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To cite this article: A M Ali and T H Al-Noor 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1046** 012006

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# Synthesis, spectroscopic study, biological activity and dyeing application of curcumin - Schiff base with various metal ions complexes

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**Abstract.** A tetradentate ( $N_2O_2$ ) Schiff base ( $H_2Ldfm$ ) was successfully synthesized via condensation of curcumin / diferuloylmethane (dfm) and L-leucine amino acid (HL). There were three different methods that used for synthesizing  $H_2Ldfm$ ; (refluxing, grading, and fusion). Ten different metal complexes were also successfully synthesized by combination of the Schiff base ( $H_2Ldfm$ ) and 1,10-phenanthroline (phen) ligand to form a hexadentate ( $N_4O_2$ ) mixed ligands ( $Ldfm$ , phen) with ten different metal salts (M) where { M= Al(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Ag(I), Cd(II), Hg(II), and Pb(II)}. The molar ratio of reactants was (1:1:1) (M:  $H_2Ldfm$  : phen). The new Schiff base and its new complexes were characterized by different physicochemical techniques such as FT-IR, UV-Visible, elemental analysis (C.H.N),  $^{13}C$ -NMR,  $^1H$ -NMR, molar conductivity, mass spectroscopy, magnetic susceptibility, and thermal analysis. All complexes exhibited octahedral geometry. The solution conductivity of (Al (III), Fe (III), and Ag(I)) complexes in DMSO shows an electrolytic behavior, while the solution conductivity of (Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Hg(II) and Pb(II)) complexes shows non-electrolytic attitude. The Schiff base ( $H_2Ldfm$ ) and its metal complexes were used for industrial and biological application such as dyeing cotton fibers testing and two types of bacteria testing like (*Staphylococcus aureus* and *Escherichia Coli*).

## 1. Introduction

Mixed ligand and Schiff bases (azometine compounds) have played important role in the development of coordination chemistry and have been implicated as a significant point in the development of inorganic biochemistry, some Schiff base compounds containing N and O are used in pharmaceutical, industrial, agricultural, biological and medical applications [1]. Curcumin ( $C_{21}H_{20}O_6$ ) = ((1E,6E)-1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6- heptadiene-3,5-dione)obtained from the rhizome of turmeric (*curcuma longa*),and it has a yellow coloring natural pigment [2] . In addition , it has many functional groups such as a polyphenol and ortho-methoxy. Compounds have widely used of diverse fields like antibacterial, antiviral, anticancer, antifungal, antioxidant activities and anti-inflammatory [3][4]. Many studies dealing with curcumin complexes have been published within the past 20 years have been used as a traditional medicine, food additive dye , and indicator [2]. Curcumin has a conjugated  $\beta$ -diketone moiety can be a powerful natural chelating agent with its safe evaluation even administered at high doses by human [3]. Recently, complexation of curcumin with metal ions have attracted the attention of researchers around the world as one of the useful requirements for the treatment of Alzheimer's disease and *in vitro* antioxidant activity [3][5]. An amino acid is a compound that generally includes two



different functional groups such as (a carboxyl and an amino), both grafted to the same carbon atom in  $\alpha$  position [6], they used in the synthesis of the Schiff base compounds [7], and amino acid based Schiff base complexes have biological importance [8]. In addition, they are used with metal ions the synthesis of complexes [9]. Moreover, Schiff base compounds are formed from the condensation any primary amine with an aldehyde or a ketone [10]. They used the synthesise complexes with different metal ions [11]. They are well known due to their applications in different fields such as analytical chemistry, coordination chemistry and agricultural applications [12]. 1,10-Phenanthroline widely used as coordinating agent for preparing of stable compounds [13].

The present work are focusing on synthesis and study Schiff base from curcumin with L-leucine, then preparing of (transitional and non-transitional) metal complexes with mixed ligands of a new Schiff base ( $H_2Ldfm$ ) and 1,10- phenanthroline (phen). The biological efficacy with two types of bacteria and tested as dyes on cotton fibers were studied

## 2. Experimental

### 2.1. Materials and methods

All chemical materials were used without further purification. The metallic ions  $MCl_n \cdot XH_2O$ , ( $M=Al(III)$ ,  $Mn(II)$ ,  $Fe(III)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$ ,  $Cd(II)$ ,  $Hg(II)$  and  $M(NO_3)_n$   $M=Ag(I)$ ,  $Pb(II)$ ), curcumin, L-leucine, DMSO and  $C_2H_5OH$  were Analar grade (BDH).

### 2.2. Physical measurements

Elemental analysis (C, H, N) of ligand were performed by Eager300 for EA1112 Thermal Finnegan C.H.N.S 2400 elemental analyzer. The (AAS) analysis in complexes were recorded by using a fair agreement method by used the device from type Shimadzu (A.A 620) atomic absorption spectrophotometer. The  $\Lambda_m$  measurements of the complexes with  $10^{-3}$  mol/L in dimethyl sulfoxide (DMSO) were reached by using a device digital conductivity series Ino.Lab.720. Magnetic measurements of the complexes were measured by using Balance Johnson Matthey. The mass spectrum of ligand was determined by using Ion source: Electron Impact (EI) 70eV mass spectra register on manufacturer company: Agilent Technology 1. MS Model: 5973 spectrometer. Ultraviolet-visible spectra were obtained by using solvent (DMSO) ( $10^{-3}$  M) for the ligand and its metal complexes by double-beam UV-visible spectrophotometry type U.V 160A (Shimadzu), between (200-1100) nm with a  $10^{-1}$  cm length of quartz cell. The Fourier-transform infrared spectra were recorded using KBr pellets on Shimadzu FT-IR 8400S spectrophotometry has a range ( $400-4000\text{ cm}^{-1}$ ).  $^1H$  and  $^{13}C$ -NMR spectra were obtained from (DMSO) - $d_6$  solution using an Inova 500 MHz, and thermal analysis (TGA-DSC) of the complexes were performed by SDT Q600 V20.9 Build 20 DSC/TG thermal system under the  $N_2$  flow with a heating rate of 10 C/min from 25 to 700°C.

### 2.3. Synthesis of Schiff base ( $N_2O_2$ ) tetradentate

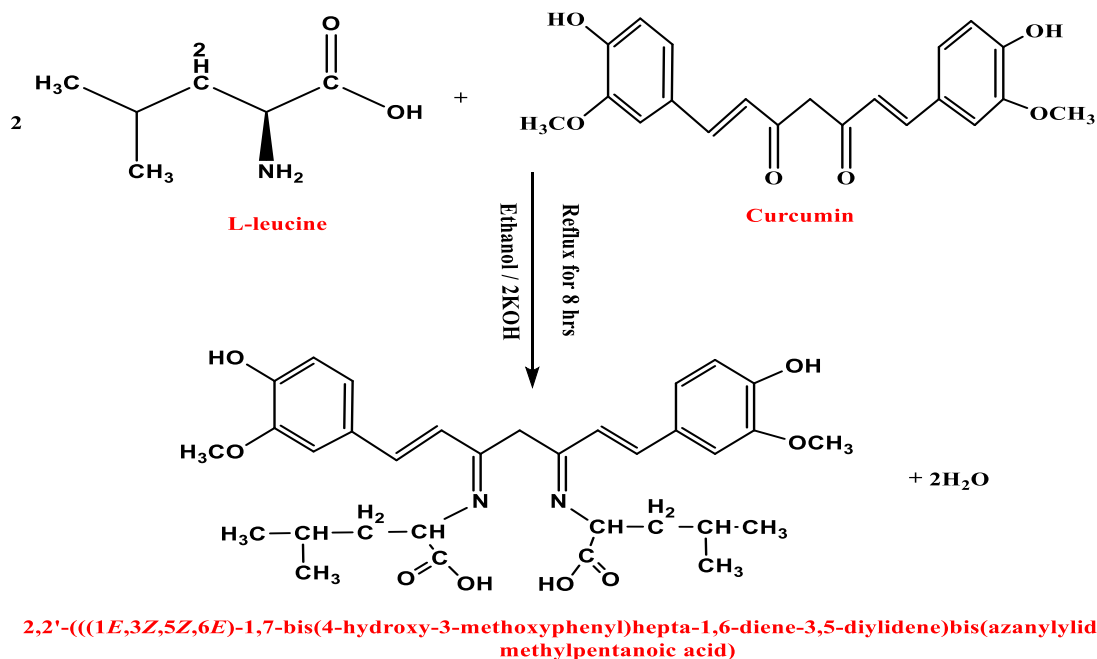
It was synthesized by reflux, grinding, and fusion methods.

**2.3.1. Reflux.** The Schiff base ligand ( $H_2Ldfm$ ) was synthesized with improvement to the common method in the literature [14]. It was prepared by condensation of HL (0.262 gm, 2 mmol) dissolved in hot ethanoic aqueous solution (25 mL) with dfm (0.368 gm, 1mmole) dissolved in hot ethanoic solution (25 mL) in a basic medium of KOH. The mixture refluxed for about eight hrs until a yellow-brown polycrystalline precipitate was obtained, the reaction monitored by TLC technique. The precipitate was filtered and washed with ethanoic aqueous solution, then recrystallized from hot ethanol. Elemental Analysis: call (found) C, 66.65(66.40); H, 7.12 (6.99); N, 4.71 (4.60); O, 21.52 (---), yield (80%). The synthesis pathway is shown in Scheme 1.

**2.3.2. Grinding.** The  $H_2Ldfm$  was also prepared by the mixing of L-leucine (0.262 gm, 2 mmol) and curcumin (0.368 gm, 1mmol) in a manual mortar [15]. Four drops of glacial acetic acid was added, then

the mixture was grinded for about (0.5-1) hour. The reaction was observed with the TLC technique. The yellow Schiff base was purified by repeated washing with ethanoic aqueous solution and recrystallized from hot ethanol afforded yield (82%).

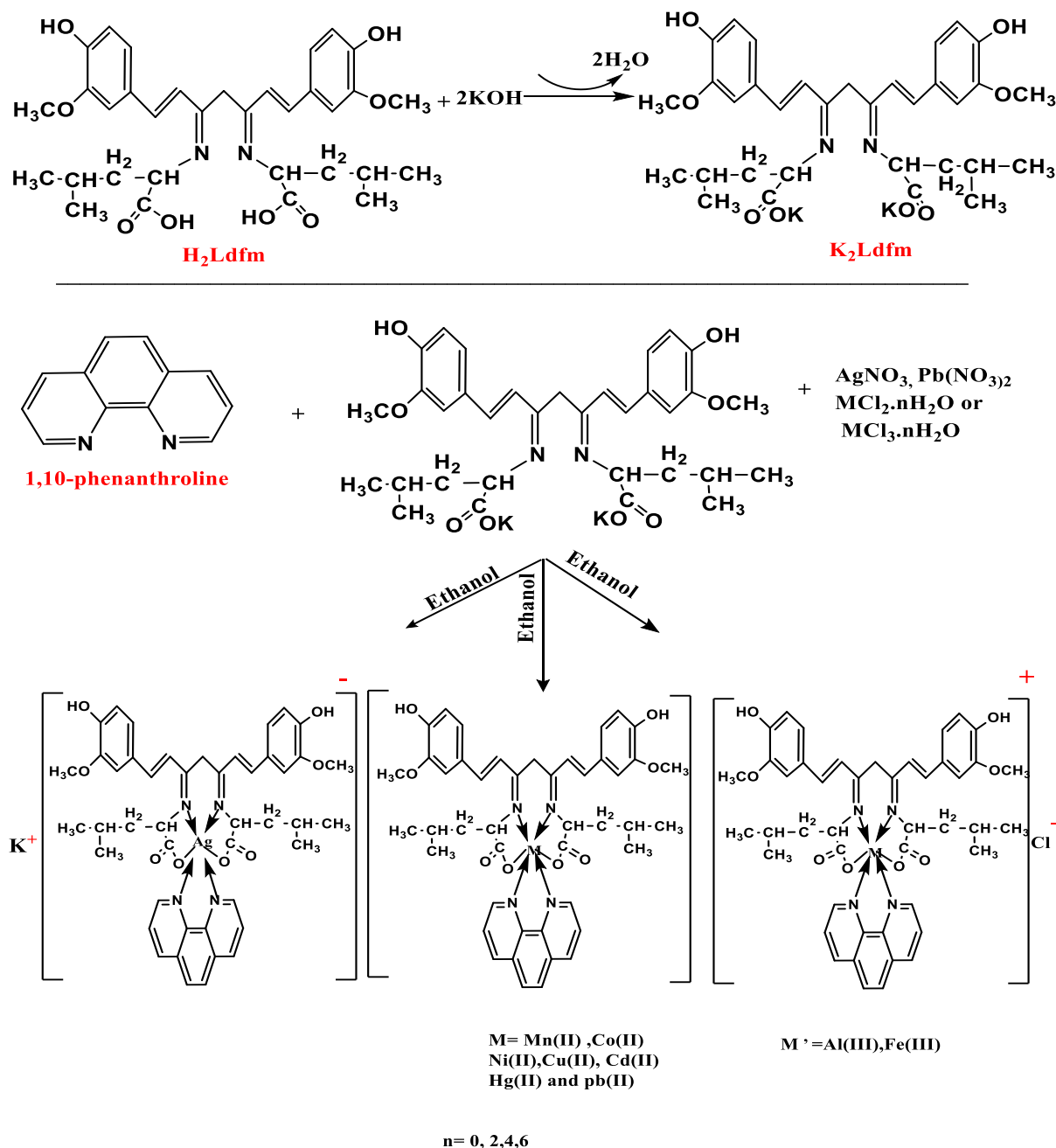
2.3.3. *Fusion*. A molar ratio of (1:2) (dfm : HL) was mixed in a round bottom flask, then 4 drops of glacial acetic acid was added [16]. The mixture was heated on oil bath for about 10 minutes until fused. The resulted yellow-brown Schiff base was dissolved in ethanol, filtered and dried, then recrystallized from hot ethanol, afforded yield (87%).



**Scheme (1):** Shows the preparation process of (H<sub>2</sub>Ldfm) Schiff base ligand.

#### 2.4. Preparation of metal complexes

As shown in Scheme 2, the metal complexes were synthesized by mixing of the ligands H<sub>2</sub>Ldfm phen and some metal ions M in the ratio of 1:1:1 (H<sub>2</sub>Ldfm: phen: M). A (0.594 gm, 1mmol) of H<sub>2</sub>Ldfm was dissolved in 15 mL of absolute ethanol, then (0.112 gm of potassium hydroxide) was added. A (0.180 gm, 1mmol) of phen was dissolved in 15 mL of absolute ethanol. The metal salts were dissolved the in 10 mL of absolute ethanol. 0.133g of aluminum(III) chloride, 0.197gm of manganese(II) chloride, 0.270 gm of iron(III) chloride, 0.237gm of cobalt(II) chloride, 0.237gm of nickel(II) chloride, 0.170 gm of copper(II) chloride, 0.169 gm of silver(I) nitrate, 0.183 gm of cadmium(II) chloride, 0.271 gm of mercury(II) chloride and 0.331 gm of lead(II) nitrate were used. The solutions of the ligands were gradually added to the above-mentioned salt solutions with constant stirring about half an hour to obtain precipitates of the complexes. The precipitates were separated and washed several times with an ethanoic aqueous solution, then re-crystallization from the hot ethanol.



**Scheme 2.** Preparation of the metal complexes

### 3. Results and Discussion

Generally, the Schiff base ligand (H<sub>2</sub>Ldfm) was attained by condensation of one equivalent of dfm with two equivalent of HL, while its complexes were prepared by reacting the metal salts with the Schiff base (H<sub>2</sub>Ldfm) and phen ligands by using (1:1:1) molar ratio. The H<sub>2</sub>Ldfm (primary ligand) behaves as a tetradentate ligand, while the phen (secondary ligand) behaves as bidentate, therefore, the resulted mixed ligand exhibited a hexadentate coordination sphere around the metal ions in the new prepared complexes. The researchers notice most of the prepared compounds have distinguished by deep color because they had a partially filled electronic arrangement (Cotton F. A, 1987). Moreover, the molar conductance (Λ<sub>m</sub>) values which were recorded in DMSO (10<sup>-3</sup>M) in the range of (6.5-19.9)

$\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$  gave an evidence that these complexes are non-electrolytes and exception of type Fe(III), Al(III) and Ag(I) complexes are electrolytes the range of (36.2-40.3)  $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$  [17]. All complexes possess high melting points ranging between (199- >250) and they are all stable at room temperatures over time. Some physicochemical characteristics of complexes are shown in (table 1).

### 3.1. Solubility test

Solubility test was performed in different types of solvents such as water, dimethyl sulfoxide, chloroform, ethanol, methanol, dimethylformamide, hexane, and acetone. All compounds were not dissolved in water, but they were easily dissolved in methanol, ethanol, chloroform, dimethylformamide, dimethyl sulfoxide and hydrochloric acid. In addition, the Al(III), Co(II), Ni(II), Cd(II), and Hg(II) complexes were poorly soluble in acetone and hexane solvents.

**Table 1.** Physicochemical characteristics data of the compounds.

Compounds	M.Wt	Color	M.P	Yield%	$\Lambda \text{ m}\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	Metal % (exp)
$\text{C}_{33}\text{H}_{42}\text{N}_2\text{O}_8(\text{H}_2\text{Ldfm})$	594.71	Yellow brown	170-172	80	---	----
[Al(Ldfm)(Phen)]Cl	835.5	Pale yellow	>260	56	36.2	3.25(3.05)
[Mn(Ldfm)(Phen)]	827.84	Dark brown	223-224	62	10.1	6.63(5.22)
[Fe(Ldfm)(Phen)] Cl	864.24	Dark brown	>260	77	40.3	6.46(6.30)
[Co(Ldfm)(Phen)]	831.83	Pale yellow	>260	61	15.5	7.08(6.96)
[Ni(Ldfm)(Phen)]	831.59	Pale yellow	>260	59	8.6	7.05(6.88)
[Cu(Ldfm)(Phen)]	836.45	Dark yellow	228-230	88	6.5	7.59(7.05)
K [Ag(Ldfm)(Phen)]	919.77	Pale brown	199 Dec	90	39.2	11.72(10.01)
[Cd(Ldfm)(Phen)]	885.31	Dark brown	>260	78	18.9	12.69(10.35)
[Hg(Ldfm)(Phen)]	973.49	Pale yellow	238-240	70	19.9	20.05(20.12)
[Pb(Ldfm)(Phen)]	980.10	Brown	228-229	79	12.2	21.14(20.11)

Phen=1,10-phenanthroline = (C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>). (H<sub>2</sub>Ldfm) = C<sub>33</sub>H<sub>40</sub>N<sub>2</sub>O<sub>8</sub>  
Dec = decomposition

### 3.2 . UV-vis spectra

The UV-vis spectra of the compounds were performed in DMSO (10<sup>-3</sup> M) solution as shown in (table 2). There was a shifting to higher wavelength that could be observed with the electronic spectra of all complexes, which supports the formation of these complexes [18]. The UV-Visible spectrum of H<sub>2</sub>Ldfm has showed two bands, the first band at 270 nm which can be assigned to  $\pi \rightarrow \pi^*$  transition in the aromatic ring and double bonds in curcumin structure, and the second band at 434 nm which can be assigned to  $n \rightarrow \pi^*$  transitions in azomethine. whilst the UV-Visible spectrum of phen (second ligand) showed only one band at 271 nm which is attributed to  $\pi \rightarrow \pi^*$  transition [19].

The UV-visible spectrum of [Al(Ldfm)(phen)]Cl complex displayed three bands, the first band with a high intensity at 268 nm due to the intra ligand charge transfer (INCT), and other two bands at 430 nm and 942 nm due to the 3p transitions in the Al $\rightarrow$  that were observed by monitoring 4s $\rightarrow$ 3p emission from Al(4s) atoms produced by pre dissociation of the excited complex [19]. The UV-visible spectrum

of [Mn(Ldfm)(Phen)] showed four bands, the first band was found in the ultraviolet region at 270 nm which assigned to ligand field while the other three bands at 426nm, 450nm and 805 nm were assigned to L→M charge transfer, L→M charge transfer, and  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ , respectively. The Mn(II) complex displayed the octahedral geometry depending on the magnetic susceptibility value (5.34 B.M) [20].

**Table 2.** Electronic spectral main data and magnetic measurements of compounds in (DMSO).

Compounds	$\lambda_{\max}$ nm	$\nu'$ $\text{cm}^{-1}$	$\epsilon$ max $\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$	Assignments	( $\mu_{\text{eff}}$ ) B.M	Geometry shape
H <sub>2</sub> Ldfm	270	37037	839	$\pi \rightarrow \pi^*$	----	---
	434	23041	2182	$n \rightarrow \pi^*$		
Phen (C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )	271	36900	801	$\pi \rightarrow \pi^*$	----	----
[Al(Ldfm)(Phen)] Cl	268	37313	369	C.T	Dia.	O.h
	430	23255	81	The 3d ← 3p		
	942	10615	7	transitions in the Al-N		
[Mn(Ldfm)(Phen)]	270	37037	1946	Ligand field	5.34	O.h
	426	23474	1835	Charge transfer		
	450	22222	1553	Charge transfer		
	805	11764	7	${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$		
[Fe(Ldfm)(Phen)]Cl	446	22421	1850	LMCT	6.02	O.h
	961	10405	1335	${}^6A_{1g} (s) \rightarrow {}^4T_{2g}$		
[Co(Ldfm)(Phen)]	267	37453	523	Ligand field	4.38	O.h
	441	22675	249	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$		
	788	12690	5	${}^4T_{2g}(f) \rightarrow {}^4A_{2g}(F)$		
	976	10245	5	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$		
[Ni(Ldfm)(Phen)]	271	36900	404	Ligand field	3.79	O.h
	989	10111	6	${}^3A_{2g}(F) \rightarrow$ ${}^3T_{2g}(f)$		
[Cu(Ldfm)(Phen)]	272	36764	1604	Ligand field	1.71	O.h
	437	22883	1868	LMCT		
	458	21834	1764	LMCT		
	825	12121	6	${}^2B_{1g} \rightarrow {}^2A_{1g}$		
k[Ag(Ldfm)(Phen)]	268	37313	1594	$\pi \rightarrow \pi^*$	Dia.	O.h
	428	23368	1072	$*n - \pi$		
	666	15015	216	C.T		
[Cd(Ldfm)(Phen)]	270	37037	1744	$\pi \rightarrow \pi^*$	Dia.	O.h
	428	23364	634	$*n - \pi$		
	858	11655	3	C. T		
[Hg(Ldfm)(Phen)]	270	37037	1819	$\pi \rightarrow \pi^*$	Dia.	O.h
	426	23474	190	$n \rightarrow \pi^*$		
	813	12300	25	C.T		
[Pb(Ldfm)(Phen)]	270	37313	1384	$\pi \rightarrow \pi^*$	Dia.	O.h
	427	23417	1218	$*n - \pi$		
	756	13227	17	C.T		

Dia. = Diamagnetic

O.h = Octahedral

The UV-Visible spectrum that outputted from [Fe(Ldfm)(phen)]Cl complex exhibited two bands, one at 446 nm and the other at 961 nm which were due to intra ligand metal charge transfer (LMCT) and  ${}^6A_{1g}({}^6S) \rightarrow {}^4T_{2g}$  transition, respectively. The ( $\mu_{\text{eff}}$ ) value of [Fe(Ldfm)(phen)]Cl [ $d^5$ ] complex was 6.02 B.M, that a tentative interpretation expects to be taken the structure of Fe(III) to be an octahedral geometry which matches the data reported by several research workers [20,21].

The UV-Visible spectrum of [Co(Ldfm)(phen)] complex was displayed four bands. The first band at 267 nm with high energy was related to the charge transfer transitions, and the other three bands were related to (d-d transitions) which appeared at 441 nm, 788 nm and 976 nm and were considered as  ${}^4T_{1g} \rightarrow {}^4T_{1g}(p)$   $\nu_3$ ,  ${}^4T_{1g} \rightarrow {}^4A_{2g}(f)$   $\nu_2$  and  ${}^4T_{2g}(f) \rightarrow {}^4A_{2g}(F)$   $\nu_1$  they also supported by magnetic sensitivity (4.38 B.M) which was a good evidence that this complex displayed an octahedral geometry [20-22].

The UV-visible spectrum of [Ni(Ldfm)(phen)] was revealed only two bands, the first band was wide and appeared at 271 due to the ligand field, and the other band was weak and related to (d-d transitions) at 989 nm attributed to  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(f)$  transition, and via measuring magnetic sensitivity (3.79 B.M) i.e., it had an electronic arrangement of three unpaired electrons that bolsters the octahedral geometry [22,23].

The UV-visible spectrum of [Cu(Ldfm)(phen)] was exhibited four bands. The first band was located in the ultraviolet region at 272 nm and related to the ligand field and other three bands were appeared in the visible region at 437nm, 458nm and 825nm related to (LMCT, LMCT and  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ), respectively. In addition, it had magnetic sensitivity (1.17 B.M) that supported the octahedral geometry [21,24].

The [Pb(Ldfm)(phen)] complex exhibited three bands in the UV-Visible spectrum, the first band was at 270 nm and the second was at 427 nm assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively, due to conjugated  $\pi$  system, while the third band was observed at 756 nm which ascribed to L-M charge transfer (C.T) transitions of the heterocyclic and COO- groups [20,25]. The spectra of Ag(I), Cd(II) and Hg(II) complexes were exhibited bands back to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  transitions. All the ions had an electronic arrangement with shell ( $d^{10}$ ); therefore, do not give the type (d-d) transition [18,23].

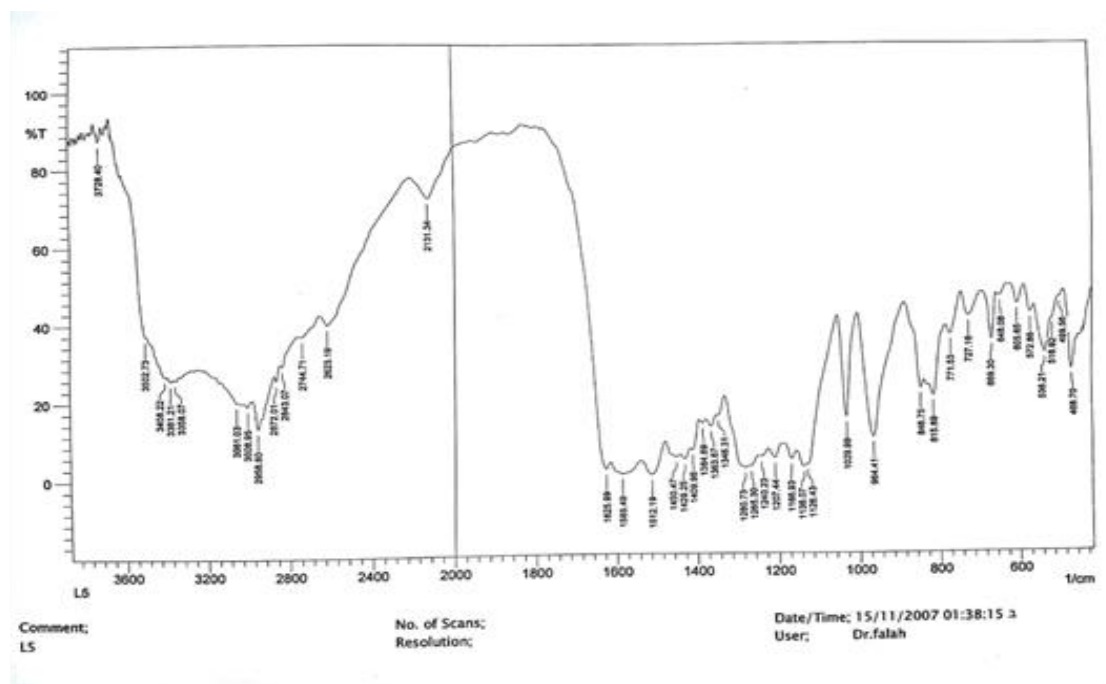
### 3.3 . IR Spectra

The FT-IR spectra data of  $H_2Ldfm$  (as shown in figure 1) and its complexes with their respective assignments as shown in (table 3). The spectrum of  $H_2Ldfm$  ligand showed a wide stretching vibration recognized at  $3508\text{ cm}^{-1}$  which could be corresponded to (O-H) carboxylic groups, while the broad band at  $3415\text{ cm}^{-1}$  indicated (O-H) phenolic groups [26,8,22].

The azomethine (HC=N) groups of  $H_2Ldfm$  appeared at  $1622\text{ cm}^{-1}$  [20,23], where it was recorded closer to the frequency of this ligand in the three different methods of synthesis .It was shifted to a lower value at ( $1602\text{-}1618\text{ cm}^{-1}$ ) in all complexes, which gives an evidence that it coordinated with different metals' ions via the nitrogen atom of (HC=N) group [23]. These results indicated that  $H_2Ldfm$  is acting as a tetradentate (NNOO) ligand when coordinating with the metal ions. Moreover, the two bands shown at  $1589\text{ cm}^{-1}$  and  $1405\text{ cm}^{-1}$  belong to ( $\text{COO}^-$ ) asymmetric and ( $\text{COO}^-$ ) symmetric, respectively [25].

The different values of the stretching vibration ( $\Delta\nu$ ) of carboxylic group ( $\text{COO}^-$ ) asymmetric and symmetric of all complexes were greater than ( $200\text{ cm}^{-1}$ ) which indicated to the monodentate coordination with the metal atoms [8,25,27]. The frequencies of phenolic (O-H) group remained without any change in most complexes indicated that OH groups did not incorporate in the process of consistency with metallic ions, while the disappearance of the frequencies of the carboxylic hydroxyl groups was a good evidence for its involvement in the process of coordination with metals. In addition, the appearance of new bands at all complexes' spectra which range from 534 - 570 and 441-466 could be assigned to the  $\nu$  (M-O) and  $\nu$  (M-N), respectively [27,28].





**Figure 1.** FT-IR spectrum of ( $H_2Ldfm$ ) Schiff base.

**Table 3.** Reprehensive results for the test of FT- IR spectra of compounds by ( $cm^{-1}$ ).

Comp	$\nu$ (O-H) <sub>carboxylic</sub> (O-H) <sub>phenolic</sub> &	$\nu$ C=N	$\nu$ as COO	$\nu$ s COO	$\Delta\nu$	$\nu$ M-O	$\nu$ M-N
$H_2Ldfm$ (Reflux)	3508&3415	1622	1589	1405	184	----	----
$H_2Ldfm$ ( Grinding)	3502 & 3400	1625	1583	1408	175	----	----
$H_2Ldfm$ (Fusion )	3512&3408	1625	1585	1409	176	----	----
Phen	----	1649	----	---	----	----	---
[Al(Ldfm) (Phen) Cl	3410	1608	1583	1361	222	534	441
[Mn (Ldfm)(Phen]	3387	1618	1585	1361	224	551	447
[Fe(Ldfm) (Phen) Cl	3388	1618	1589	1342	247	555	459
[Co(Ldfm) (Phen]	3417	1608	1585	1359	226	557	443
[Ni(Ldfm) (Phen)]	3427	1602	1582	1382	200	534	443
[Cu(Ldfm) (Phen)]	3406	1612	1589	1338	251	570	443
K[Ag(Ldfm) (Phen)]	3419	1607	1582	1365	218	536	441
[Cd (Ldfm) (Phen)]	3417	1618	1581	1352	229	549	466
[Hg(Ldfm) (Phen)]	3417	1604	1568	1354	214	549	460
[Pb(Ldfm) (Phen)]	3417	1616	1581	1374	207	551	460

### 3.4. $^1H$ -NMR Spectrum of $H_2Ldfm$ ligand

The  $^1H$ -NMR spectrum of the Schiff base ( $H_2Ldfm$ ) was recorded in the  $DMSO-d_6$  solvent. The  $^1H$  NMR spectrum of  $H_2Ldfm$ , (figure 2), was exhibited multiple signals at 7.56-6.66 that allotted to the aromatic protons of the benzene ring [29]. The three sharp signals at 3.8, 3.3 and 2.08 ppm were assigned to the  $OCH_3$ ,  $CH_2$  and  $CH_3$  groups, respectively [30], also the proton's signal of  $COOH$  group was absent in the spectrum due to hydrogen bonding [31].

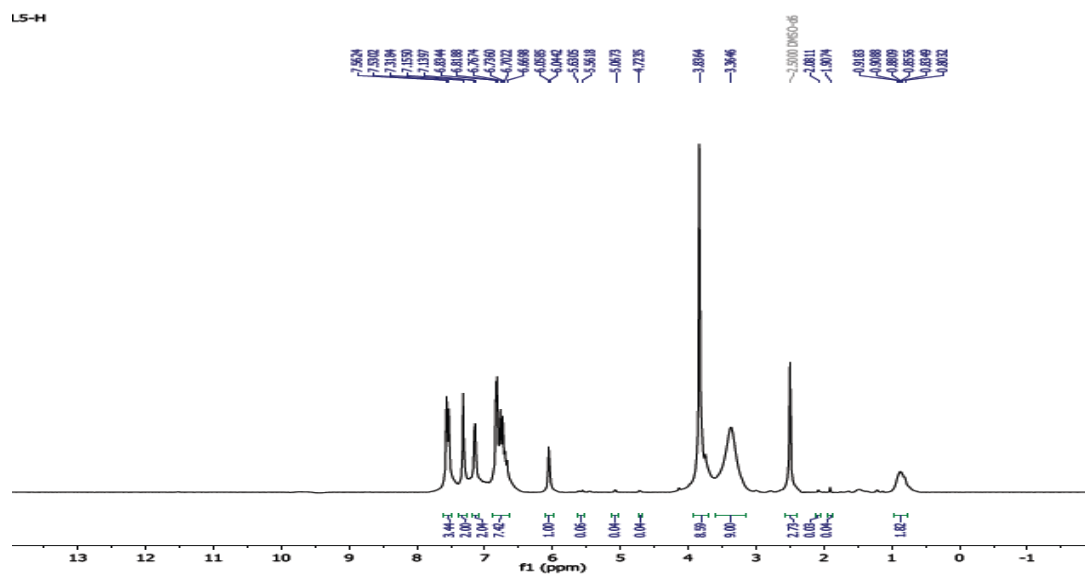


Figure 2.  $^1\text{H}$ -NMR spectrum of  $\text{H}_2\text{Ldfm}$  ligand.

### 3.5. $^{13}\text{C}$ -NMR Spectrum of $\text{H}_2\text{Ldfm}$

The  $^{13}\text{C}$ -NMR spectrum of ( $\text{H}_2\text{Ldfm}$ ) showed two signals at (183.20 and 159.73 ppm) ascribed to  $\text{C}=\text{O}$  (carboxylic) and  $\text{C}=\text{N}$  (azomethine) groups, respectively [22, 32]. The other bands that appeared at the region (149 and 140 ppm) correspond to the carbons that attached with  $=\text{C}-\text{N}$  and  $=\text{C}-\text{C}$  groups, respectively [22]. The bands in the range at 100.83-130.33 ppm were attributed to aromatic ring groups [33]. In addition, the band at (55.70 ppm) was assigned to two methyl carbons [34], as shown in (figure 3).

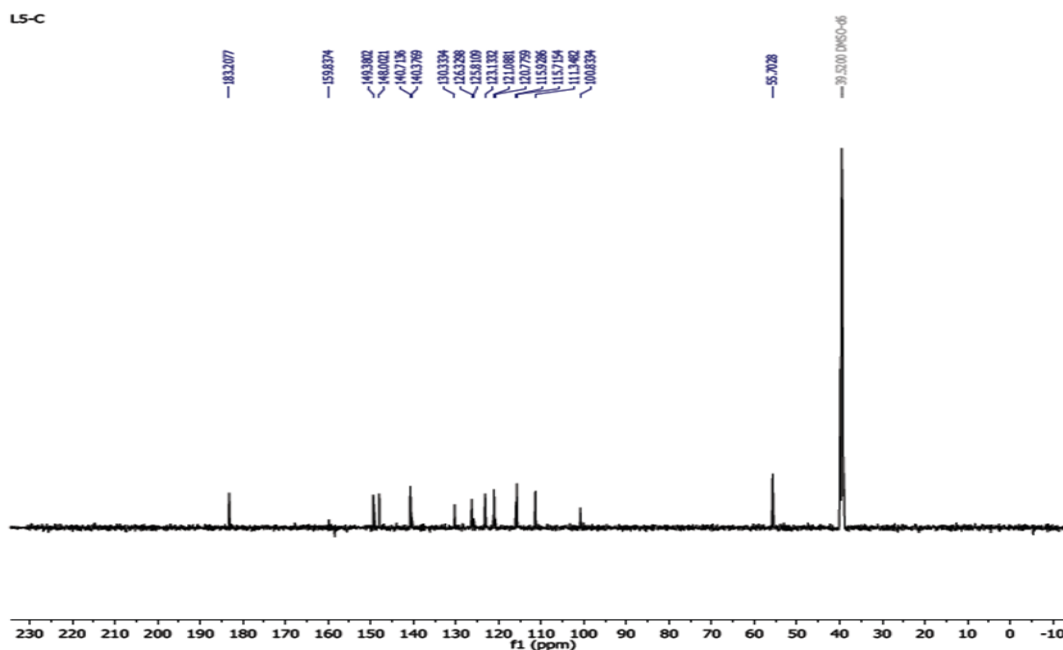
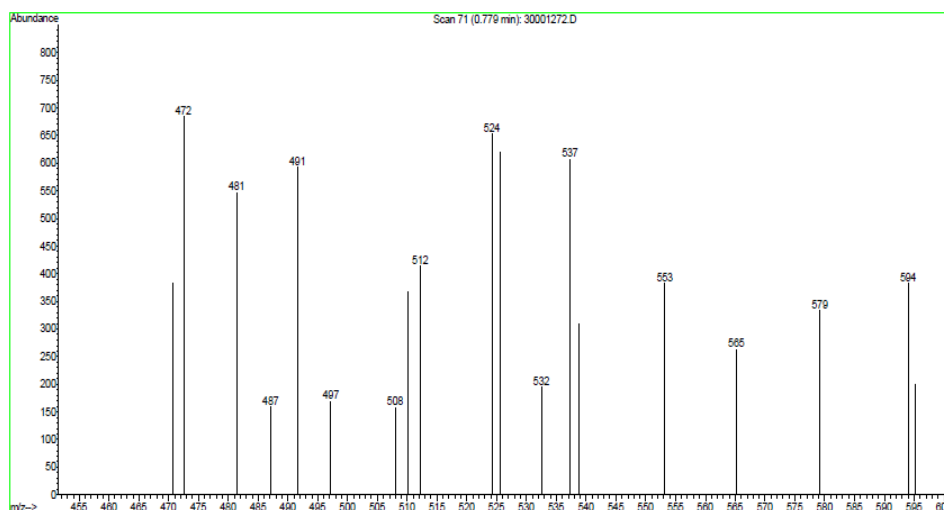


Figure 3.  $^{13}\text{C}$ -NMR spectrum of  $\text{H}_2\text{Ldfm}$  ligand.

### 3.6. Mass Spectrum of $H_2Ldfm$ Ligand

The mass spectrum fragmentations of  $H_2Ldfm$  ligand is shown in (figure 4). The peak that appeared at  $m/e+ = 594$  due to the ligand  $[C_{33}H_{42}N_2O_8]$  molecular weight. The peaks at  $m/e+ = 579, 564, 524, 491$  and  $472$  corresponded to the fragments  $C_{33}H_{42}N_2O_7, C_{33}H_{44}N_2O_6, C_{32}H_{48}N_2O_4, C_{32}H_{46}N_2O_2$  and  $C_{31}H_{40}N_2O_2$ , respectively. This proves the structure of Cur-leucine ligand ( $H_2Ldfm$ ).



**Figure 4.** Mass spectrum of  $H_2Ldfm$  ligand.

### 3.7. Thermal Analysis

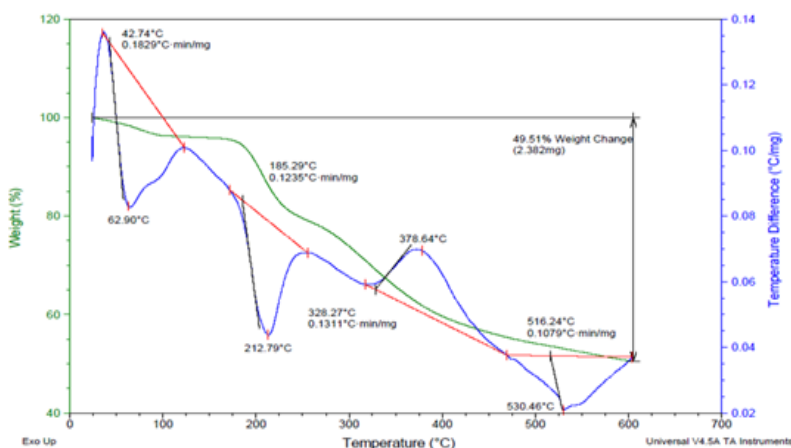
TGA is used to investigate the thermal degradation of inorganic compounds [26]. The TGA and DSC analysis for all the prepared complexes are studied where the heating rates are suitably controlled at 10 deg/min under  $N_2$  gas flow and weight loss is measured from ambient temperature to 600 °C. Figures (5-8) showed the TGA& DSC curves and the thermal degradation were conducted to (Mn (II), Co(II), Ni(II) and Cu(II)) complexes. TGA curve of the  $[Mn(Ldfm)(phen)]$  showed four decomposition peaks, the first peak observed at 42 to 110 °C, with accompanying by a mass loss of 3% (calc.2.99) to elimination of ( $-OH$  and  $H_2$ ) molecules. The second peak detected at 185 to 250 °C, with accompanying by a mass loss 22% (calc.19.99) due to the elimination of ( $CH_3OH, CO_2$  and  $CH_4$ ) molecules. Whilst the third peak observed at 328-468 °C with elimination of 21% (calc.20.95) corresponding to the decomposition of ( $C_{12}H_8N_2$ ) molecule, and the forth peak located at 516-600 °C, with accompanying by a mass loss of 6% (calc 5.96) due to the decomposition of ( $C_2H_2$  and  $H_2$ ) molecules. The DSC curve showed a peak at 378.64 °C, which represented its melting point. Moreover, the TGA curve of  $[Co(Ldfm)(phen)]$  complex displayed four decomposition peaks, the first peak located at 216 to 274 °C, with accompanying by a mass loss of 16% (calc.16) related to loss of ( $CO$  and  $CH_4$ ) molecules. The second peak observed at 302 to 348 °C, with accompanying by a mass loss of 10% (calc.10) corresponded to elimination of ( $CO_2, CH_3OH$  and  $H_2$ ) molecules. Whilst the third peak was detected at 399-423 °C, and matched a mass loss of 8.5% (calc.8.4) that compatible with loss of ( $CH_3COOCH_3$ ) molecule and the forth peak was located at 524-540 °C, with accompanying of a mass loss of 4.5% (calc. 4.4) that compatible with the loss of ( $CO$  and  $CH_4$ ) molecules.

The TGA curve of the  $[Ni(Ldfm)(phen)]$  showed two peaks. The first peak detected at 68 to 127 °C, with accompanying of a mass loss of 6.8 % (calc. 6.8) which related to mass loss of ( $OH$  and  $H_2$ ) molecules. The second peak detected at 185 to 250 °C, with accompanying of a mass loss of 53% (calc. 52.99) which related to decomposition of ( $phen, CO, CO_2, CH_3COOCH_3, C_2H_2$  and  $CH_4$ ) molecules. While the DSC curve exhibited a peak in 306.70°C which represented its melting point. The TGA curve of the  $[Cu(Ldfm)(phen)]$  showed only one peak at 221 to 240 °C, with accompanying of a mass loss of

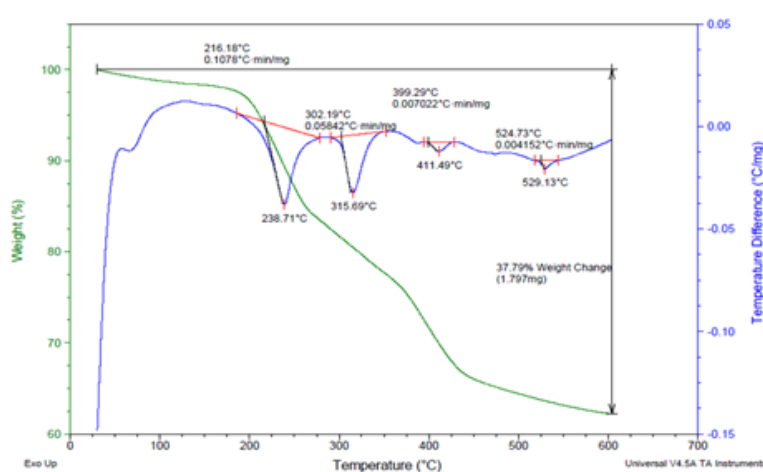
47% (calc. 47) to an approximate mass loss of (phen,CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>) molecules. The DSC curve displayed a peak in 221.68°C which represented melting point.

**Table 4.** Thermal analysis (TGA) abridgment data of Mn(II) , Co(II), Ni(II) and Cu(II)) complexes.

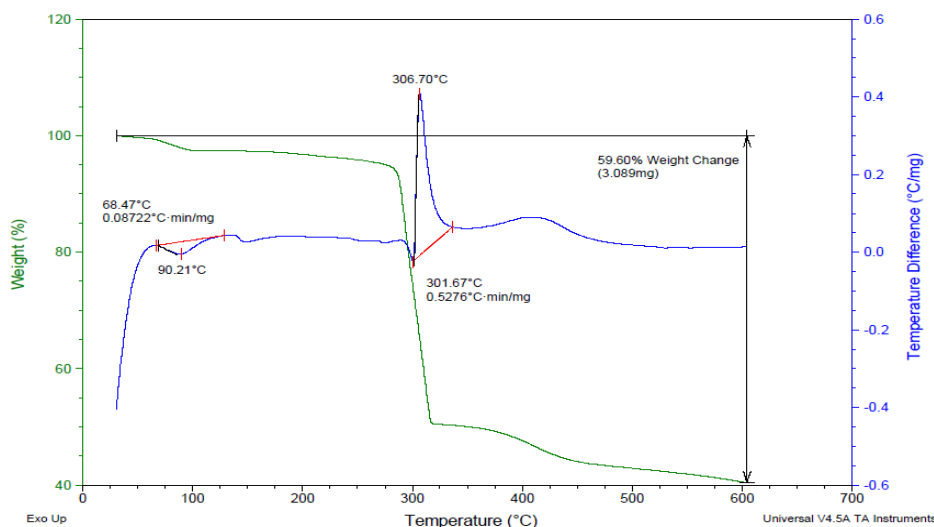
Compounds	Stage	T <sub>max</sub> (°C)	(% )Estimated (calculated)		Assignment Loss
			Mass loss	Total mass loss	
[Mn(Ldfm)(Phen)]	I	62.90	3(2.99)	49.51	OH,3H <sub>2</sub>
	II	212.79	22(19.99)	(49.89)	2CH <sub>3</sub> OH,2CO <sub>2</sub> ,4CH <sub>4</sub>
	II	378.64	21(20.95)		Leaving (C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )
	IV	530.46	6(5.96)		2C <sub>2</sub> H <sub>2</sub> , H <sub>2</sub>
[Co(Ldfm)(Phen)]	I	238.71	16(16)	37.79	3CO,3CH <sub>4</sub>
	II	315.69	10(10)	(38.89)	CO <sub>2</sub> ,CH <sub>3</sub> OH, 3H <sub>2</sub>
	III	411.49	8.5(8.4)		CH <sub>3</sub> COOCH <sub>3</sub>
	IV	529.13	4.5(4.4)		CO,CH <sub>4</sub>
[Ni(Ldfm)(Phen)]	I	90.21	6.8(6.8)	59.60	3OH,4H <sub>2</sub>
	II	301.67	53(52.99)	(59.79)	Phen,CO,CO <sub>2</sub> , CH <sub>3</sub> COOCH <sub>3</sub> ,2C <sub>2</sub> H <sub>2</sub> ,CH <sub>4</sub>
[Cu(Ldfm)(Phen)]	I	221.69	47 (47)	47.92	Phen,5CH <sub>4</sub> ,5C <sub>2</sub> H <sub>2</sub>



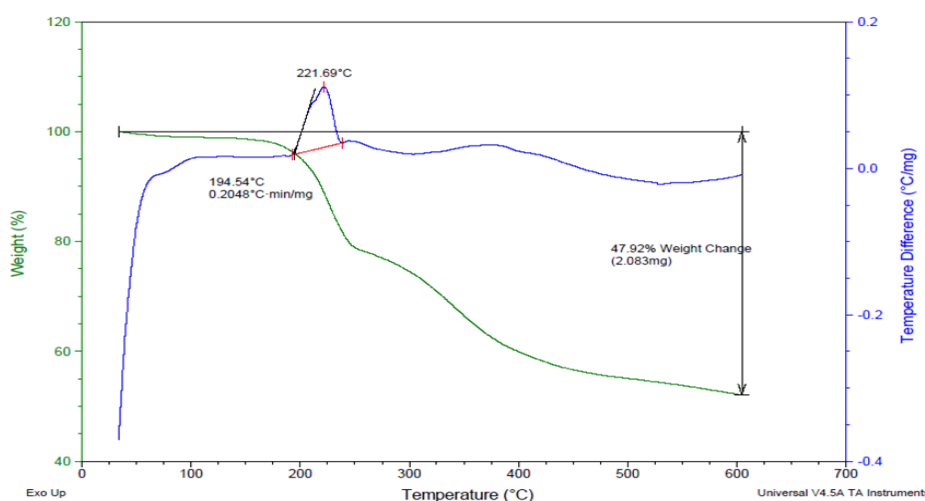
**Figure 5.** TGA -DSC curves of [Mn(Ldfm)(Phen)].



**Figure 6.** TGA -DSC curves of [Co(Ldfm)(Phen)].



**Figure 7.** TGA- DSC curves of [Ni(Ldfm)(Phen)].



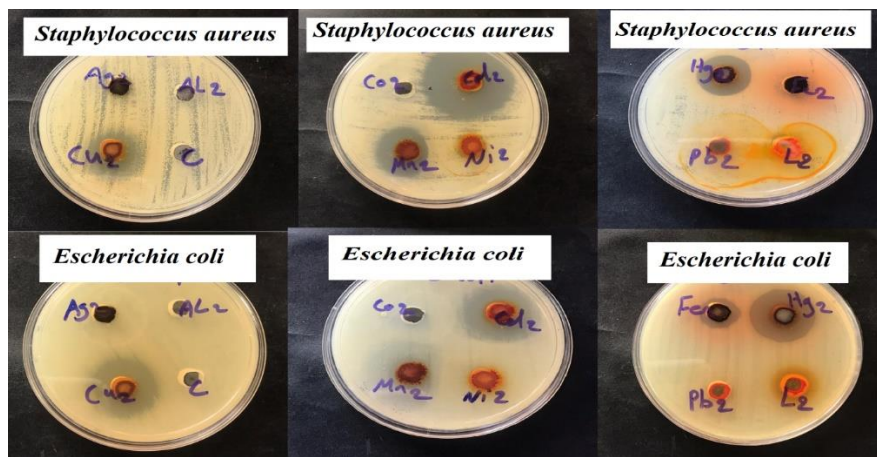
**Figure 8.** TGA -DSC curves of [Cu(Ldfm)(Phen)].

### 3.8. Antibacterial activities

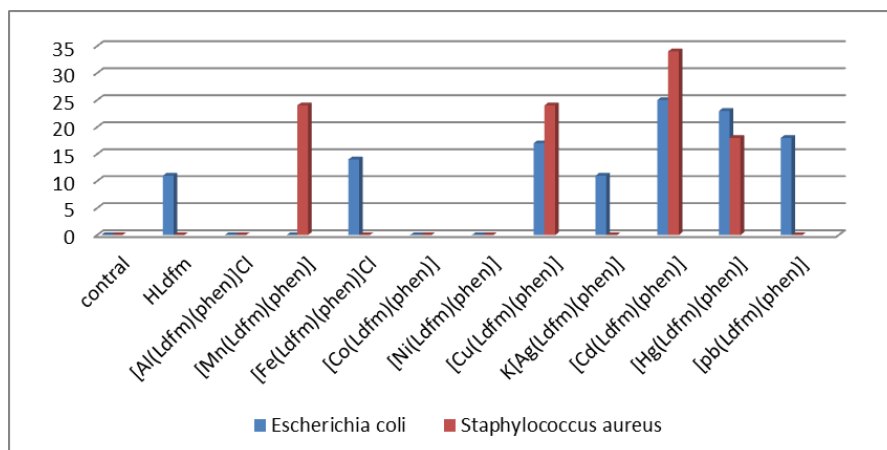
The prepared compounds were screened against the growth of two types of bacteria *Staphylococcus aureus* and *Escherichia Coli*. The sensitivity of the prepared compounds was measured by using the propagation method and incubated at a temperature of 37 °C for 24 hours. It was noted that most compounds have the ability to inhibit the two type of bacteria by using the disk diffusion method [35].

It is known, that anion ligands were reducing the polarity of the central atom that carries a positive charge because they were participating by partial charges with metal in the coordination process. This characteristic can be taken as advantage by entering the compounds of the fatty layers of the membrane cell and affecting on the minerals that present in the structure of enzymes of microorganisms [36,37]. Furthermore, it can increase the biological activity of the compounds like solubility, conductivity, and bond distance between the central atom and the ligand. It was expected that the ligand and its complexes are involving in the formation of a H- bonding through (azomethine CH=N) groups with active centers of the cell and so do hydroxyl groups that have almost the same effect [37]. The results which gained from the experimental section showed that the Cu(II), Cd (II) and Hg(II) complexes have higher inhibition (as shown in figure 9) for both types of bacteria than the other complexes. The (Fe(III), Ag(I),

Cd(II), and Hg(II)) complexes that had a higher degree of toxicity towards bacteria cells. Therefore, they had high inhibition the direction of bacteria. The antibacterial activity of all compounds is depicted on the figure 10.



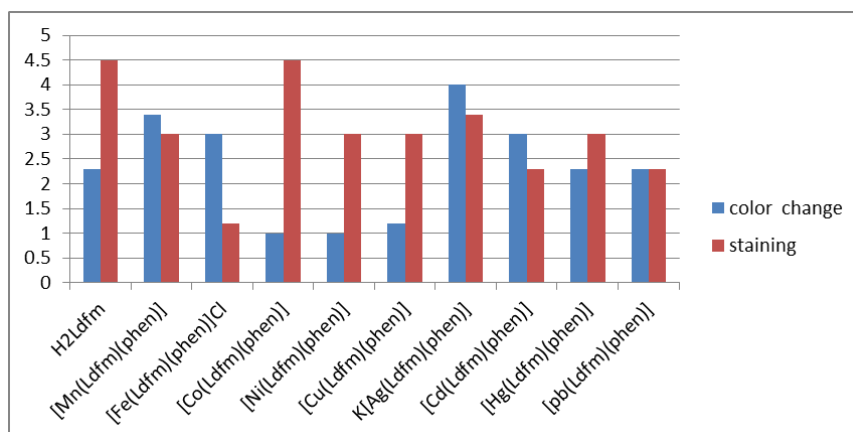
**Figure 9.** Photograph of zone of inhibition in mm for antibacterial activity of the prepared compounds.



**Figure 10.** Histogram of antibacterial activities of compounds.

### 3.9. Dyeing realization

Several studies have demonstrated the use of Schiff bases and complexes in the manufacture of dyes and inks [12,38]. In this study, the prepared compounds were used in the process of dyeing cotton fibers. Wash stabilization dyes of the ligand and its complexes were tested according to ISO 105-CO3 method via three steps: (1) Production of dyeing solution – the ligand and its complexes were dissolved in ethanoic aqueous solution and soaked in a dyeing bath with mordant (alum or sodium carbonate), then some drops of (NaOH) solution was added. (2) Dyeing process – the cotton fibers was delivered in the mixture which was prepared in the step 1, then heated to 40 °C for 20 minutes with continuous stirring until getting a homogenous dye. It was extracted from the mixture, then washed with cold water and left to dry. (3) Dye stability was tested by using a solution containing (5 g/L (soap liquid) through 38°C for 30 min. After dyeing of the cotton fibers, some compounds such as ligand and (Co(II), Ag(I), Hg(II) and Mn(II)) complexes gave good results as clarified in figure (11,12) and table 5.



**Figure 11.** Fastness properties of cotton fibers for compounds.

**Table 5.** Fastness properties of cotton fibers dyeing for compounds.

No.	Comp.	Color change	Staining
1	H <sub>2</sub> Ldfm	2.3	4.5
2	[Mn(Ldfm)(Phen)]	3.4	3
3	[Fe(Ldfm)(Phen)]Cl	3	0.5
4	[Co(Ldfm)(Phen)]	1	4.5
5	[Ni(Ldfm)(Phen)]	1	3
6	[Cu(Ldfm)(Phen)]	0.5	3
7	K[Ag(Ldfm)(Phen)]	4	3.4
8	[Cd(Ldfm)(Phen)]	3	2.3
9	[Hg(Ldfm)(Phen)]	2.3	3
10	[pb(Ldfm)(Phen)]	2.3	2.3

Wash fastness 5- very good , 4-4.5 good , 0.5-1 , 2-2.3 poor



**Figure 12.** Shapes of cotton fibers dyeing to Schiff base and complexes. 1-H<sub>2</sub>Ldfm, 2-[Mn(LdfmL)(Phen)], 3-[Co(Ldfm)(Phen)], 4-[Fe(Ldfm)(Phen)]Cl, 5- [Ni(Ldfm)(Phen)]6-[Cu(Ldfm)(Phen)],7-K[Ag(Ldfm)(Phen)],8- [Cd(Ldfm)(Phen)], 9- [Hg(Ldfm) (Phen)], 10-[Pb(Ldfm)(Phen)].

#### 4. Conclusions

A Schiff base ligand was prepared by using three different ways (refluxing, fusion, and grading) and its metal complexes with another ligand were prepared and identified. The ligands coordinated with metals ions through the nitrogen atom of azomethine group and oxygen of carboxylic atoms. All complexes possessed an octahedral geometric shapes. Applications of this Schiff base and its complexes have been carried out, including biological activity against two types of bacteria (*Staphylococcus aureus* and *Escherichia*) which showed greater effectiveness of Fe (III), Cd (II) and Hg(II) complexes. All compounds were tested as dyes on the cotton fibers and gave distinct results, especially the Schiff base and (Ag(I), Fe(III), and Cd(II)) complexes.

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