



Metal Complexes Derived from Mixed Azo-linked Schiff-base Ligand with Dithiocarbamate Derivative: Formation, Spectral Characterization and Biological Study

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ABSTRACT

The study includes preparation and characterisation of mixed azo-linked Schiff-base and DTCs ligands and their complexes. The starting material was isolated from the mixing of naphthyl amine diazonium salt with 2-aminophenol in a 1:1 mole ratio in water. In this work, the formation of azo-linked Schiff-base and DTCs ligands are reported. Ligand of the azo-linked Schiff-base was achieved by the reaction of starting material with 4-(dimethylamino)benzaldehyde (HL¹). The DTCs was isolated by the reaction of (C₆H₅)₂NH with carbon disulphide in potassium hydroxide (L²). The complexes were prepared by mixing the azo-linked Schiff-base ligand and DTCs ligand with the metal salts; Co^{II}, Ni^{II}, Zn^{II} and Cd^{II} in a 1:1:1 mole ratio. Ligands and complexes were characterised by analytical and spectroscopic analyses including; microanalysis, chloride content, thermal analysis, magnetic susceptibility for complexes, conductance, FTIR, UV-Vis and ¹H-NMR spectroscopy. Physico-chemical techniques indicated complexes demonstrated four and six coordinate structures in the solid and solution state. Biological activity of the ligands and their metal complexes were screened for their antimicrobial activity against four bacterial species (*Escherichia coli* and *Enterobacter Gram - ve*, (*Bacillus subtilis* and *Staphylococcus aureus Garam + ve*).

Keywords: Mixed ligands, Metal complexes, Dithiocarbamates (DTCs), Biological activity, Thermal analysis.

INTRODUCTION

Azo compounds are an interesting materials that have shown a range of applications including; food technology, analytical chemistry, pharmaceutical application and dyeing or textile industry. Their role in coloring approach has been

widely investigated and a range of compounds are fabricated¹. The biological activity of azo-compounds allowed them to be used in the treatment of textile materials, also azo-compounds are well known for their medicinal importance and have shown a variety of applications as antitumor, antibacterial, antiseptics and antineoplastics². Variety of ligands



type Schiff-base and their metal complexes have been isolated, these compounds have very flexible and diverse structures, therefore their properties have been studied³. Dithiocarbamates (DTCs) are class of organic compounds that are capable to chelate to metal ions^{4,5}. DTCs compounds have a significant role in coordination chemistry. This may due to the metal ion stabilization ability in many oxidation states, and permitting the metal ion to implement its desirable structure⁶. DTCs have shown a significant biological activity including their role as antibacterial, antitumor and antifungal agents. They have other potential applications in materials science and supramolecular chemistry^{7, 8}. In our research, we report here the preparation of mixed azo-linked Schiff-base and DTCs ligands and their metal(II) dithiocarbamate complexes.

EXPERIMENTAL

All chemicals in this work are commercially available and used as received. Solvents were distilled using appropriate protocol before use.

Physical measurements

Elemental micro-analyses (carbon, hydrogen, nitrogen and sulphur) for ligand and its metal complexes were conducted on a Euro EA 3000. Electrothermal Stuart SMP40 apparatus was used to record melting points. FT-IR spectra were recorded as potassium bromide discs with a Shimadzu 8300s in the range 4000-400 cm^{-1} and as CsI discs in the range 400-200 cm^{-1} . UV-Vis spectra were obtained with 10-3 M solutions between 200-1100 nm in dimethylsulfoxide (DMSO) spectroscopic grade solvent at 25 °C using a Perkin-Elmer spectrophotometer Lambda. TGA was carried out using a STA PT-1000 Linseis. NMR spectra (¹H-NMR) were acquired in DMSO- d_6 and CDCl_3 using a Bruker-400 MHz and a Bruker-300 with tetramethylsilane (TMS). A Shimadzu (A.A) 680 G atomic absorption spectrophotometer was implemented to determine metal content in complexes. Conductivity measurements were performed using a Jenway 4071 digital conductivity meter with DMSO solutions at room temperature. Chloride was determined using potentiometer titration method on a (686-Titro processor-665 Dosimat-Metrohm Swiss). A magnetic susceptibility balance (Sherwood Scientific) was used to determine magnetic moments of complexes.

Synthesis Preparation of the precursor

The compound was prepared according to the literature^{9,10} 1-naphthyl amine (1 g, 6.98 mmol) was dissolved in H_2O (10 ml) and hydrochloric acid conc. (2.14 ml, 60.98 mmol) mixture with stirring, a clear solution was obtained. Temperature of (0–5) °C have been kept, then aqueous solution of sodium nitrite (0.48g, 6.98 mmol) dissolved in (5 ml) water, was dropwise slowly added, keeping the temperature below 5 °C, followed by mixture stirring for 1 h, using ice bath, then little amount of urea was added, the pH was adjusted to 6–7 using sodium acetate [solution(1)]. $\text{H}_2\text{NC}_6\text{H}_4\text{OH}$ (0.762 g, 6.98 mmol) was dissolved in 12 ml KOH 10 mmol aqueous solution, cooled by ice bath to (0–5) °C solution(2). Gradually the last solution was mixed with cooling with (solution1), the mixture resulted was stir red at (0–5) °C continually for 2h, the precipitate resulted was then filtered using acidification, cold H_2O used to wash several times after drying, a brown solid precipitate was obtained, Yield:1.35 g (73.7%), melting point 132°C.

Synthesis of free ligands

Preparation of [HL¹]

The compound was prepared according to the literature¹². A solution of the derivative[2-amino-6-(naphthalen-1-yl diazenyl)phenol] (1g, 3.798 mmol) in 25 ml ethanol was mixed with (0.566 g, 3.798 mmol) of $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CHO}$ dissolved in (10 ml) ethanol. After adding glacial acetic acid (3-5) drops, the mixture resulted was refluxed for 2h, filtered off, and after washing by ethanol and drying; it was obtained a light brown product. The product solid was recrystallized using EtOH. Yield:1.23 g, 82.5%, melting point(190-192 °C).

Preparation of [L²]

The compound was prepared according to the literature¹³. Ethanolic solution of KOH (1.32 g, 23.6 mmol, 4eq) was added to solution of diphenyl amine (1g, 5.90 mmol) dissolved in (10 mL) ethanol. The resulted mixture was stirred keeping the temperature at (0-5), dropwise with stirring it was added carbon disulphide solution(1.34 g, 17.7 mmol, 3eq) keeping the temperature at 0 °C for 2 hours. The solid DTCS yellow salt was obtained, Yield :1.48 g, 88.6%. Melting point (238- 240 °C).

Synthesis of complexes

A one pot approach reported in¹⁴ was used to prepare the mixed ligand metal complexes.

Preparation of [Coll(HL¹)(L²)(H₂O)₂]

To a mixture of HL1 (0.2 g, 0.506 mmol) dissolved in (10 ml) was added (0.0568 g, 1.0139 mmol) of potassium hydroxide dissolved in 10 ml ethanol. While, the solution was allowed to stirring, a mixture of Coll salt (0.120 g, 0.506 mmol) in 10 ml ethanol with (0.143 g, 0.506 mmol) of dithiocarbamate ligand (L²) was added to the above solution. The reaction mixture was kept stirring for two h, during which time a green product was filtered off. Washed with absolute ethanol and recrystallized from ethanol to give the pure product. Yield: 0.187 g, 50.33%, (Dec. over 320).

Preparation of Ni(II), Zn(II) and Cd(II) complexes

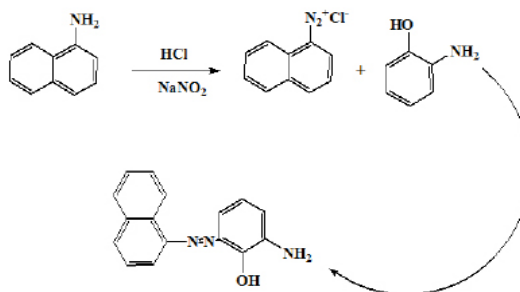
An analogous method to that reported for the synthesis of Coll complex was implemented to prepare Ni(II), Zn(II), and Cd(II) mixed ligands complexes. **Table 1** displays the physical properties of the complexes and their reactant amount.

RESULTS AND DISCUSSION

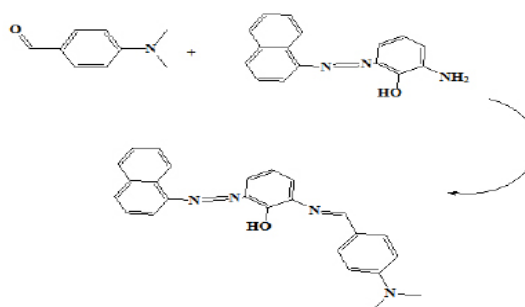
Synthesis

The precursor was obtained using a standard azo dye approach. The reaction of naphthyl amine diazonium salt with 2-amino-phenole in a 1:1 mole ratio in water solvent gave the required compound, see Scheme 1. Two sorts of ligands were prepared; (i) Azo-linked Schiff-base ligand, which isolated by reaction of the precursor with (CH₃)₂NC₆H₄CHO and (ii) DTCs ligand that obtained from the reaction of (C₆H₅)₂NH with carbon disulphide using KOH base (Schemes 2 and 3). The complexes were prepared by mixing the ligands with the metal salts in a 1:1:1 mole ratio (Scheme 4). A range of analytical and spectroscopic techniques were used to confirm the entity of compounds including; CHNS, FT-IR, UV-Vis, magnetic susceptibility and ¹H-NMR spectra. The infra-red spectrum of [HL¹], Fig. (1), exhibited bands at 3423 and 2978 cm⁻¹ attributed to the OH phenolic group^{15,16} and ν(C-H) aliphatic stretching, respectively. Bands related to ν(C=N) imine and ν(C-N) are observed at 1630 and 1257cm⁻¹, respectively. The formation of Schiff-base ligand can be indicated by the absence of amine

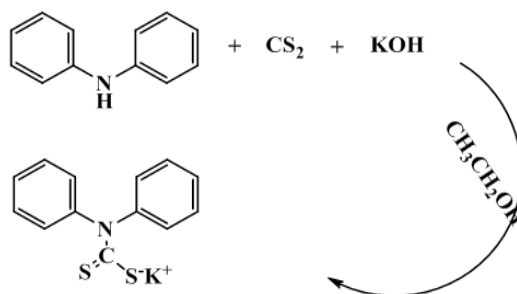
(NH₂) and aldehydic CHO bands and appearance of the new imine (C=N) band in the ligand spectrum¹⁷⁻¹⁹.



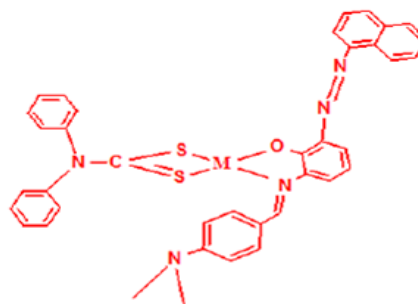
Scheme 1. Preparation path for Precursor



Scheme 2. Preparation route for ligand [HL¹]



Scheme 3. Preparation route of ligand [L²]

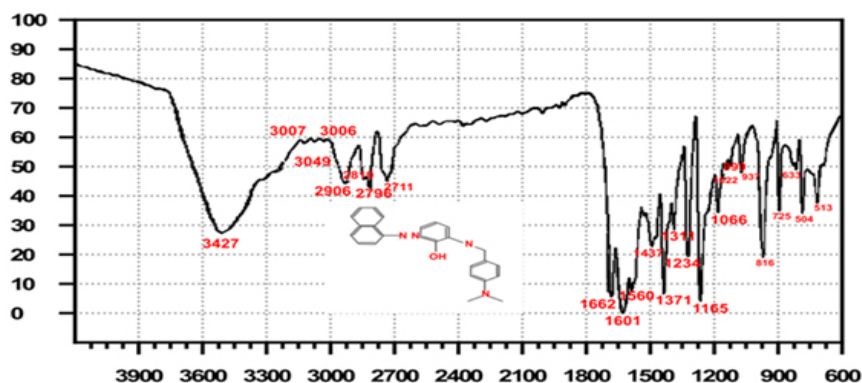


Where M = Co^{II}, Ni^{II}, Zn^{II} and Cd^{II}

Scheme 4. Structure of mixed ligand complexes of mixed ligand complexes

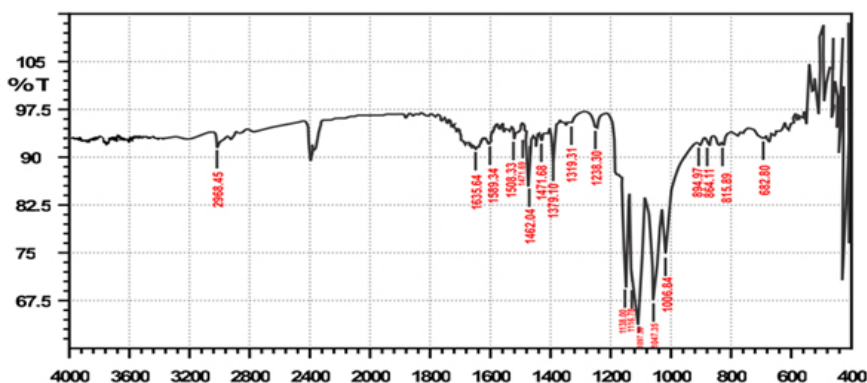
Table1: Melting points, yields, metal salts quantities and colours of ligands and their complexes

Compound	Dec. (°C)	Weight of metal salt(g)	Weight of complex(g)	Yield (%)	Colour
[Co(L ¹)(L ²)(H ₂ O) ₂]	Over 320*	0.123	0.188	51	Light green
[Ni(L ¹)(L ²)]	Over 320*	0.121	0.172	49	Green
[Zn(L ¹)(L ²)(H ₂ O) ₂]	Over 320*	0.07	0.148	40	Dark brown
K ₂ [Cd(L ¹)(L ₂)Cl ₂]	Over 320*	0.103	0.185	41	light yellow

Fig. 1. FT-IR spectrum of ligand [HL¹]

Band related to stretching $\nu(\text{N}=\text{N})$ azo group are detected at 1460 cm^{-1} ^{16,20}. The FT-IR spectrum of [L²] is displayed in Fig.(2). The $\nu(\text{C}-\text{N})$ of (N-CS₂) moiety shows a band at 1471 cm^{-1} ²¹. The spectrum indicates a couple of new bands at (894) and (1047) cm^{-1} , which designated to $\nu_s(\text{CS}_2)$ and $\nu_{as}(\text{CS}_2)$ respectively²². The characteristic bands are summarised in (Table 3). The ¹H-NMR spectrum of [HL¹], Fig.(7), displays peak related to the azomethine group at $\delta=10.1\text{ ppm}$ (H,s,N=C-H)²³. Chemical shift at $\delta=10.809\text{ ppm}$ (OH, S, H) correlated to the

phenolic proton. The spectrum indicated that the non-equivalent two CH₃ groups appeared at $\delta=2.2$ and $3.3\text{--}3.4\text{ ppm}$ (2CH₃, S,6H). That may probably resulted from the position alternation of the two CH₃ groups in the proposed structure of the molecule. An averaged symmetrical spectrum may resulted from rapid rotation process. On the other hand, two non-equivalent conformations may resulted from the slow rotation. The ¹H-NMR spectrum of [L²] is depicted in (Fig.8). The spectrum shows peaks at $\delta=5.561\text{ ppm}$ (2H, m) (C1, 1', 5, 5'-H), $\delta=6.789\text{--}$

Fig. 2. FT-IR spectrum of ligand [L²]

6.805 ppm (2H, m) (C3, 3'-H) and $\nu = 7.685-7.694$ ppm (2H, m) (C2, 2', 4, 4'-H) attributed to the aromatic ring protons. The complexes are air stable solid. The entity of new complexes was confirmed by elemental analysis, FT-IR, electronic spectra

and magnetic susceptibility. The analytical data (Table 2) support the proposed formulae. The molar conductance of the complexes in DMSO solvents is indicative of non-electrolyte and 1:2 electrolyte behaviour^{24,25}.

Table 2: Colours, Yields, (C, H, N, S) analysis and chloride content values for ligands and complexes

Compound	M.wt	Yield %	colour	Found (Calc.) %					
				M%	C	H	N	S	Cl
HL ¹	394.47	82.5	Light brown	-	75.74 (76.12)	5.38 (5.62)	14.04 (14.2)		
L ²	283.46	88.6	yellow	-	53.38 (55.08)	3.38 (3.56)	4.65 (4.94)	22.34 (22.63)	
[Co(L ¹)(L ²) (H ₂ O) ₂]	732.78	51	Light green	7.12 (8.04.)	-	-	-	-	-
[Ni(L ¹)(L ²)]	696.51	49	Light green	7.55 (8.42.)	-	-	-	-	-
[Zn(L ¹)(L ²) (H ₂ O) ₂]	739.23	40	Dark brown	8 (8.84.)	-	-	-	-	-
K ₂ [Cd (L ¹)(L ²)Cl ₂]	898.33	41	Light yellow	12.01 (12.51)	50 (50.76)	3.11 (3.45)	6.89 (7.79)	7.44 (7.21)	7 (7.89)

FTIR and NMR spectra for complexes

The FTIR spectra of complexes show bands at rang (1606-1639) cm⁻¹ were assigned to of imine $\nu(C=N)$ group, with alower frequency shift. This may be related to the engagement of the nitrogen atom of the iminic moiety in the coordination reaction²⁶⁻²⁸. The shift also may explained by delocalisation process of the d-10 (metal electron density) to the ligand (ν system)^{29,30}. Spectra for complexes appeared bands at rang (1500-1510) cm⁻¹ that attributed to (N-CS₂)²¹. This confirms that the $\nu(N-C)$ double bond character may increase as a consequence of the moving of electrons to the metal centre as a result of coordination to the DTCs²². Band located in the range (1454-1469) cm⁻¹ is assigned to $\nu(N=N)$ azo. Finally, the spectra showed new bands in the range (609-673) and (416-489) cm⁻¹ that attributed to $\nu(M-N)$ and $\nu(M-O)$, respectively. The appearance of these bands supported the involvement of the nitrogen of imin and oxygen phenolic atoms in the coordination of the ligand to the metal centre. These results are in accordance with that reported in literature^{31,32}. Bands detected at (1043-1053) and (948-997) cm⁻¹ are due to ν as(CS₂)

asymmetric and ν s(CS₂) symmetric mode of the DTCsmoiety, respectively. This is in agreement with an anisobidentate chelation mode of the ligand to the metal ion²². The anisobidentate mode of chelation of the ligand, may confirmed by the bands observed in the range (302-393) cm⁻¹ which may attributed to $\nu(M-S)$ bond³³. The spectra of Co, see Fig. (3), and Zn complexes exhibited a broad band that assigned to $\nu(OH)$ of the hydrated water molecule¹⁶. Table (3) includes the prominent FTIR bands of complexes. The ¹H-NMR spectrum of K₂ [Cd(L¹)(L²)Cl₂], (Fig. 9), displays peak at $\delta=10.9$ ppm related to the proton of the iminic moiety (1H, s, N=C-H)²³. The chemical shift at $\delta= 2.2$ ppm that equivalent to six protons assigned to the methyl groups (2CH₃,s, 6H).

UV-Vis Spectral data and magnetic susceptibility of the complexes

The electronic spectra of the complexes exhibited peaks in the range 262-305 nm attributed to $\pi \rightarrow \pi^*$ transition of the aromatic rings³⁴. The spectra of complexes revealed peaks around 349 nm related to ($n \rightarrow \pi^*$) transition of azo moiety. The blue shift recorded may attribute to the energy

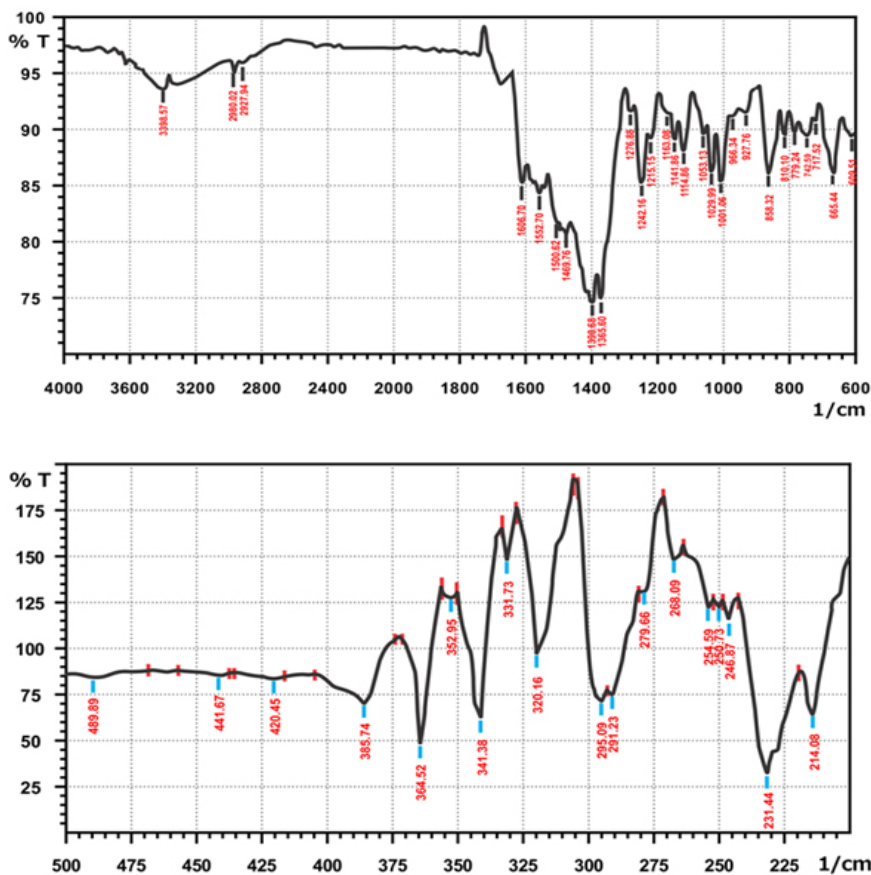


Fig. 3. FT-IR spectrum of [Co(L¹)(L²)(H₂O)₂] complex

Table 3: FT-IR spectral data for ligands and complexes

Compound	$\nu(\text{C-H})_{\text{ar}}$	$\nu(\text{C-H})_{\text{ali}}$	$\nu(\text{C=N})_{\text{im}}$	$\nu(\text{N-CS2})_{\text{di}}$	$\nu(\text{N=N})_{\text{azo}}$	$\nu(\text{CS2})_{\text{as}}$ $\nu(\text{CS2})_{\text{s}}$	$\nu(\text{M-N})$ $\nu(\text{M-O})$	$\nu(\text{M-S})$	$\nu(\text{M-Cl})$
HL¹	3097, 3049, 3008	2906	1642	-	1437	-	-	-	-
L²	2968	-	-	1471	-	1,047, 894	-	-	-
[Co(L¹)(L²)(H₂O)₂]	2980	2927	1606	1500	1469	1,053, 966	665,609 489,420	385, 320	-
[Ni(L¹)(L²)]	3035	29, 832, 891	1639	1510	1462	1,051, 993	673,619 464,420	387, 302	-
[Zn(L¹)(L²)(H₂O)₂]	2981	2895	1622	1506	1454	1,043, 997	671 489, 457	385, 302	-
K₂[Cd(L¹)(L²)Cl₂]	3035	29, 832, 889	1624	1504	1458	1,050, 948	621 457, 416	393, 304	298, 268

change of the conjugated chromophore ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) electronic transitions, due to the chelation between metal ions and azo ligand³⁵. The spectrum of Co(II) complex, see (Fig. 6), reveals peaks at 886 and 528 nm assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively which may confirm a distorted octahedral structure for Co(II) complex³⁶⁻³⁹, this result was confirmed by the magnetic moment value μ_{eff} of 5.07 B.M for the Co(II)-complex⁴⁰. The Ni(II) complex shows a peak at 617 nm attributed to ${}^1A_{1g}(f) \rightarrow {}^1A_{2g}(F)$, revealing a distorted square planar arrangement about Ni atom. This result was confirmed by the diamagnetic moment behavior of the Ni(II)-complex⁴⁰. The spectra of Zn(II) and Cd(II) compounds revealed peaks attributed to ligand field $\pi \rightarrow \pi^*$ and $M \rightarrow L$ charge transfer⁴¹. These data along with other analytical results indicated that the Zn(II) and Cd(II) complexes adopt octahedral arrangement about metal centre⁴². The six-coordinate number for the Zn(II) and Cd(II) compounds may be due to sort of ligands that surrounding metal centre and their steric and

electronic interaction that occurred upon complex formation⁴³. The electronic data of the complexes are tabulated in (Table 5).

Thermal analysis

The thermogram chart indicated the stability of $[\text{Co}(\text{L}^2)(\text{L}^4)(\text{H}_2\text{O})_2]$ up to 97 °C, see (Fig. 10). peak detected at 297 °C may due to the loss of $(\text{HCN}, 2\text{H}_2\text{O}, \text{NO}$ and $\text{CS}_2)$ moieties, (obs.=4.86 mg, 23.15 %; Calc. = 4.85 mg. 23.1%). While second step at (594) °C may refers to the loss of $(\text{C}_6\text{H}_6$ and $\text{N}_2)$ fragment, (det.=3.06 mg, 14.56%; Calc.= 3.07 mg.14.46%). The final residue from the compound which may assigned to the $(\text{Co}, \text{CH}_3\text{NCH}_3, 2\text{C}_6\text{H}_4, \text{C}_6\text{H}_3,$ and $\text{C}_{10}\text{H}_7)$, Calc. =13.1 mg. 62.4%). The dithiocarbamates analysis thermogram showed peaks at 97, 310, 320, 398 and 594 may assigned to an exo and endo thermal decomposition process. The peak at 320 (exothermic) may due to combustion process of the organic ligand part(in an argon atmosphere). While metal-ligand bond breaking may signified by

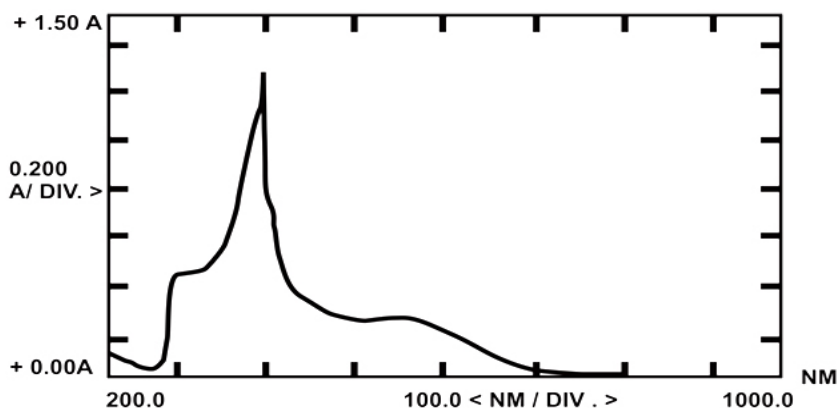


Fig. 4. Electronic spectrum of $[\text{HL}^1]$

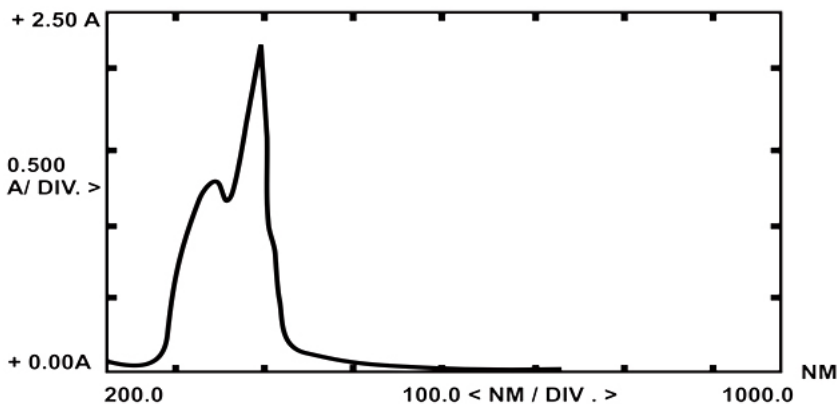


Fig. 5. Electronic spectrum of $[\text{L}^2]$

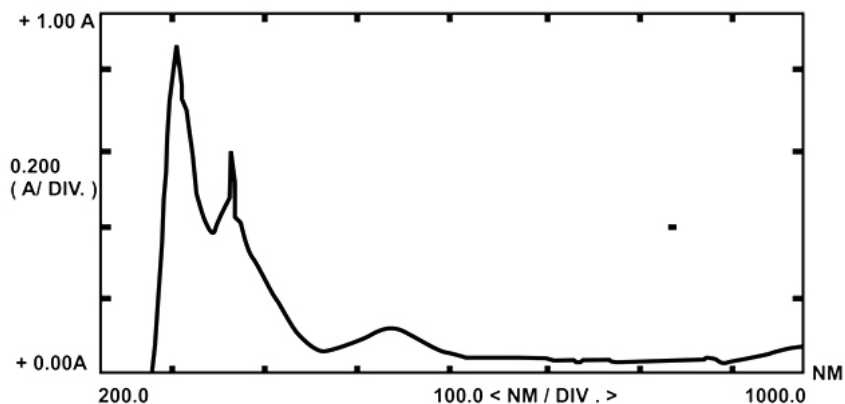
Fig. 6. Electronic spectrum of $[\text{Co}(\text{L}^1\text{L}^2)(\text{H}_2\text{O})_2]$

Table 4: Electronic spectral data of complexes in DMSO solutions

Compound	Wave number λ nm	Wave number (cm^{-1})	ϵ max molar $^{-1}$ cm^{-1}	Assignment	Suggested structure
$[\text{Co}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	287	34843	828	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	Distorted octahedral
	348	28735	559	C.T	
	528	19047	107	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	
	886	11286	16	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$	
$[\text{Ni}(\text{L}^1)(\text{L}^2)]$	295	33898	351	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	Square planar
	348	28735	551	C.T	
	617	16207	26	${}^1\text{A}_{1g}(\text{F}) \rightarrow {}^1\text{A}_{2g}(\text{F})$	
$[\text{Zn}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	262	38167	33	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	Distorted octahedral
	349	28653	124	C.T	
$\text{K}_2[\text{Cd}(\text{L}^1)(\text{L}^2)\text{Cl}_2]$	305	32786	811	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	Distorted octahedral
	346	28901	1113	C.T	

Table 5: Biological activity of compounds

Compounds	Gram negative		Gram positive	
	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i> (G+)	<i>Escherichia coli</i> (G-)	<i>Enterobacter</i> (G-)
Control	—	—	—	—
HL ¹	—	—	—	—
L ²	22	12	—	—
$[\text{Co}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	12	—	—	—
$[\text{Ni}(\text{L}^1)(\text{L}^2)]$	—	—	—	—
$[\text{Zn}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	13	—	—	—
$\text{K}_2[\text{Cd}(\text{L}^1)(\text{L}^2)\text{Cl}_2]$	14	—	—	—

endothermic peaks at 97, 310, 398 and 594 °C^{44,45}.

Biological activity

The synthesized ligands and its complexes were screened for their biological activity against some

bacterial strains (*Escherichia coli* and *Enterobacter* (G-) *Bacillus subtilis* and *Staphylococcus aureus* (G+)). The involvement of dimethylsulphoxide in the bacterial test was confirmed by individual tests that

conducted with the DMSO alone that indicated no activity towards any bacterial species⁴⁶. The measured size of inhibition zones against growth of different microorganisms are summarised in that displays the effect of the prepared compounds on bacterial species. From collected data, it is clear that, compared with the free ligands, the ligands (HL¹ and L²) showed no antimicrobial activity against *Escherichia coli* and *Enterobacter*. Hence, formation of complexes enhances the antimicrobial activity.

Such increased activity of complexes may be related to the chelation theory³³. Therefore, the chelation decreases the polarity of the metal atom that resulted in the partial sharing of its positive charge with donor group and possible π -electron delocalisation over the whole ring. Zinc and cadmium complexes showed almost the higher antibacterial activity, compared with other compounds. This due to their molecular weight and their electronic configuration (d¹⁰ system), compared with other metal complexes (Figures.11-14)^{47, 48}.

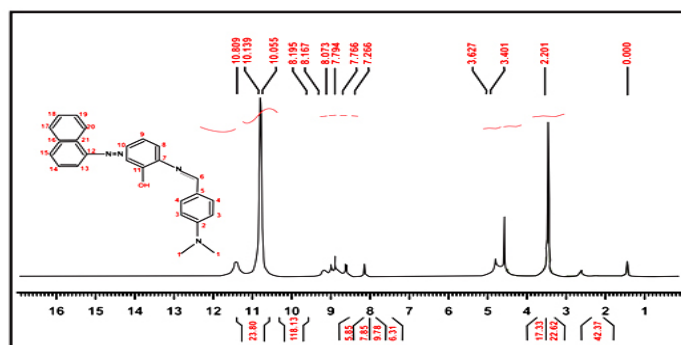


Fig. 7. ¹H-NMR spectrum of ligand HL¹ in CDCl₃

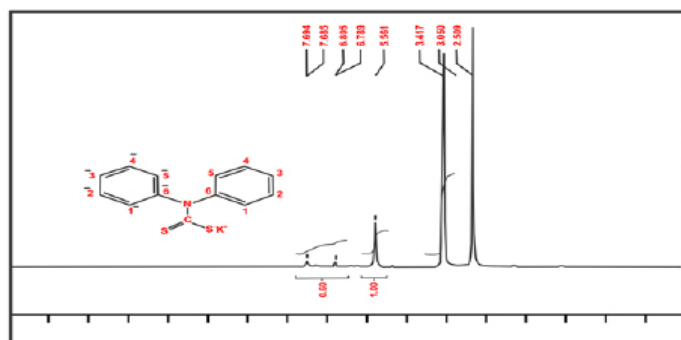


Fig. 8. ¹H-NMR spectrum of ligand L² in DMSO-d₆

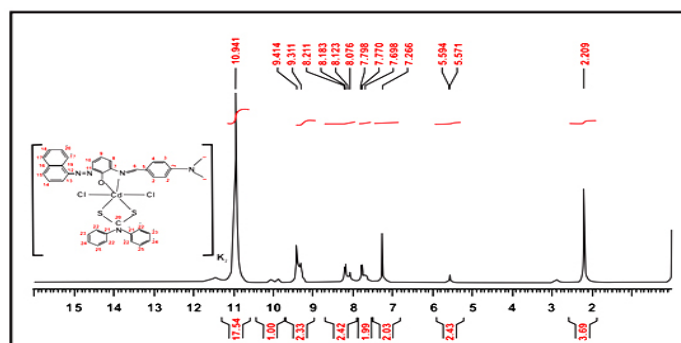


Fig. 9. ¹H-NMR spectrum of K₂[Cd(L¹)(L²)Cl₂] in CDCl₃

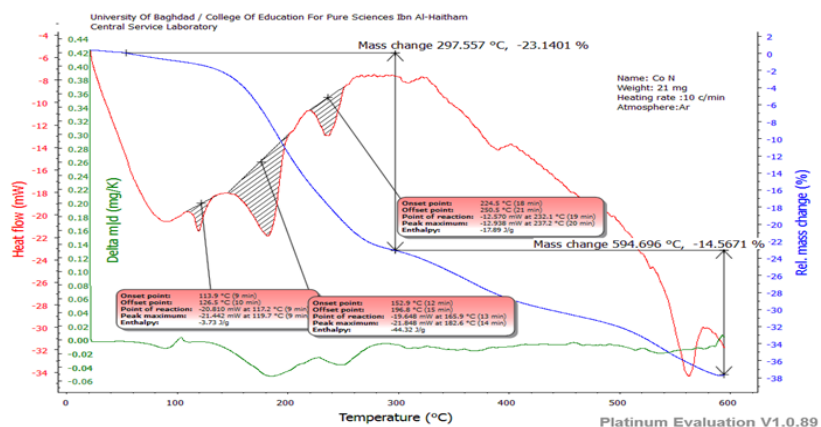


Fig. 10. (TGA/ DTA and DSC) thermogram of $[\text{Co}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$ in an argon atmosphere

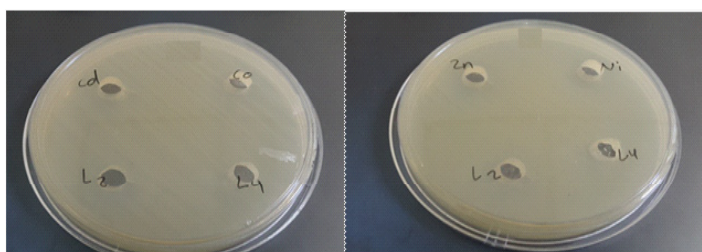


Fig. 11. The effect of L^1 L^2 and its complexes on *Escherichia coli*

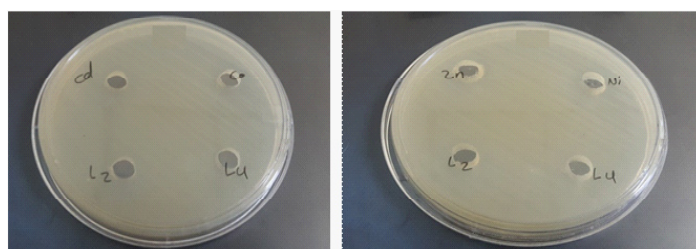


Fig. 12. The effect of L^1 L^2 and its complexes on *Enterobacter*

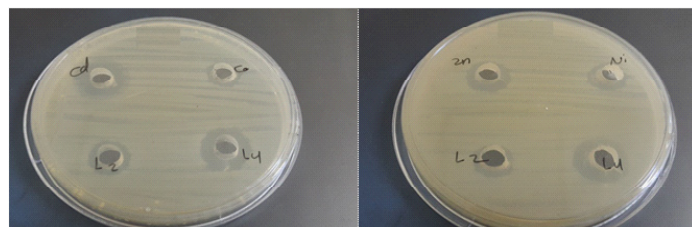


Fig. 13. The effect of L^1 L^2 and its complexes on *Bacillus subtilis*

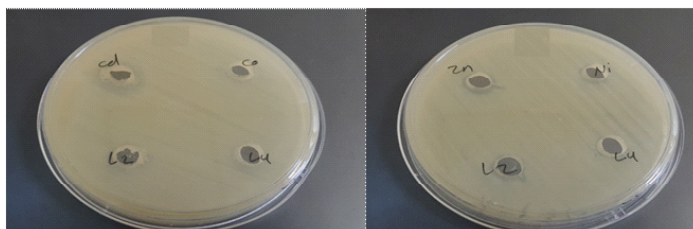


Fig. 14. The effect of L^1 L^2 and its complexes on *Staphylococcus aureus*

CONCLUSION

The preparation and characterisation of mixed ligands and their complexes are described. This was based on the preparation of two sorts of ligands; (i) the azo-linked Schiff-base ligand that obtained by reaction of the precursor with $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CHO}$ and (ii) the DTCs ligand that fabricated by reaction of

$(\text{C}_6\text{H}_5)_2\text{NH}$ with carbon disulphide. The mixed ligand complexes were achieved by adding the HL¹ and L² with the appropriate metal salt in a 1:1:1 mole ratio. Physico-chemical and spectroscopic methods were implemented to confirm mode of bonding and over all structure of the complexes. These results lead to the preparation of four and six coordinate complexes.

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