”. *J. Chem. Pharm. Res.* 2013, 5(7), 272-277.
9. Kumar V., Singh V., Gupta A. N., Manar K. K., Drew M. G., Singh N., Influence of ligand environments on the structures and luminescence properties of homoleptic cadmium (II) pyridyl functionalized dithiocarbamates., *J. Cryst. Eng. Comm.*, 2014. 16(29), 6765-6774.
10. Stowell, J. C. “New gamma-keto Aldehyde synthesis”. *The Journal of Organic Chemistry.*, (1976). 41(3) 560–561.
11. Safaa A.R. , “Synthesis and characterization of new ligand of Dithiocarbamate derived from “2-Aminopyridine” with some metal ions”, *Kerbala journal of pharmaceutical sciences.*,(2017).12: P.84-91.
12. Lijuan J., Yayang W., Sufan W., Xiaoke H., Ping Z., Changjiang Y., Kebing C., Qianli M., Erhong H., and M. Graca H. V., “Accessing Near-Infrared Absorbing BF2Azadipyrrromethenes via a Push-Pull Effect”, *The Journal of Organic Chemistry .*,(2014).79(4): P.1830-1835.
13. Hasan A. H. Enaam I. Y., “Formation of New Macrocyclic Complexes with Bis (Dithiocarbamate) Ligand:Preparation, Structural Characterisation and Bacterial Activity”, *Ibn Al-Haitham Jour. for Pure & Appl. Sci.*,(2016), 29(3): P.146-166.
14. Choppara, P., Prasad, Y. V., Rao, C. V., Hari Krishna, K., Trimoorthulu, G., Maheswara Rao, G. U., Venkateswara Rao,J., Bethu,M.S., Murthy, Y. L. N., “Design, synthesis of novel N prenylated indole-3-carbazones and evaluation of in vitro cytotoxicity and 5-LOX inhibition activities”, (2015). *Arabian Journal of Chemistry .*, (2015).
15. Riyadh M. A., “Co(II) and Cd(II) Mixed-Ligands Complexes Prepared From N’-(4-methylsulfanylbenzoyl)-hydrazine Carbodithioic Acid Methyl Ester; Synthesis and Physico-Chemical Characterisation”, *Ibn Al-Haitham Jour. for Pure & Appl. Sci.*,(2016), 29(3): P.195-208.
16. Keter,F.K., Guzei,I.A.,Nell,M.,Zyl, W. E. van, and Darkwa, J., “Phosphinogold(I) Dithiocarbamate Complexes: Effect of the Nature of Phosphine Ligand on Anticancer Properties”, *Inorganic Chemistry*, (2014). 53(4): P.2058–2067.
17. Anderson, G. K., Lin, M., Sen, A., and Gretz, E., “ Bis(Benzonitrile)Dichloro Complexes of Palladium and Platinum”. *Inorganic Syntheses*, (2007). P. 60–63.
18. Sebastian S., Sylvestre S., Sundaraganesan B., Amalanathan M., Ayyapan S., Oudayakuma K and Karthikeyan B., “Vibrational spectra, molecular structure, natural bondorbital, first order hyperpolarizability, TD-DFT and thermodynamic analysis of 4-amino-3-hydroxy-1-naphthalenesulfonic acid by DFT approach”, *J. Spectrochimica Acta Part A: Mol. Bio. Spec.*, (2013). 107: P.167-178.
19. Amir, M. K., Zia-ur-Rehman ., Z.-R., Hayat, F., Khan, S. Z., Hogarth, G., Kondratyuk, T and Tahir, M. N., “Monofunctional platinum(ii) dithiocarbamate complexes: synthesis, characterization and anticancer activity”. *RSC Advances*, (2016) .6(112): P.110517–110524.
20. Damian C. O and Anthony C. E., “Synthesis, characterization, thermal, antimicrobial and antioxidant studies of some transition metal dithiocarbamates”, *Springer Science+Business Media Dordrecht* (2016).43(3): P.1465-1485.

21. Sykes A. G., Wilkinson G., Gillard R. D and Mcleverty J.A., “Comprehensive Coordination Chemistry”. Pergamon Press: Oxford, UK, (1987), 229.
22. Muthu, S., Uma Maheswari, J and Sundius, T., “Molecular structural, non-linear optical, second order perturbation and Fukui studies of Indole-3-Aldehyde using density functional calculations”. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, (2012)106: P. 299–309.
23. Pavia,L.D.,Lampman,S.G., Vyvyan,R.J., “Introduction to spectroscopy” ., Department of chemistry ., Western Washington University ., Bellingham, Washington (2008).
24. Cric´-Marjanovic G., Trchova M., Matejka P., Holler P., Marjanovic B and Juranic I., “ Electrochemical oxidative polymerization of sodium 4-amino-3-hydroxynaphthalene-1-sulfonate and structural characterization of polymeric products”., *Reactive & Functional Poly.*,(2006). 66 : P.1670-1683.
25. Kalia S. B., Kausha G., Kumar M., Kumar S., Khanduja K L., “Physicochemical studies on some 4-methylpiperazine-1-carbodithioate complexes of zinc(II), cadmium(II) and mercury(II)”., *Indian J. Chem.A.*, 2008. 47(9), 1323-1332.
26. Khan H., Badshah A., Rehman Z., Said M., Murtuza G., Shah A., Ahmed S., Butler I. S and Fontaine F. G., “New dimeric and supramolecular mixed ligand palladium(II) dithiocarbamates as potent DNA binders”., *J. Polyhedron*, (2012). 39: p. 1-8.
27. Al-Shemary R. K., Al-Khazraji A. M. Fadhil sulaiman A. F., Sajid M. Lateef S. M., “Synthesis, Characterization and Antimicrobial Activity Studies of Mixed-1,10-phenanthroline- Mn(II), Co(II), Cu(II), Ni(II) and Hg(II) Complexes with Schiff Base[2,2'-(1Z,1'Z)-(biphenyl-4,4'- diylbis (azan-1-yl-1-ylidene)) bis(methan-1-yl-1-ylidene) diphenol]”., *Inter. J. Sci. and Res.*, 2016. 5(5) .,1787-1793.
28. W.J. Geary. The use of conductivity measurements in organic solvents for the characterization of coordination compounds. *Coord. Chem. Rev.*, 1971,7, 81.122.
29. Myunghyun Paik Suh, Il Soon Kim, Boo Yong Shim, Daewon Hong, and Tae-Sung Yoon , Extremely Facile Template Synthesis of Gold(III) Complexes of a Saturated Azamacrocyclic and Crystal Structure of a Six-Coordinate Gold(III) Complex , *Inorg. Chem.* 1996, 35, 3595-3598.
30. Srivastava K. P., Singh S. K., Mishra B. P., Green synthetic approach and antimicrobial activity of bidentate schiff base ligands and their Ni(II) complexes under microwave irradiation., *J. Chem. Pharm. Res.*, 2015. 7(1), 197-203.