

Synthesis, Characterization and Antibacterial Studies of Some Transition Metal Complexes Containing New Dithiocarbamate Ligand

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Abstract

The synthesis of some transition metal complexes with dithiocarbamate as a ligand of general formula $[M(L)_2]$ where $M = Mn(II), Co(II)$ and $Ni(II)$. The dithiocarbamate ligand and its complexes were described by FT-IR, UV-Vis and $^1H, ^{13}C$ -NMR, Mass spectra, elemental micro analysis C.H.N.S., magnetic susceptibility, molar conductivity, melting points, and atomic absorption. The antibacterial Studies of synthesized compounds were studied versus [*Escherichia coli* (gram negative) and *Staphylococcus aureus* (gram positive)]. The conductivity data affirm the nonelectrolyte nature of the complexes.

Keywords: Dithiocarbamate (Dtc), 4-aminophenazone, Transition metal.

Introduction

Dithiocarbamate (DTC) are multilateral ligands with a wide range of chemistry and numerous applications in different courts such as medicine, biologically active they can act as fungicides to save crops from fungal diseases and in industrial enforcement as a catalyst in the vulcanization of rubber [1, 3]. Some dithiocarbamate complex used to strip NO in which the absorbed NO is reduced to nitrogen. In different direction, the most polluting industries such as wastewater emptying by textile industries are known to contain large numbers of toxic dyes, which can be extracted by Dtc modified starch materials.

Around the global, there are a domain of commercial Dtc based compounds that can be employ for managing fungal diseases in agriculture [4,5]. DTC have shown a set of applications in analytical chemistry. They have the capacity to form a stable compound with transition metals and delegate elements.

They have been employing in solvent extraction, spectrophotometric determination of trace elements and eclectic chromatographic determination of metal ions [6, 8]. The selectivity and precision of determination method used is tuned by chemical entity of DTC reagents and reaction conditions (PH, solvent), derivatives of DTC are applied as precursors for nano compounds

Furthermore DTC compounds have a figure of other applications in photochemistry[9,10]. In view of the vast range of application of DTC. Report in this search the synthesis and characterization of Mn, Co, and Ni complexes of potassium [(1,5-dimethyl-3-oxo-2-phenyl-2,3- dihydro-1H- pyrazol-4-yl) (5,5- dimethyl-3-oxocyclohex-1-en-1-yl) carbamodithioate (KL¹)].

Experimental

All chemicals used were of highest purity (Fluka or Merck, BDH) and used out furthermore purification. Elemental analyses (C.H.N.S) were carried out on a (EURO EA 3000 Single). 1H and ^{13}C -NMR spectra were acquired in DMSO using Bruker, Model: Ultra 300 MHz, Switzerland for tetramethylsilane (TMS).

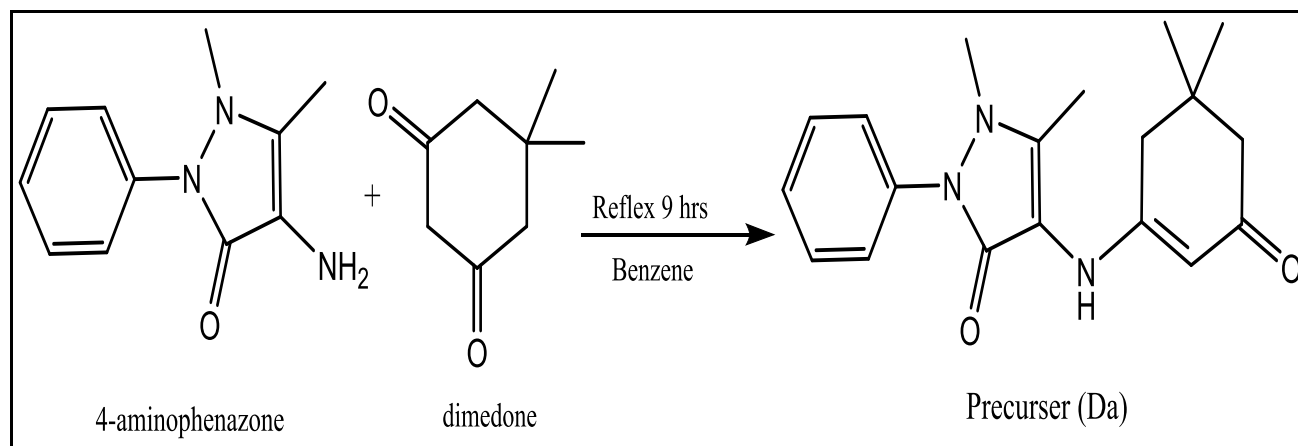
Mass spectra were acquired by GC-Mass QP-2010, IR spectra were recorded with FT-IR-8000 Shimadzu, in the scope of (4000-400) cm^{-1} . Absorption spectra were recorded using Shimadzu UV-Vis 1700 spectrophotometer, conductivity evaluate by Digital conductivity meter WTW, 720 with solute concentration of 10^{-3} M in DMSO at room temperature. Magnetic moments were evaluate with a magnetic susceptibility (Xg) were carried out at 20° C by Faraday and atomic absorption by

atomic absorption spectrophotometer-5000, Perkin-Elmer.

Preparation of [4-((5, 5-Dimethyl-3-Oxocyclohex-1-en-1-yl) Amino)-1, 5-DIMETHYL-2-Phenyl-1, 2-Dihydro-3H-pyrazol-3-One] (Da) [11]

The compound (Da) was prepared using the following of dimedone (7.15mmol) was grinded together with 4-amino phenazone (7.11mmol), then adding (25 mL) of benzene. The mixture was allowed to continuous stirring until

complete dissolution and formation of yellow light colour solution. To the solution (3-4) drops of glacial acetic acid was added, then resulting solution was refluxed for (9) hrs until the dark yellow precipitate was behold, the reaction was monitored by TLC. The reaction mixture was allowed to cool at room temperature, a dark yellow product was remote by filtration and washed various times with benzene and dried to give a yellow precipitate. The preparation is shown in Scheme (1). Yield 1.52g (65.5%), M.P. (220-222 °C).

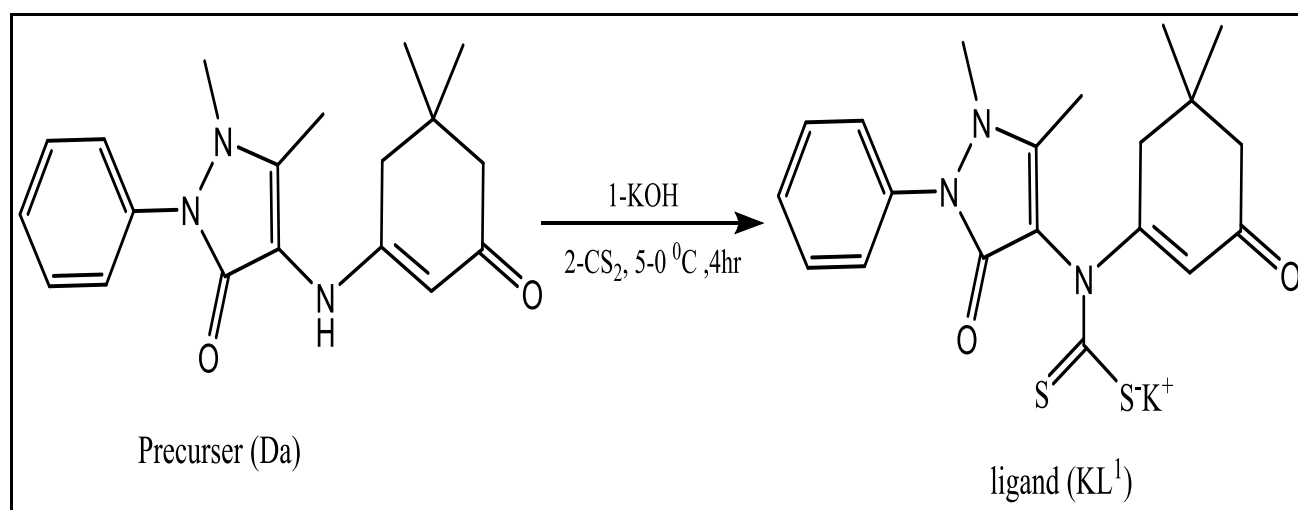


Scheme 1: Synthesis of precursor (Da)

Preparation of Potassium [(1, 5-Dimethyl-3-Oxo-2-Phenyl-2, 3- Dihydro-1H- Pyrazol-4-yl) (5, 5- Dimethyl-3-Oxocyclohex- 1- en- 1- yl) Carbamodithioate] (KL¹)

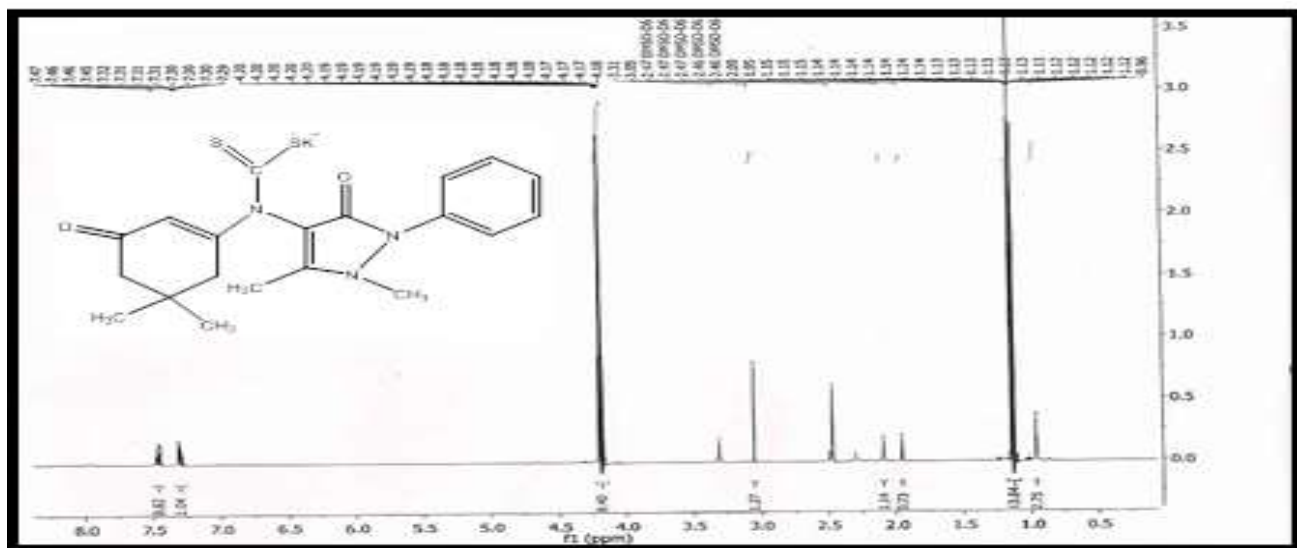
The new ligand was make by mixture compound (Da) (0.30mol) was dissolved in 10 ml of ethanol was added an excess of KOH (0.07 g, 1.25 mmol, 4eq) dissolved in ethanol

(2 ml). The mixture was allowed to stir in an ice bath, and then a solution of carbon disulfide (0.07 g, 0.92mmol, 3eq) was added drop wise with stirring. The mixture was pliable to stir at 0 °C for 2 h, during which the formation of the potassium dithiocarbamate salt was obtained as a yellow solid. The preparation is shown in Scheme (2). Yield: (0.11)g, (81.5%) with m.p. (176-178) °C.

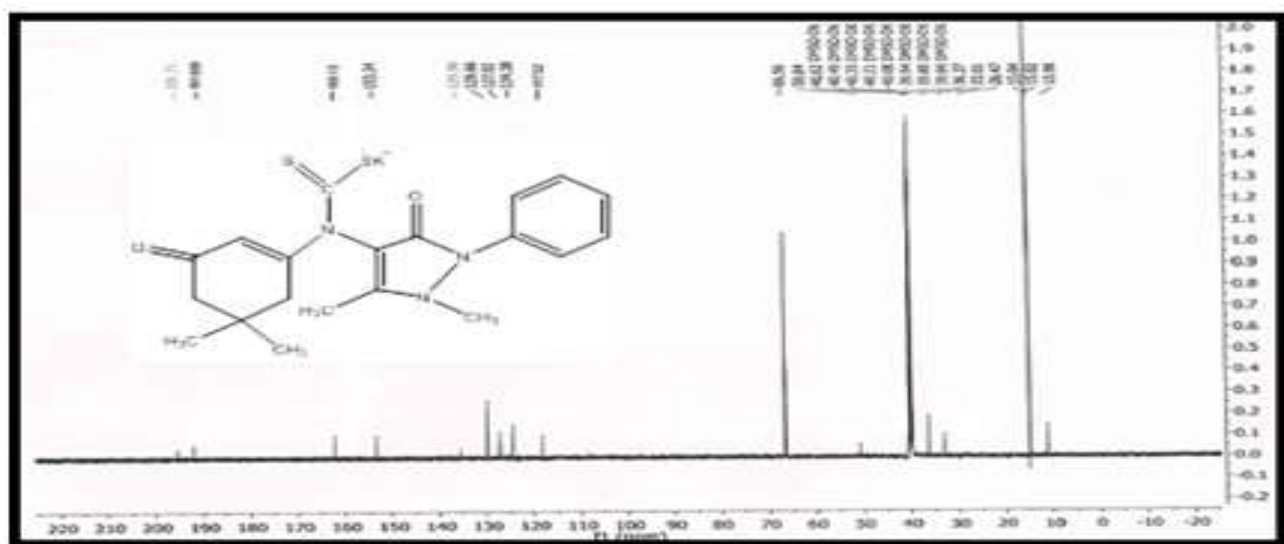


Scheme 2: Synthesis of Ligand(KL¹)

¹H NMR data (ppm) Fig.(1): Ar-H 3H(C₄) 3.315, 2H(C_{5,6}) 3.05 s, 3H(C₇) 2.09, (C_{1,C2})(7.47-7.29)s, 1H(C₃) (4.20-4.10)m, 6H(C₈)(1.15)m [12].

Fig.1: ^1H NMR spectrum of ligand KL¹ in DMSO

^{13}C NMR data (ppm) Fig.(2): C_1 195.25 , C_{11} 66.56 , ($\text{C}_{12,13}$) 50.84, 40.62 respectively
 C_2 185.21 , C_3 160.50 , C_4 153.34 , ($\text{C}_{5,6}$) 135.50 , C_{14} 36.37 , C_{15} 33.01 , C_{16} 15.04 , C_{17} 10.98 [13].
 C_7 127.02 , C_8 124.38 , C_9 129.66 , C_{10} 115.01

Fig. 2: ^{13}C NMR spectrum of ligand KL1 in DMSO

The mass spectrum Fig. (3) of the ligand KL¹ showed the peaks at $m/z = 439.3$ (5%) corresponding to parent ion. The other two

peaks detected at $m/z = 184.2$ (20%), 76.0 (98%) corresponding to $[\text{C}_8\text{H}_{13}\text{N}_3^+]$, $[\text{C}_2\text{H}_5^+]$, respectively [14].

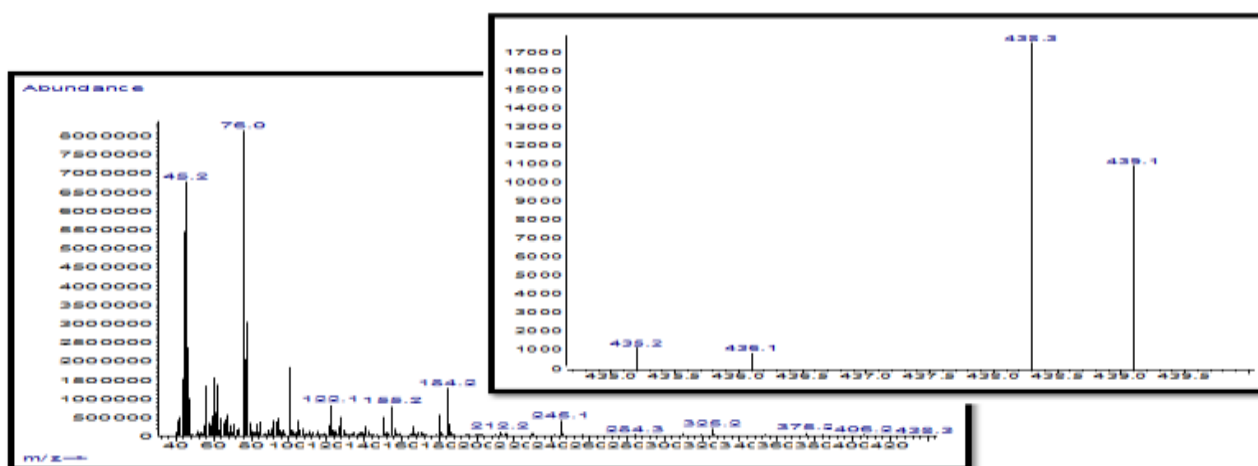


Fig.3: Mass spectrum of ligand KL1

Preparation of Metal Complexes

A solution of (0.034g, 0.2mmol) metal salt in (3ml) ethanol was added to solution of (0.177g, 0.4mmol) (KL¹) in (10ml) ethanol. The mixture was refluxed for 3 hrs with constant stirring, the precipitate was collected by filtration, washed with (1:1) mixture of water: ethanol, then with diethyl ether and dried at room temperature precipitate. Weight (0.0735), yield (79%).

Results and Discussion

The analytical data in Table (1) indicates that KL¹ and all complexes were found to be stable in air and insoluble in water but soluble in common organic solvent. The notice molar conductance values of the complexes in DMSO were non-electrolytic nature. The mole ratio method was used to determine the ratio of metal and ligand. The study shows the ligand coordinated to metal in 1:2 ratios. Physical data and analysis of ligand and its complexes are listed in Table (1).

Table 1: Physical data and analysis of ligand and its complexes

Complex, mol, Formula, mol. wt.	Color, Yield (%)	Decomposition temp. (°C)	Analyses % Found (Cal.)				
			C	H	N	S	M
C ₂₀ H ₂₂ KN ₃ O ₂ S ₂ 439.63	Yellow 81.5	(176-178)	54.01 (54.64)	5.10 (5.04)	9.99 (9.56)	14.38 (14.58)	-
[Mn(L ¹) ₂] 858.19	Green 76.68	>300*	55.77 (55.93)	5.01 (5.12)	10.06 (9.78)	14.72(14.91)	6.36 (6.40)
[Co(L ¹) ₂] 862.19	Brown 81.16	>300*	55.59 (55.67)	5.09 (5.10)	9.95 (9.74)	14.73 (14.84)	6.59 (6.83)
[Ni(L ¹) ₂] 861.92	Olive green 66.98	>300*	55.51 (55.68)	5.00 (5.10)	9.95 (9.74)	14.61 (14.85)	6.72 (6.80)

*decomposition

Infrared Spectra

The ligand KL¹ and its metal complexes were show a characteristics absorption bands, the difference between them is probably due to the complexation of the metal to the ligand through sulphur atoms of the DTC group. The obtain data are given in Table (2) and shown in Fig. (4-7). substantial absorption infrared spectrum of the free ligand exhibited strong high intensity bands due to C-N, C-S_{sy} and C-S_{as}, at 1493, 945 and 1003 cm⁻¹, respectively. A strong band remarked in the range 1456-1495cm⁻¹ in these complexes is

attributed to C-N stretching vibration that are intermediate between (C-N) (1250-1350 cm⁻¹) single band and (C=N) (1630-1690 cm⁻¹) double bands, due to π electron delocalization within the DTC functions [15]. Otherwise a strong intensity bands was observed in the range (1003-1053 cm⁻¹), which due to CS₂ vibration. These values are increased and shifted to higher frequencies comparison to ligand (KL¹). Which specify that the DTC ligand coordinating with metal through (S) atoms [16]. The complexes exhibited band (250-400 cm⁻¹), which are assigned to the ν (M-S) stretching mode [17].

Table 2: FTIR spectral data of complexes (cm⁻¹)

Compound	$\nu_{\text{aro.}}$ (C-H)	$\nu_{\text{alph.}}$ (C-H)	$\nu_{\text{vin.}}$ (C=C)	$\nu(\text{N-CS}_2)$ (C-N)	$\nu(\text{C-N})$	$\nu(\text{C-S})_{\text{sy.}}$ $\nu(\text{C-S})_{\text{asy.}}$
KL ¹	3107(w)	2954(m)	1527(w)	1493(w)	1244(s)	945 (s) 1003(w)
[Mn(L ¹) ₂]	3248(w)	2956(m)	1589(s)	1456(s)	1217(w)	1003(s) 1053(m)
[Co(L ¹) ₂]	3236(w)	2958(m)	1529(w)	1495(w)	1238(s)	1003(s) 1036(w)
[Ni(L ¹) ₂]	3242(w)	2954(m)	1527(w)	1495(w)	1236(s)	1003(w) 1020(s)

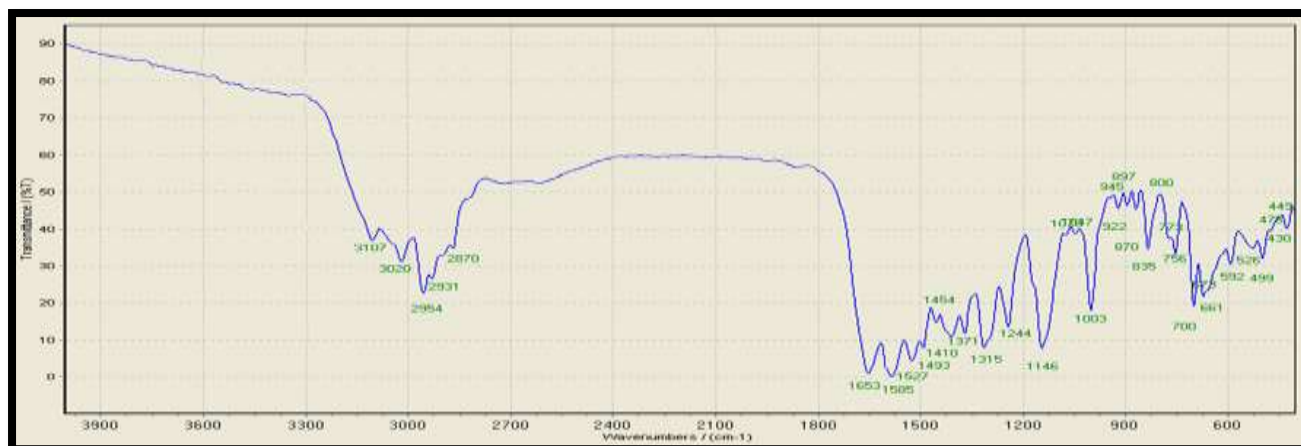


Fig.4: IR Spectrum of ligand KL1



Fig.5: IR Spectrum of [Mn(L¹)₂] complex



Fig.6: IR Spectrum of [Co (L¹)₂] complex

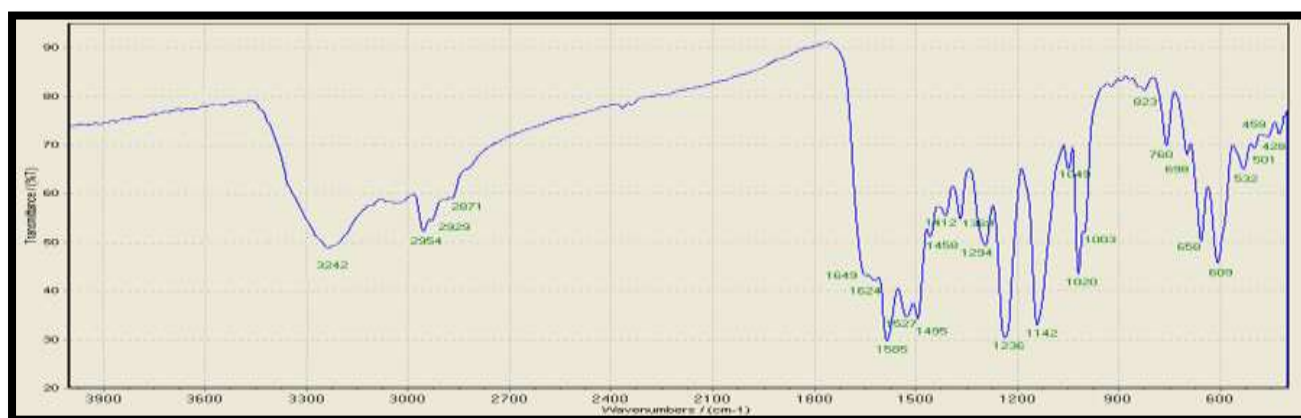


Fig.7: IR Spectrum of [Ni (L¹)₂] complex

Electronic Spectra

The electronic spectrum of the ligand (KL¹) offering strong absorption bands at (32258, 41841 cm⁻¹) assigned to transition $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ respectively. The electronic spectrum of Mn(II) complex shows addition bands in the region of d-d transition at 16233 cm⁻¹ which is assigned to ${}^6A_1 \rightarrow {}^4E, {}^4T_{(G)}$ characteristic for tetrahedral geometry. The electronic spectrum of Co (II) complex showed one

absorption band at 35087 cm⁻¹ which is assigned to ${}^4A_2 (F) \rightarrow {}^4T_1$ transition and other band at 25000 cm⁻¹ which is assigned to C.T transition. Finally the Ni (II) complex showed two absorption bands at 10204 cm⁻¹ for ${}^3T_1 \rightarrow {}^3T_2 (P)$ transition and the second was assigned to charge transfer transition at 22222 cm⁻¹. These complexes were tetrahedral geometry [18-20]. It is shown in Fig. (8-11), Table (3).

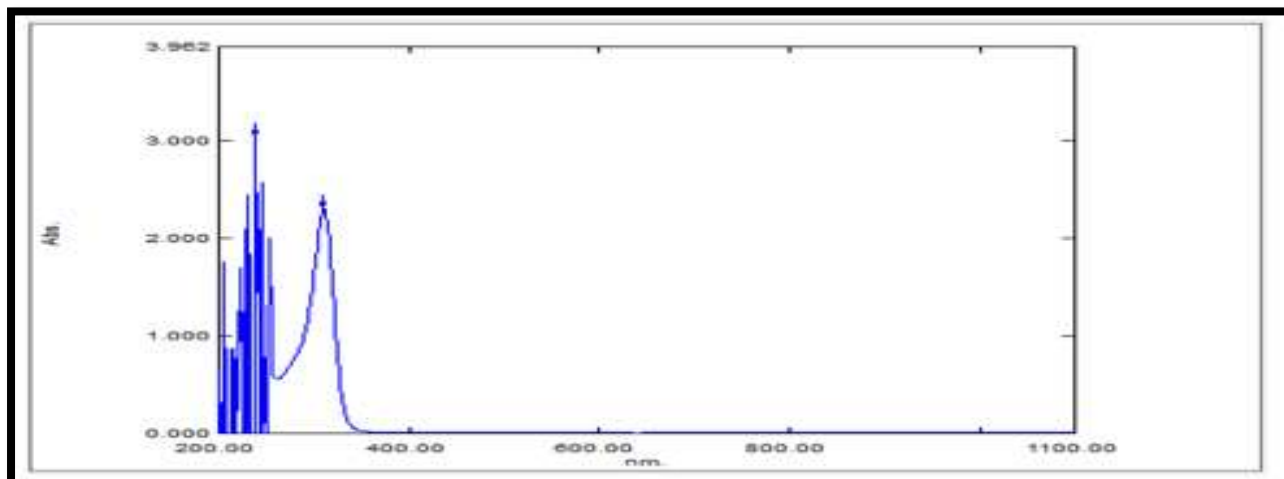


Fig.8: Electronic spectrum of ligand KL1

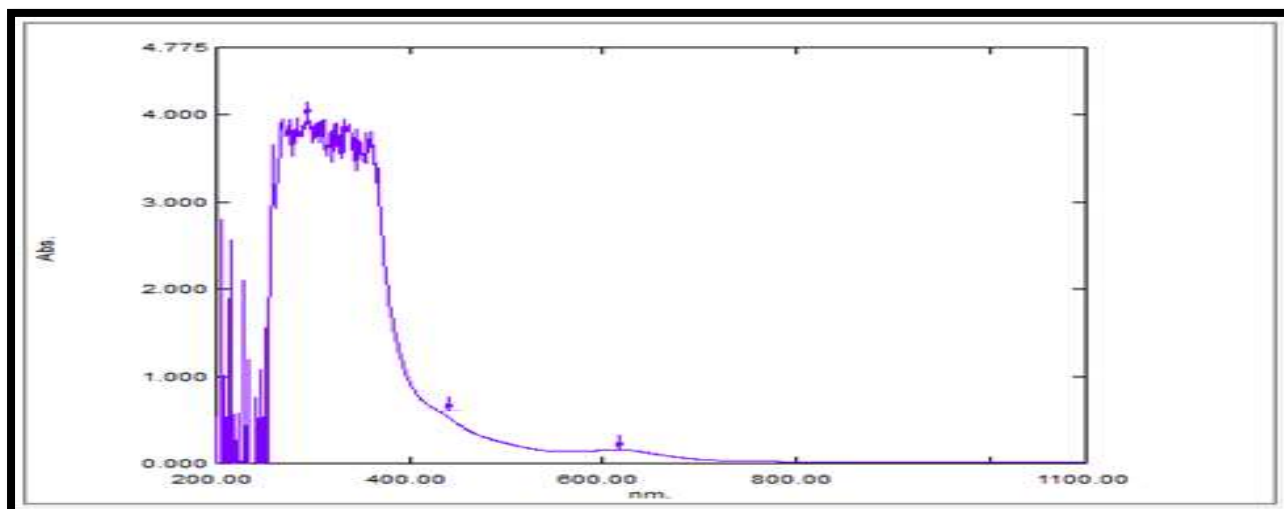


Fig.9: Electronic spectrum of [Mn(L¹)₂] complex

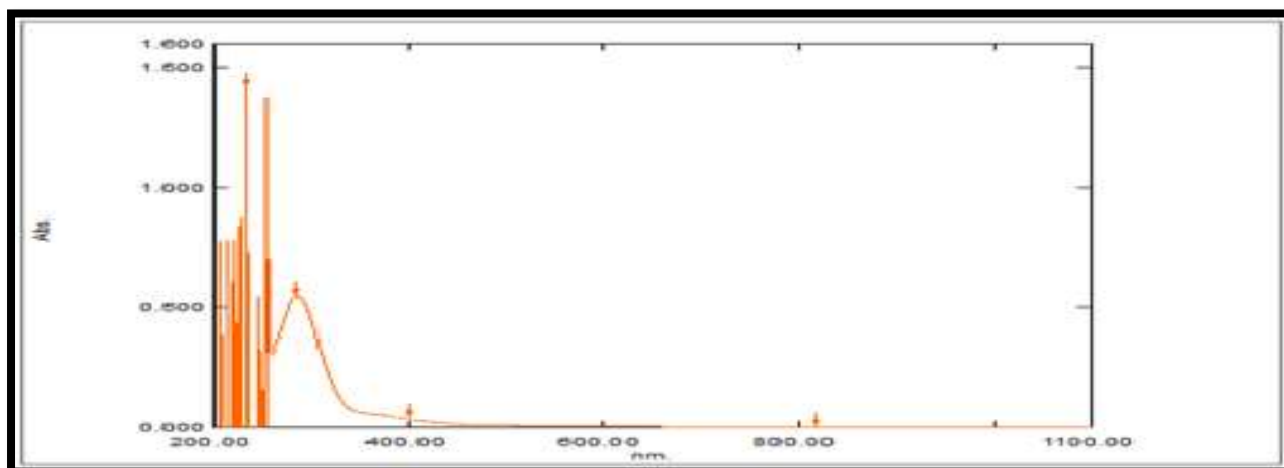


Fig.10: Electronic spectrum of [Co (L¹)₂] complex

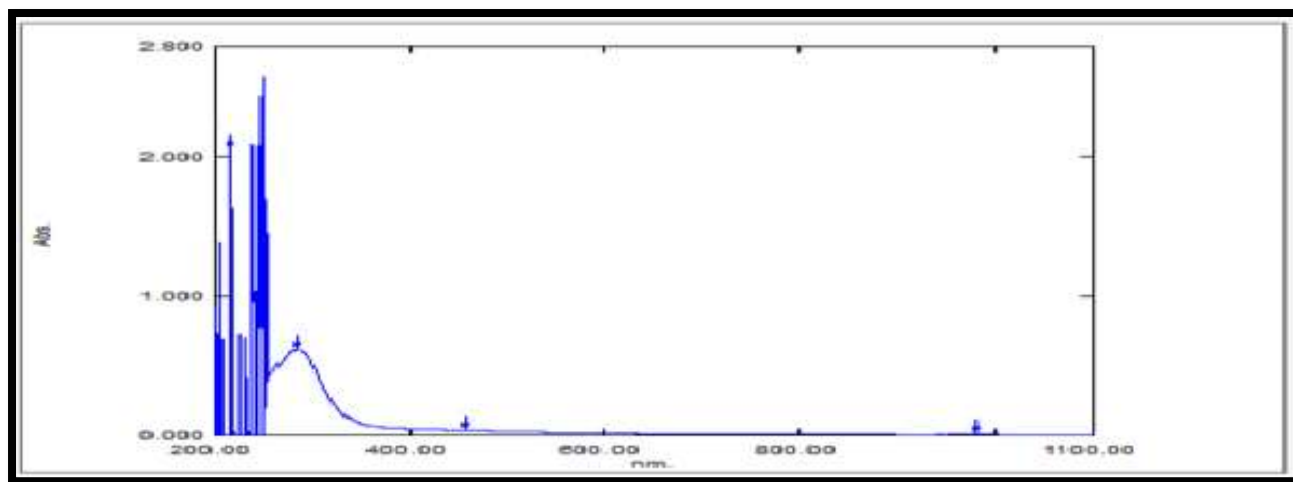


Fig.11: Electronic spectrum of [Ni (L¹)₂] complex

Table 3: UV-Vis spectral data of KL¹ complexes in DMSO solutions

Compound	Wave length λ_{nm}	Wave number (cm ⁻¹)	ϵ_{max} (moler ⁻¹ .cm ⁻¹)	Assignment	Suggested geometry
KL¹	239 310	41841 32258	3037 2304	$\pi \rightarrow \pi^* n \rightarrow \pi^*$	-
[Mn(L¹)₂]	295 435 617	33898 22988 16207	3977 550 155	Intra Ligand C.T ${}^6A_1 \rightarrow {}^4T_{1(G)}$	Tetrahedral
[Co(L¹)₂]	234 285 400 813	42735 35089 25000 12300	1421 547 98 57	Intra Ligand C.T ${}^4A_1 \rightarrow {}^4T_{1(P)}$	Tetrahedral
[Ni(L¹)₂]	216 283 450 981	46296 35335 22222 10204	2061 613 100 50	Intra Ligand C.T ${}^3T_1 \rightarrow {}^3T_{1(P)}$	Tetrahedral

Magnetic Susceptibility

The experimentally determined value of magnetic moment and the suggested

structure [21] for all these complexes are listed in Table (4).

Table 4: Magnetic moment of complexes

Compound	μ_{eff} (B.M.)	Suggested Structure
[Mn(L¹)₂]	5.89	Tetrahedral
[Co(L¹)₂]	4.81	Tetrahedral
[Ni(L¹)₂]	3.56	Tetrahedral

Biological Activity

The author in this sitting investigation attempted to find out the antibacterial activity of ligand their metal complexes versus *Staphylococcus* and *E. coli* select suggested disc method Table (5). The results of the biological activity of the metal complexes suggest the following facts. A

comparative study of the ligand and their complexes suggest that the metal chelates exhibited higher antibacterial activity than that of the ligand [22, 23]. The regions of inhibition of the ligand metal complexes were in the Table (5), Fig (12, 13). The activity was contrasted with a region of inhibition was measured in mm.

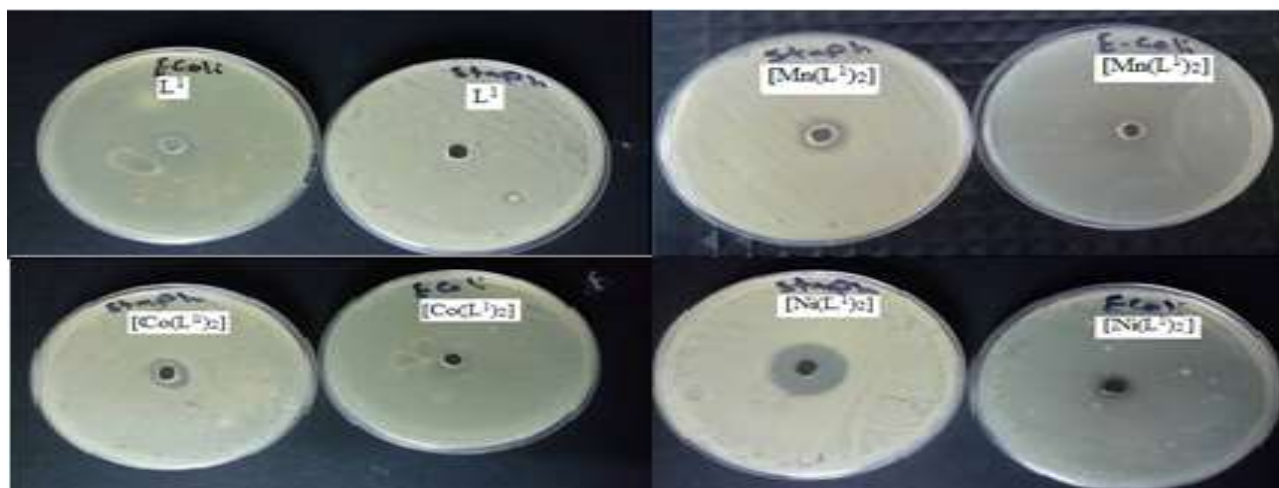


Fig.12: The effect of mix ligand complexes on [Escherichiacoli and Staphylococcus Aureus].

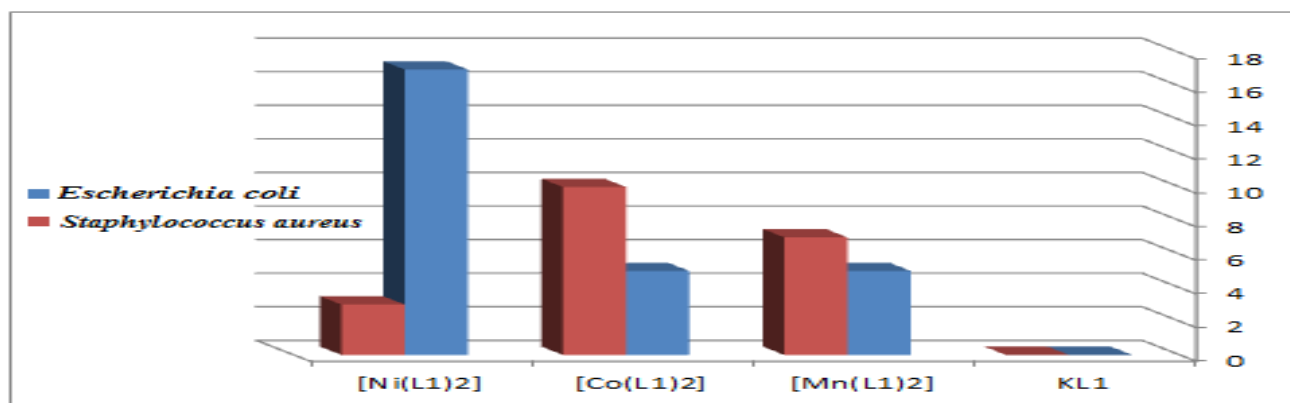


Fig. 13: The antibacterial activity of compounds against [*Escherichiacoli* and *Staphylococcus Aureus*].

Table 5: Antibacterial activity of the metal complexes total area of zone of clearance in mm

Compounds	<i>Escherichia coli</i> (G-)	<i>Staphylococcus aureus</i> (G+)
KL ¹	-	-
[Mn(L ¹) ₂]	5	7
[Co(L ¹) ₂]	5	10
[Ni(L ¹) ₂]	17	3

Conclusion

This present work account the synthesis and identification of new Dtc ligand (KL¹) and its complexes with Mn(II), Co(II), Ni(II) metal ions. These compounds were described by

accessible techniques. In synopsis, we have shown that all of these complexes have the tetrahedral suggested structure. The structural formula of these complexes is suggested in Fig. (14).

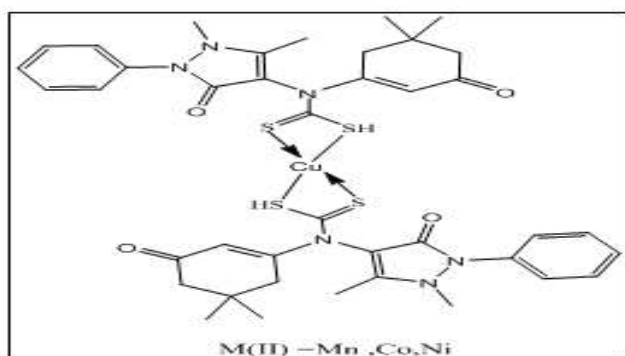
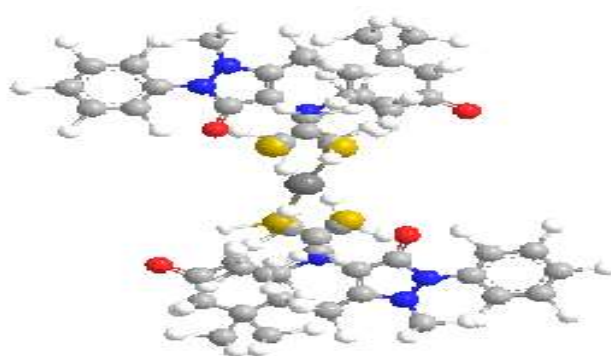


Fig.14: Suggested structure of tetrahedral geometry [M (L2)]



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