



## Synthesis, Characterization and Biological Study of Mixed Ligand Complexes Derived from Dithiocarbamate and Azo

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### Abstract

The formation, structural characterisation of mixed ligand complexes of  $\text{Co}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  metal ions with dithiocarbamate, azo and 1, 10-phenanthroline are reported. Ligands and complexes were characterised by analytical and spectroscopic analyses including; FTIR, electronic and  $^1\text{H}$ ,  $^{13}\text{C}$ -NMR spectroscopy, microanalysis, chloride content, thermal analysis, magnetic susceptibility and conductance. Physico-chemical techniques indicated complexes demonstrated six coordinate structures in the solid and solution state. Biological activity of the prepared ligands and their mixed metal complexes were screened for their antimicrobial activity against four bacterial species ((*Bacillus subtilis* and *Staphylococcus aureus* (G+)), *Escherichia coli* and *Enterobacter* (G-)). Biological data showed that complexes become potentially more active against these tested bacteria compared with the free ligands

**Keywords:** *Mixed ligand complexes; Structural characterization; Thermal analysis; Biological activity.*

### Introduction

Dithiocarbamates (DTCs) are a class of organic compounds that are capable to chelate to metal ions [1, 2]. Dithiocarbamates are essential materials that have been widely explored due to their applications in coordination chemistry [3], medicine and radiopharmaceutical chemistry [4, 5], sensing technology [6], materials science [7], and in the industry [8].

DTCs have shown a significant biological activity including their role as antibacterial, antitumor and antifungal agents. Azo compounds are interesting materials that have shown a range of applications including; food technology, analytical chemistry, pharmaceutical application and dyeing or textile industry.

Their role in colouring approach has been widely investigated and a range of compounds are fabricated [9]. The biological activity of azo-compounds allowed them to be used in the treatment of textile materials. Further, azo-compounds have the role in medicinal chemistry and have pronounced a range of applications as antitumor, antibacterial, antiseptics and antineoplastics [10].

In our research, we report here the preparation of mixed azo, dtc and 1, 10-phenanthroline ligands with their metal complexes and studying their biological activity.

### Experimental

All chemicals in this work are purchased from Aldrich-Sigma and used as received. Solvents were distilled adopting an 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  $4000\text{-}400\text{ cm}^{-1}$  and as CsI discs in the range  $400\text{-}200\text{ cm}^{-1}$ . UV-Vis spectra were obtained with  $10^{-3}\text{ M}$  solutions between 200-1100 nm in dimethylsulfoxide (DMSO) spectroscopic grade solvent at  $25\text{ }^{\circ}\text{C}$  using a Perkin-Elmer spectrophotometer Lambda. TGA was carried out using a STA PT-1000 Linseis.

NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ -NMR) were acquired in DMSO- $d_6$  solutions using a Bruker-300 for  $^1\text{H}$ -NMR and 75 MHz for  $^{13}\text{C}$ -NMR, respectively with tetramethylsilane (TMS) for  $^1\text{H}$  NMR. 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. A magnetic susceptibility balance (Sherwood Scientific) was used to determine magnetic moments of complexes.

## Synthesis

### Synthesis of ligands

#### Preparation of the ligand [ $\text{HL}_{\text{azo}}$ ]

4-Amino pyridine (0.9g, 9.56mmol) was dissolved in  $\text{H}_2\text{O}$  (10ml) and conc. hydrochloric acid (2.93ml, 90.56mmol) were mixed with stirring, and a clear solution was obtained.

The mixture was kept at (0–5) $^\circ\text{C}$  using an icy bath. An aqueous solution of sodium nitrite (0.65g, 9.56mmol) dissolved in (5ml) water was slowly added (keeping the temperature below 5 $^\circ\text{C}$ ).

Then a little amount of urea was added, the pH was adjusted to (6–7) using sodium acetate [solution (1)]. 2-amino-phenole (1.04g, 9.56mmol) was dissolved in (10ml) aqueous sodium hydroxide (10mmol) solution, cooled in ice bath to (0–5) $^\circ\text{C}$  [solution (2)].

Gradually the last solution was mixed with cooling with (solution 1), the mixture resulted was stirred at (0–5) $^\circ\text{C}$  continually for 2hrs, the precipitate resulted was then filtered using acidification, cold  $\text{H}_2\text{O}$  used to wash several times after drying, a dark brown solid precipitate was obtained, Yield:1.89g (93 %), melting point 171 $^\circ\text{C}$  [11,12].

### Preparation of the Ligand [ $\text{L}_{\text{dtc}}$ ]

A standard procedure for the formation of DTC compounds [13] was adopted as follows

An ethanol solution of KOH (3.34g, 59.62mmol, 4eq) was added to a solution of pyrrole (1.00g, 14.90mmol) dissolved in (10mL) of ethanol. The resulted mixture was stirred (keeping the temperature at (0-5)), and then carbon disulphide (3.40g, 44.71mmol, 3eq) was added slowly. The reaction mixture was kept with stirring at 0  $^\circ\text{C}$  for 2 hrs. The white sold salt was collected by filtration and air dried. Yield: 1.5g, 51.36%, melting point (210- 212 $^\circ\text{C}$ ).

### Synthesis of Complexes

#### Preparation of [ $\text{Co}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}})(\text{phen})$ ]

To a mixture of  $\text{HL}_{\text{azo}}$  (0.3g, 1.40mmol) dissolved in (10 ml) was added (0.15g, 2.80mmol) of potassium hydroxide dissolved in 10 ml ethanol.

While, the solution was allowed stirring, a mixture of  $\text{Co}^{\text{II}}$  salt (0.33g, 1.40mmol) in 10ml of ethanol with (0.27gm, 1.40mmol) of dithiocarbamate ligand (L) was added to the above solution along with (0.25gm, 1.40mmol) of 1,10-phenanthroline in 10 mL.

The reaction mixture was kept stirring for two hrs, during which time a brown product was filtered off. Washed with absolute ethanol and recrystallized from ethanol to give the pure product. Yield: 0.72g, 84.7%, melting point (280-282 $^\circ\text{C}$ ).

#### Preparation of $\text{Zn}^{\text{II}}$ and $\text{Cd}^{\text{II}}$ complexes

An analogues method to that reported for the synthesis of  $\text{Co}^{\text{II}}$  complex was implemented to prepare  $\text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  mixed ligands complexes. Table (1) displays the physical properties of the complexes and their reactant amount.

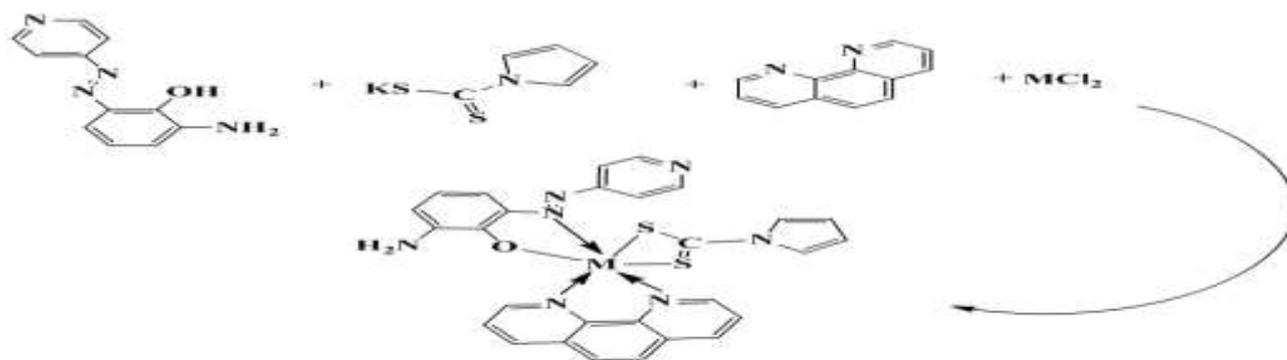
**Table 1: Melting points, yields, metal salts quantities and colours of complexes**

Compound	m.p ( $^\circ\text{C}$ )	Wt of metal salt(g)	Wt of complex(g)	Yield (%)	Colour
$[\text{Co}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}})(\text{phen})]$	280-283	0.33	0.72	84.7	Brown
$[\text{Zn}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}})(\text{phen})]$	300-302	0.19	0.65	73.8	Dark yellow
$[\text{Cd}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}})(\text{phen})]$	263-266	0.32	0.89	93.6	Pale brown

## Results and Discussion

The formation of ligands was obtained using a standard azo dye approach or DTC procedure (see experimental section). The complexes were prepared by mixing the two ligands  $[HL_{azo}]$  and  $[L_{dtc}]$  and 1, 10-phenanthroline with the metal salts in a 1:1:1:1 mole ratio (Scheme 1). A range of

analytical and spectroscopic techniques were used to confirm the entity of compounds including; magnetic susceptibility, CHNS, FT-IR, electronic and  $^1H$ ,  $^{13}C$  -Nuclear magnetic resonance (NMR) spectra. The analytical data, colours, yields and (C, H, N, S) analysis are listed in (Table 2).



Where  $M^{+2} = Co, Zn$  and  $Cd$

Scheme 1: Mixed Ligand Metal Complexes

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

Compound	M.wt	Yield %	colour	Found (calc.) %				
				M	C	H	N	S
$HL_{azo}$	215	93	Brown	-	60.22 (61.67)	4.01 (4.71)	26.00 (26.15)	-
$L_{dtc}$	181.32	51.36	White	-	33.03 (33.12)	1.88 (2.22)	7.00 (7.73)	34.89 (35.36)
$[Co(L_{azo})(L_{dtc}) (phen)]$	594.58	84.7	Brown	9.26 (9.91)	56.14 (56.56)	3.21 (3.56)	15.90 (16.49)	10.41 (10.78)
$[Zn(L_{azo})(L_{dtc}) (phen)]$	601.02	73.8	Dark yellow	10.66 (10.88)	55.16 (55.96)	3.11 (3.52)	15.88 (16.31)	10.10 (10.67)
$[Cd(L_{azo})(L_{dtc}) (phen)]$	648.06	93.6	Pale brown	17.12 (17.35)	51.34 (51.89)	3.00 (3.27)	14.85 (15.13)	9.13 (9.89)

### FTIR and NMR Spectra

The FT-IR spectral data is collected in Table (3). The FT-IR spectrum of the azo  $[HL_{azo}]$  exhibits peak at  $3440\text{cm}^{-1}$  due to  $\nu$  (OH) stretching of the OH phenolic group [14, 15]. Bands related to  $\nu$  ( $\text{NH}_2$ ) amine and  $\nu$  ( $\text{N}=\text{N}$ ) azo group are detected at  $3377$ ,  $3305$  and  $1460\text{ cm}^{-1}$ , respectively [15, 16]. The FT-IR spectrum of the dtc ligand  $[L_{dtc}]$  exhibits peak related to  $\nu$  (C-N) of ( $\text{N-CS}_2$ ) moiety at  $1516\text{ cm}^{-1}$  [17]. The spectrum reveals a couple of new bands at  $1054$  and  $894\text{cm}^{-1}$ , which designated to  $\nu_s(\text{CS}_2)$  and  $\nu_{as}(\text{CS}_2)$ , respectively [18]. While, the FT-IR spectrum of complexes exhibits bands at  $1504$ - $1512\text{ cm}^{-1}$  that resulted from the stretching of the C-N-S bond indicated a partial delocalization of  $\pi$ -electron density within the

dithiocarbamate moieties [17]. Peaks detected at  $1029$ - $1072\text{cm}^{-1}$  and  $906$ - $950\text{cm}^{-1}$  were assigned to  $\nu_{as}(\text{CS}_2)$  and  $\nu_s(\text{CS}_2)$ , respectively. Band located in the range ( $1448$ - $1452$ )  $\text{cm}^{-1}$  assigned to  $\nu$  ( $\text{N}=\text{N}$ ) azo. Finally, the spectra showed new bands in the range ( $565$ - $698$ ) and ( $408$ - $476$ )  $\text{cm}^{-1}$  that attributed to  $\nu$  (Metal-N) and  $\nu$  (Metal-O), respectively. The appearance of these bands supported the involvement of the nitrogen of azo and oxygen phenolic atoms in the coordination of the ligand to the metal centre. These results are in accordance with that reported in literature [19, 20]. Complexes exhibited two sets of bands around ( $304$ - $385$ )  $\text{cm}^{-1}$ , which attributed to  $\nu$  (Metal-S) vibration mode, and supporting the

asymmetrical chelation mode of the ligand [21]. This is in agreement with an anisobidentate chelation mode of the ligand to the metal ion [18]. The entity of new complexes was confirmed by elemental analysis, FT-IR, electronic spectra and magnetic susceptibility. The molar conductance of the complexes in DMSO solvents is indicative of their non-electrolyte behaviour [22,23]. The  $^1\text{H}$  NMR spectrum of the ligand [HLazo] Fig.(1), exhibited signals related to the various protons indicating the formation of the ligand. The  $^1\text{H}$ -NMR spectrum in DMSO- $d_6$  solution of the ligand shows peak at 11.8ppm (H, s, OH), which may be assigned to the phenolic proton. Chemical shift at  $\delta = 9.5\text{ppm}$  (2H, s, NH) can

assign to the amine protons. Signal at  $\delta = 6.8\text{--}8.6\text{ppm}$  attributed to (aromatic ring protons). The  $^1\text{H}$ , NMR spectrum of the ligand [Ldtc] Fig.(2), shows chemical shifts at  $\delta = 7.6\text{ppm}$  (2H, m) ( $C_{1,4}\text{-H}$ ) and  $7.5\text{ppm}$  (2H, m) ( $C_{2,3}\text{-H}$ ) attributed to (aromatic ring protons). While, the  $^1\text{H}$ -NMR spectrum for [Cd(Lazo)(Ldtc)(phen)] complex Fig.(3), in DMSO- $d_6$  solution displays chemical shift at  $\delta = 10.5\text{ppm}$  (2H, s, NH), which may be assigned to the amine proton. The signal at  $\delta = 6.9\text{--}8.7\text{ppm}$  attributed to (aromatic ring protons). The  $^{13}\text{C}$ -NMR spectrum of [Cd(Lazo)(Ldtc)(phen)] complex exhibits resonance at 192 ppm that assigned to C=S moiety, indicating the formation of the Cd-complex [24] ( see Fig (4)).

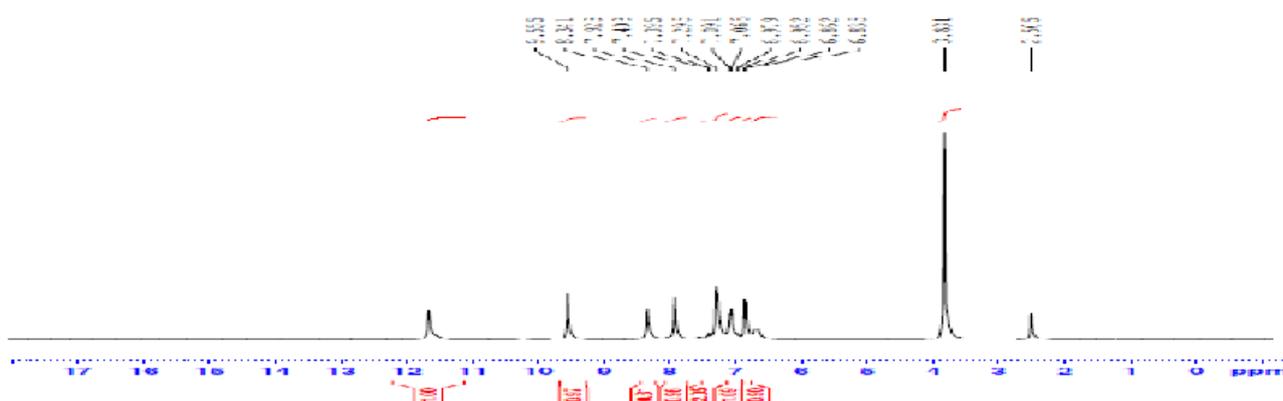


Fig 1:  $^1\text{H}$ -Nuclear magnetic resonance spectrum of HLazo

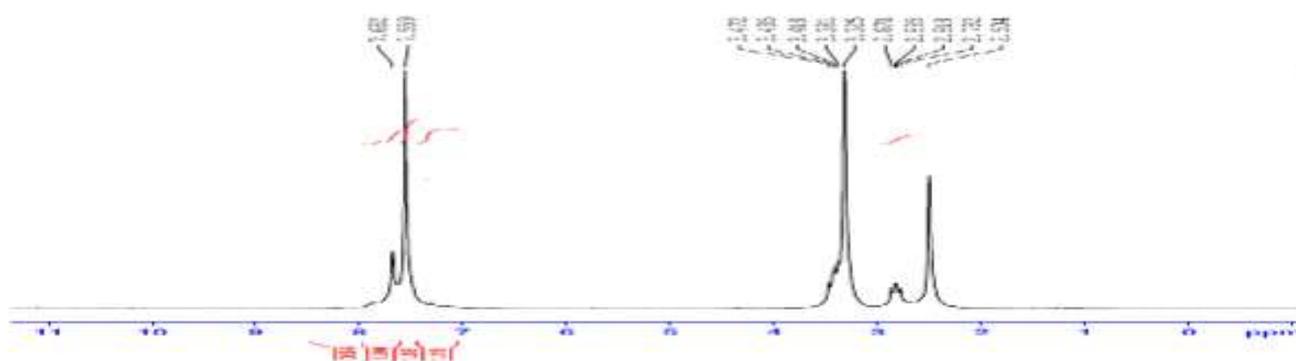


Fig 2:  $^1\text{H}$ -Nuclear magnetic resonance spectrum of Ldtc

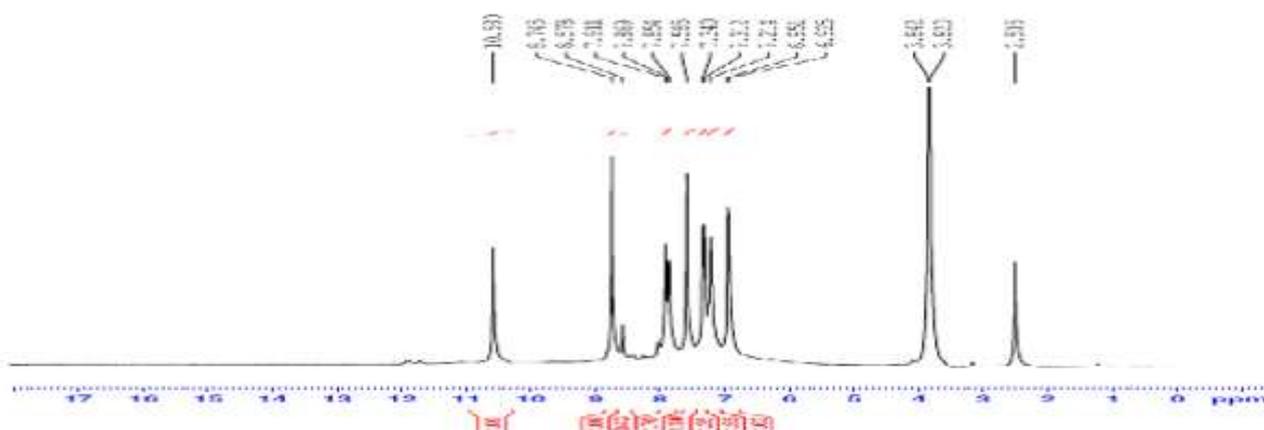


Fig 3:  $^1\text{H}$ -Nuclear magnetic resonance spectrum of [Cd(Lazo)(Ldtc)(phen)]

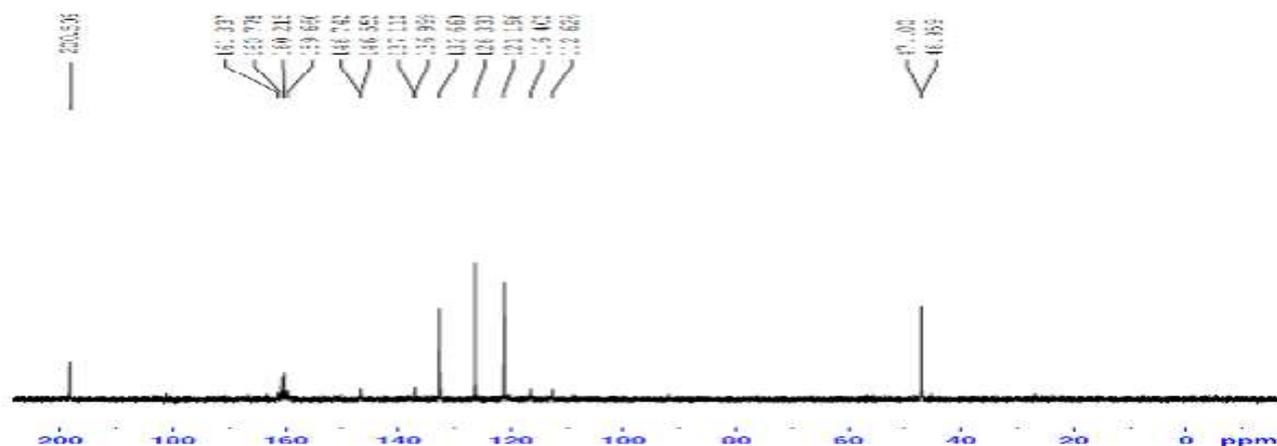
Fig 4:  $^{13}\text{C}$ -Nuclear magnetic resonance spectrum of  $[\text{Cd}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}}) (\text{phen})]$ 

Table 3: FT-IR spectral data for complexes

Compound	$\nu(\text{OH})$	$\nu(\text{NH}_2)$	$\nu(\text{N-CS}_2)$	$\nu(\text{N=N})_{\text{azo}}$	$\nu(\text{CS}_2)_{\text{as}}$ $\nu(\text{CS}_2)_{\text{s}}$	$\nu(\text{Metal - N})$ $\nu(\text{Metal - O})$	$\nu(\text{Metal - S})$
$\text{HL}_{\text{azo}}$	3440	3377,3305	-	1460	-	-	-
$\text{L}_{\text{dtc}}$	-	-	1516	-	1054,894	-	-
$[\text{Co}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}}) (\text{phen})]$	-	3305,3139	1512	1450	1072,925	684,665 476,416	379,304
$[\text{Zn}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}}) (\text{phen})]$	-	3338,3265	1504	1452	1074,906	698,606 455,408	383,307
$[\text{Cd}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}}) (\text{phen})]$	-	3369,3232	1504	1448	1029,950	667,565 476,416	385,308

## UV-Vis Spectral Data

The UV-Vis spectra of ligands  $[\text{HL}_{\text{azo}}]$  and  $[\text{L}_{\text{dtc}}]$  in DMSO solution revealed peaks at (282, 320) and (266,304) nm assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively [2527]. The electronic spectra of the complexes exhibited bands at (268-271) nm due to the ligand field  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. Bands at (301-443) nm attributed to the charge transfer transitions (CT) in complexes [28]. The Co (II) complex exhibits an additional peak at 670 nm correlated to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  transition. The  $\mu_{\text{eff}}$  value 4.38 B.M for Co-complex indicates an octahedral arrangement about metal centre [29, 30]. The spectra of Zn<sup>II</sup> and Cd<sup>II</sup> compounds revealed

peaks attributed to ligand field  $\pi \rightarrow \pi^*$  and  $\text{M} \rightarrow \text{L}$  charge transfer [31]. These data along with other analytical results indicated that the Zn<sup>II</sup> and Cd<sup>II</sup> complexes adopt octahedral arrangement about metal centre [32]. The six-coordinate number for the Zn<sup>II</sup> and Cd<sup>II</sup> compounds may be due to the sort of ligands that surrounding metal centre and their steric and electronic interaction that occurred upon complex formation [33]. The electronic data, molar conductance and magnetic moment measurements of complexes with their assignments are listed in (Table 4).

Table 4: Electronic spectral data of complexes in DMSO solutions

Compound	Wave number $\lambda_{\text{nm}}$	Wave number ( $\text{cm}^{-1}$ )	$\epsilon_{\text{max}}$ molar <sup>-1</sup> $\text{cm}^{-1}$	Assignment	Suggested structure
$\text{HL}_{\text{azo}}$	282 320		1739 1855	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-
$\text{L}_{\text{dtc}}$	266 304		722 2142	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-
$[\text{Co}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}}) (\text{phen})]$	271 301 443 816		1915 1834 1109 108	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$	Distorted octahedral
$[\text{Zn}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}}) (\text{phen})]$	273 301 416		2090 2152 1350	$\pi \rightarrow \pi^*, n \rightarrow \pi^*$ C.T	Distorted octahedral
$[\text{Cd}(\text{L}_{\text{azo}})(\text{L}_{\text{dtc}}) (\text{phen})]$	268 313 396		1157 2011 355	$\pi \rightarrow \pi^*, n \rightarrow \pi^*$ C.T	Distorted octahedral

## Thermal Analysis

The TGA thermal analysis curve for [Co (L<sub>azo</sub>) (L<sub>dtc</sub>)(phen)] reveals is stable up to 183.4°C. Peak observed at 243.8 °C due to the loss of (CS<sub>2</sub>) fragment, (obs. =1.02418 mg, 12.8008%; calc.=1.0225 mg, 12.7823%).

The second step at 342 °C attributed to the loss of (CO, N<sub>2</sub>) fragment, with a weight loss of (obs.=0.753217 mg, 9.4152%; calc.=0.7534 mg, 9.4185%). The third step occurs at 594°C is related to the loss of (C<sub>6</sub>H<sub>3</sub>, 3C<sub>5</sub>H<sub>4</sub>N, C<sub>4</sub>H<sub>4</sub>N) fragment (obs. =5.04706 mg, 63.0881%; calc.=5.0456 mg, 63.0707%). The residue of the complex that assigned to the (NH<sub>2</sub>, C and Co) (Calc. = 1.3154 mg, 14.6150% ). The DSC analysis endothermic peaks at 183.4, 243.8 may refer to decomposition process of the organic ligand in nitrogen atmosphere. The endothermic peak observed at 477.8°C may signify metal-ligand bond breaking [34,35].

## Biological Activity

The preparation ligands and their mixed complexes were screened of their biological activity against some bacterial strains (*Bacillus subtilis* and *Staphylococcus aureus*(G+) *Escherichia coli* and *Enterobacter*(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 species [36]. The measured size of inhibition zones against growth of different microorganisms are summarized in (Table 5). Biological data showed that complexes become potentially more active against these tested bacteria compared with the free ligands (HL<sub>azo</sub> and L<sub>dtc</sub>). Zinc and cadmium complexes showed almost the higher antibacterial activity, compared with other compounds. This is due to their molecular weight and their electronic configuration (d<sup>10</sup> system), (Fig (5 and 6)) [37, 38].



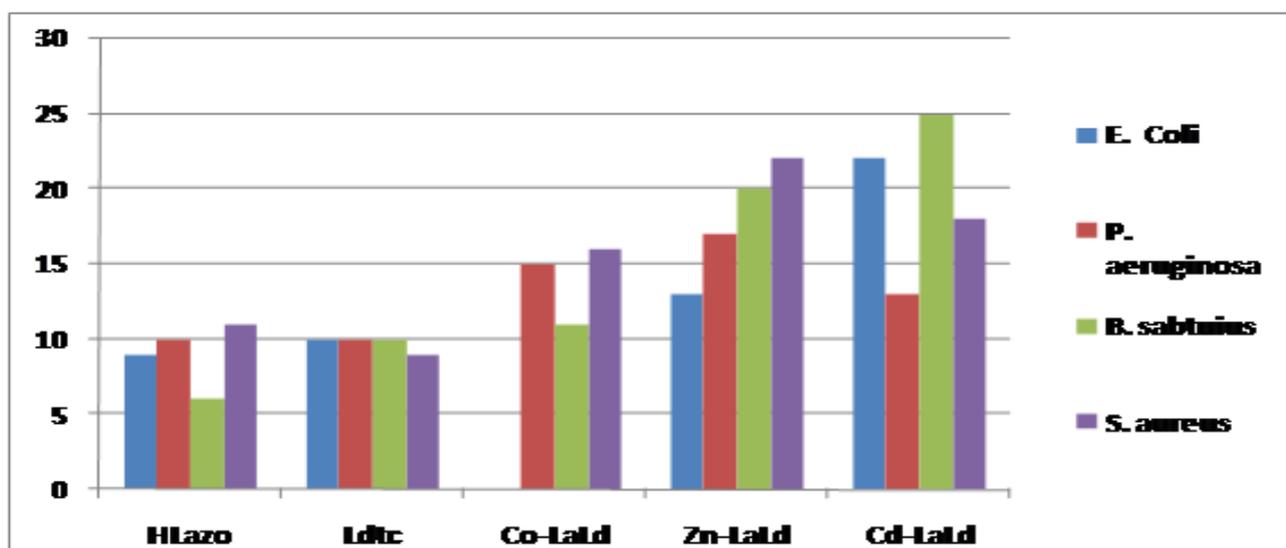
Fig 5: the effect of Lazo L<sub>dtc</sub> and their complexes on *Escherichia coli* and *Enterobacter*



Fig 6: The effect of Lazo L<sub>dtc</sub> and their complexes on *Bacillus subtilis* and *Staphylococcus aureus*

**Table 5: Biological activity of compounds**

Compounds	Gram negative (G+)		Gram negative (G-)	
	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i> (G+)	<i>Escherichia coli</i> (G-)	<i>Enterobacter</i> (G-)
Control	—	—	—	—
HL <sub>Lazo</sub>	6	11	9	10
L <sub>dtc</sub>	9	10	10	10
[Co(L <sub>Lazo</sub> )(L <sub>dtc</sub> ) (phen)]	16	11	15	—
[Zn(L <sub>Lazo</sub> )(L <sub>dtc</sub> ) (phen)]	22	20	17	13
[Cd(L <sub>Lazo</sub> )(L <sub>dtc</sub> ) (phen)]	18	25	13	22

**Chart 1: The zone (mm) of (L<sub>Lazo</sub>L<sub>dtc</sub>) and their complexes**

## Conclusion

The preparation and characterisation of mixed ligands and their complexes are described. The mixed ligand complexes were achieved by adding the HL<sub>Lazo</sub> and L<sub>dtc</sub> and 1, 10-phenanthroline with the appropriate metal salt in a 1:1:1:1 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 six

coordinate complexes. Biological activity of the compounds was screened for their antimicrobial activity against four bacterial species (*Escherichia coli*, *Enterobacter*, *Bacillus subtilis* and *Staphylococcus aureus*). Biological data showed that complexes become more active against these tested bacteria compared with the free ligands

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