



# CO<sup>II</sup>, NI<sup>II</sup> AND CD<sup>II</sup> COMPLEXES DERIVED FROM MIXED AZO-LINKED SCHIFF-BASE LIGANDS: FORMATION, CHARACTERISATION, THERMAL ANALYSIS AND BIOLOGICAL STUDY

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## Abstract

The study includes preparation and characterisation of mixed azo-linked Schiff-base ligands and their complexes. The starting material was isolated from the mixing of 2-amino pyridine diazonium salt with 2-amino-phenole and 4-amino-3-hydroxy-1-naphthalene sulfonic acid respectively in 1:1 mole ratio in water. In this work, the formation of azo-linked Schiff-base ligands are reported. Ligands of the azo-linked Schiff-base was achieved by the reaction of starting material with 4-(dimethylamino) benzaldehyde (HL<sup>1</sup> and HL<sup>2</sup>) The complexes were prepared by mixing the azo-linked Schiff-base ligands with the metal salts; Co<sup>II</sup>, Ni<sup>II</sup> and Cd<sup>II</sup> 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 <sup>1</sup>H-NMR spectroscopy. Physico-chemical techniques indicated complexes demonstrated 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* (G-)), (*Bacillus subtilis* and *Staphylococcus aureus* (G+)).

**Key words :** Mixed azo-linked Schiff-base ligands, metal complexes; 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 fabricated Thoraya *et al.*, 2008. 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 antineoplastics Chandravadivelu *et al.*, 2011. 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 studied Hakimi *et al.*, 2012. More, Schiff base compounds have a range of applications in

the biological system, clinical biochemistry, analytical and industrial aspects Kumar *et al.*, 2009. Further, metal complexes of azomethine ligands exhibit remarkable antibacterial, antitumor activities and antifungal Spange *et al.*, 1999; Tumer *et al.*, 1999. Recently, we reported the formation of mixed azo-linked Schiff-base ligands and their metal (II) complexes Enaam *et al.*, 2018; Enaam *et al.*, 2018.

## Materials and Methods

### Materials

2-amino pyridine, 2-amino-phenole, Ethanol, Sodium nitrite, 4-amino-3-hydroxy-1-naphthalenesulfonic acid, KOH, 4-dimethylaminobenzaldehyde, and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich and used without further purification. Solvents were distilled prior to use.

### Physical Measurements

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Elemental analyses (carbon, hydrogen and nitrogen) for compounds were carried using Euro Vector, model EA 3000. Melting points of compounds were conducted using an Electro-Thermal Stuart melting point apparatus. Fourier transform infrared spectra (FTIR) were recorded on a Shimadzu (FT-IR) – 8400S spectrophotometer in the range (4000–400  $\text{cm}^{-1}$ ). Spectra were obtained as KBr. The UV-Vis for ligands and their complexes were measured using a Shimadzu UV-Visible 160A Spectrophotometer, in DMSO solutions, with ( $10^{-3}$ – $10^{-5}$ M) concentration. NMR spectra ( $^1\text{H-NMR}$ ) were recorded on a Bruker 300 for  $^1\text{H-NMR}$  with tetramethylsilane (TMS) for  $^1\text{H-NMR}$ . Mass spectra was obtained by positive (lc/ms-ms) using agilent q\_trap3200 mass spectroscopy Mashhad University of Medical Sciences, Iran. TGA was carried out using a STA PT-1000 Linseis. Metal content of complexes were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. The conductivity measurements of the complexes were recorder at (25  $^{\circ}\text{C}$ ) for ( $10^{-3}$  mole  $\text{L}^{-1}$ ) solution of the samples in DMSO using a Jenway conductivity meter model 4070. Chloride was determined using potentiometer titration method on a (686-Titro processor-665Dosimat-Metrohm Swiss). Magnetic moments were determined at room temperature with a Sherwood Scientific Apparatus.

## Synthesis

### Preparation of the precursors

The compound was prepared according to the literature Enaam *et al.*, 2018; Enaam *et al.*, 2018.

### Preparation of 2-amino-6-(pyridin-2-yl diazenyl)phenol(1)

2-amino pyridine (0.9g, 9.56mmol) was dissolved in  $\text{H}_2\text{O}$  (10ml) and Hydrochloric acid Conc.(2.93ml, 90.56mmol), the mixture was stirring, a clear solution was obtained. Temperature of (0–5) $^{\circ}\text{C}$  have been kept, then aqueous solution of sodium nitrite (0.65g, 9.56mmol) dissolved in (5ml) water, was dropwise slowly added, keeping the temperature below 5 $^{\circ}\text{C}$ , followed by mixture stirring for 1hrs using ice bath, then 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 (12ml) KOH (10mmol) aqueous solution, cooled by ice bath to (0–5) $^{\circ}\text{C}$  [solution(2)]. Gradually

the last solution was mixed with cooling with (solution1), 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 (92.6 %), m.p 170 $^{\circ}\text{C}$ .

### Preparation of 4-amino-3-hydroxy-2-(pyridin-2-yl diazenyl)naphthalene-1-sulfonic acid(2)

Precursor (2) was prepare in a similar method to that mentioned in preparation of precursor (1), Table (1): displays the physical properties of the synthesised precursors.

### Synthesis of free ligands

Preparation of azo-linked schiff bases 2-(((E)-4-(dimethylamino) benzylidene)amino)-6-(pyridin-2-yl diazenyl)phenol [ $\text{HL}^1$ ]: The compound was prepared according to the literature Uppadine *et al.*, 2001. A solution of the derivative 2-amino-6-(pyridin-2-yl diazenyl)phenol (1) (0.945g, 4.413mmol) in 25ml ethanol was mixed with (0.65g, 4.413mmol) of 4-dimethylaminobenzaldehyde dissolved in (10ml) ethanol. After adding glacial acetic acid (3-5) drops, the mixture resulted was refluxed for 2hrs., filtered off, and washing with ethanol and drying; the resulted was obtained as green product. The product solid was recrystallised using EtOH. Yield: 1.1g, 72.3%. m.p (98-100 $^{\circ}\text{C}$ ).

### Preparation of azo linked schiff base ligand 4-(((E)-4-(dimethylamino)benzylidene)amino)-3-hydroxy-2-((E)-pyridin-2-yl diazenyl)naphthalene-1-sulfonic acid [ $\text{HL}^2$ ]

The method used was similar to [ $\text{HL}^1$ ], but with precursor (2) in place of precursor (1).Table(2) shows some physical properties of the prepared ligands.

### Synthesis of complexes

A one pot approach reported in Cookson *et al.*, 2010. was used to prepare the mixed ligand metal complexes.

### Preparation of $\text{Co}^{\text{II}}$

The mixed ligand  $\text{Co}^{\text{II}}$  complex was prepared by addition of a mixture of The ligand ( $\text{HL}^1$ ), (0.22g, 0.579mmol) and of the ligand ( $\text{HL}^2$ ) dissolved in (20ml) of ethanol and (0.06 g, 1.15mmol) of potassium hydroxide dissolved in (10ml) ethanol with continuous stirring for few minutes, to (0.120g, 0.579mmol) of  $\text{Co}^{\text{II}}$  salt dissolved

**Table 1:** Weight, colours, melting points and yields of the synthesised precursors.

Compound	Starting material	Colour	Weight (g)	Yield (%)	m.p. $^{\circ}\text{C}$
Precursor (1)	2-amino pyridine with 2-amino-phenole	dark brown	1.89	92.6	170
Precursor (2)	2-amino pyridine with 4-amino-3-hydroxy-1-naphthalenesulfonicacid	brown	2.2	85.9	155

**Table 2:** Colours, yields, melting points and weight of azo linked schiff base ligands (HL<sup>1</sup> and HL<sup>2</sup>).

m.p. °C	Colour	Yield (%)	Weight of Free ligand (g)	Weight of precursor (g)	Free ligand
97-99	green	72.	1.1	0.945	HL <sup>1</sup>
187	purple	65.	1.63	1.8	HL <sup>2</sup>

**Table 3:** Metal salts quantities, Colours, yields and melting points of complexes of HL<sup>1</sup>, HL<sup>2</sup> mixed ligand.

m.p. °C	Colour	Yield (%)	Weight of complex (g)	Weight of metal salt (g)	Comp.
305	light green	46	0.245	0.120	[Co(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]
310	dark green	45	0.238	0.120	[Ni(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]
290	Pale yellow	39	0.219	0.115	[Cd(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]

in (10ml) ethanol in a one pot step. The resulting mixture was stirred for 2 hrs. Filtered off, washed with absolute ethanol and recrystallised from ethanol, Yield :0.245g, 46.36%, m.p (305 °C).

### Preparation of Ni<sup>II</sup> and Cd<sup>II</sup> complexes

An analogues method to that reported for the synthesis of Co<sup>II</sup> complex was implemented to prepare Ni<sup>II</sup> and Cd<sup>II</sup> mixed ligands complexes. (Table 3) 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 2-amino pyridine diazonium salt with 2-amino-phenole and 4-amino-3-hydroxy-1-naphthalene sulfonic acid, respectively, in 1:1 mole ratio in water. See Scheme 1. Ligands were prepared; the ligand of azo-linked Schiff-base was achieved by the reaction of starting material with 4-(dimethylamino) benzaldehyde (HL<sup>1</sup> and HL<sup>2</sup>) (Schemes 1 and 2). The complexes were prepared by mixing the azo-linked Schiff-base ligands with the metal salts; Ni<sup>II</sup>, Cu<sup>II</sup> and Cd<sup>II</sup> in a 1:1:1 mole ratio. (Scheme 3). The entity of new complexes was confirmed by elemental analysis, FT-IR, electronic spectra and magnetic susceptibility. The analytical data table 4 support the proposed formulae. The molar conductance of the complexes in DMSO solvents is indicative of non-electrolyte behaviour Canpolat *et al.*, 2005; Geary *et al.*, 1971.

### NMR spectra for ligands

The <sup>1</sup>H-NMR spectrum for HL<sup>1</sup> displays chemical shifts of two methyl groups are non-equivalent that detected at δ= 2.18 and 2.84-3.37 ppm (6H, s, 2CH<sub>3</sub>) equivalent to 6 protons, which assigned to (C1, 1'-H). This is may be due to the rotation of the dimethyl segment

of the molecule. Quick rotation resulted in an averaged symmetrical spectrum. However, slow rotation could result in two conformations that are non equivalent. Chemical shift at δ= 10.93 ppm (1H, d, OH) which may be assigned to the phenolic proton Swati *et al.*, 2011. The other signals at δ= 6.74-6.80 ppm (2H, m) (C<sub>3,3'</sub>-H), δ= 7.00 ppm (1H, m) (C<sub>11</sub>-H), δ= 7.58-7.37 ppm (2H, m) (C<sub>10,10'</sub>-H), δ= 7.78-7.76 ppm (2H, m, J<sub>HH</sub>=8.8Hz) (C<sub>4,4'</sub>-H), δ= 7.90-7.88 ppm (1H, m, J<sub>HH</sub>=10Hz) (C<sub>15</sub>-H), δ= 8.13 ppm (1H, m) (C<sub>14</sub>-H), δ= 8.435 ppm (1H, m) (C<sub>13</sub>-H) and δ= 8.61ppm (1H, s)(C<sub>16</sub>-

H) attributed to (aromatic ring protons) Silverschtién *et al.*, 1981. The signal at δ=10.01ppm (H,s,NCH) is due to the proton of the azomethine group (N=C-H) Tunçel *et al.*, 2006. Signal observed at δ=7.27 ppm is related to the solvent residual for CDCl<sub>3</sub>, While the <sup>1</sup>H-NMR spectrum for HL<sup>2</sup> displays chemical shift at δ=1.70 ppm (H, s, OH) may be due to OH proton of sulfonic acid group Swati *et al.*, 2011. The signal at δ=3.10-3.13 ppm (6H, s, 2CH<sub>3</sub>) equivalent to 6 protons, which assigned to (C<sub>1,1'</sub>-H). Chemical shift at δ= 9.73 ppm (H, s, OH) which may be assigned to the phenolic proton. The signal at δ= 6.86-6.83 and 7.76-7.73 ppm (4H, d, J<sub>HH</sub>= 9.2 Hz) attributed to (aromatic ring protons)[16]. The signal at δ= 8.93 ppm (H, s, NCH) can be attributed to the proton of the azomethine group (N=C-H) Tunçel *et al.*, 2006. The chemical shift at δ= 2.56-2.57 and 3.47 ppm are due to the NMR solvent dimethyl sulfoxide-d<sub>6</sub> and water residual in the solvent.

### FTIR and NMR spectra for complexes

The FTIR spectra of complexes show bands at rang (1618-1627) cm<sup>-1</sup> were assigned to of imine u(C=N) group. (Table 5) includes the prominent FTIR bands of complexes frequency shift. This may be related to the engagement of the nitrogen atom of the iminic moiety in the coordination reaction Nejati *et al.*, 2003; Mikuraya *et al.*, 1992 ; Lee *et al.*, 1999.

The shift also may explained by delocalisation process of the d<sup>10</sup> (metal electron density) to the ligand (p-system) Agrawal *et al.*, 2004; Al-Janabi *et al.*, 2005. Band located in the range (1436-1454) cm<sup>-1</sup> was assigned to u (N=N) azo group. Finally, the spectra showed new bands in the range (621-678) and (421-514)cm<sup>-1</sup> that attributed to u(M-N) and u(M-O) group, respectively. The appearance of these bands supported the involvement of the nitrogen of imine and oxygen phenolic atoms in the coordination of the ligand to the metal centre. These results are in accordance with that reported in literature

**Table 4:** Elemental microanalysis data and some physical properties for ligands and complexes.

Comp.	Empirical formula	MWg/mol	Yield %	Colour	Microanalysis (calc) %				
					M%	C	H	N	S
HL <sup>1</sup>	C <sub>20</sub> H <sub>19</sub> N <sub>5</sub> O	345	72	green	-	68.56 (69.55)	4.48 (5.54)	19.22 (20.28)	-
HL <sup>2</sup>	C <sub>24</sub> H <sub>21</sub> N <sub>5</sub> O <sub>4</sub> S	475	65.	purple	-	60.6 (60.62)	4.27 (4.45)	13.23 (14.73)	5.07 (6.74)
[Co(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]	C <sub>44</sub> H <sub>42</sub> N <sub>10</sub> CoO <sub>7</sub> S	912	46.	light green	5.45(6.45)	-	-	-	-
[Ni(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]	C <sub>44</sub> H <sub>42</sub> N <sub>10</sub> NiO <sub>7</sub> S	912	45.	dark green	5.33(6.43)	-	-	-	-
[Cd(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]	C <sub>44</sub> H <sub>42</sub> N <sub>10</sub> CdO <sub>7</sub> S	966	39.	Pale yellow	10.00(11.63)	-	-	-	-

**Table 5:** FTIR spectral data (wave number) cm<sup>-1</sup> for complexes HL<sup>1</sup>, HL<sup>2</sup> mixed ligand metal (azo linked Schiff-bases).

v(M-O)	v(M-N)	SO <sub>3</sub> Has SO <sub>3</sub> Hs	v(C-N)	v(C-O)	v(N=N)	v <sub>ar</sub> (C=C)	v(C=N)	v <sub>ali</sub> (C-H)	v <sub>ar</sub> (CH)	v(O-H)	Comp.
-	-	-	1257	1385	1460	1491	1630	2978	3033	3423	[HL <sup>1</sup> ]
-	-	1134,1056	1176	1276	1458	1627,1558	1654	2910	3005	3441	[HL <sup>2</sup> ]
471,442	652,621	1167,1016	1194	1275	1454	1577	1619	2937,2852	3003	3346	[Co(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]
480,426	671,622	1100,1056	1321	1375	1444	1595,1564	1627	2989,2925	3025	3404	[Ni(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]
514,472	678,621	1051,1018	1181	1272	1436	1575	1618	2929	3010	3394	[Cd(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]

**Table 6:** Electronic spectral data of complexes in DMSO solutions.

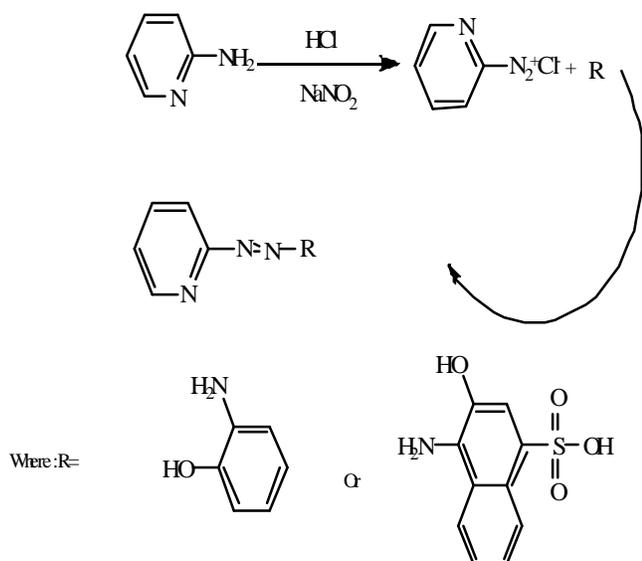
Suggested geometry	Assignment	Extinction coefficient $\epsilon_{\max} \text{ (dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}\text{)}$	Band Position $\lambda_{\text{nm}}$	Comp.
Distorted octahedral	Intra-ligand $\pi \rightarrow \pi^*$ , $n \rightarrow \pi^*$	1867	272	[Co(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]
	C.T.	1845	345	
	${}^4T_1g^{(F)} \rightarrow {}^4T_2g^{(F)}$	21	810	
Distorted octahedral	Intra-ligand $\pi \rightarrow \pi^*$ , $n \rightarrow \pi^*$	834	267	[Ni(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]
	C.T.	844	348	
	${}^3T_2g \rightarrow {}^3T_1g^{(F)}$	19	660	
	${}^3A_2g \rightarrow {}^3T_1g^{(F)}$	12	764	
Distorted octahedral	Intra-ligand $\pi \rightarrow \pi^*$ , $n \rightarrow \pi^*$	1157	268	[Cd(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]
	C.T.	355	396	

Addison *et al.*, 1967; Preti *et al.*, 1977. The <sup>1</sup>H-NMR spectrum of [Cd(L<sup>1</sup>L<sup>2</sup>)(H<sub>2</sub>O)<sub>2</sub>], displays peak at  $\delta = 8.76$  ppm related to the proton of the iminic moiety (1H, s, N=C-H) Tunçel *et al.*, 2006. The chemical shift at  $\delta = 4.61$  ppm (H, s, OH) may be due to OH proton of sulfonic acid. The chemical shift at  $\delta = 2.12$  ppm that equivalent to six protons assigned to two methyl groups (2CH<sub>3</sub>, s, 6H).

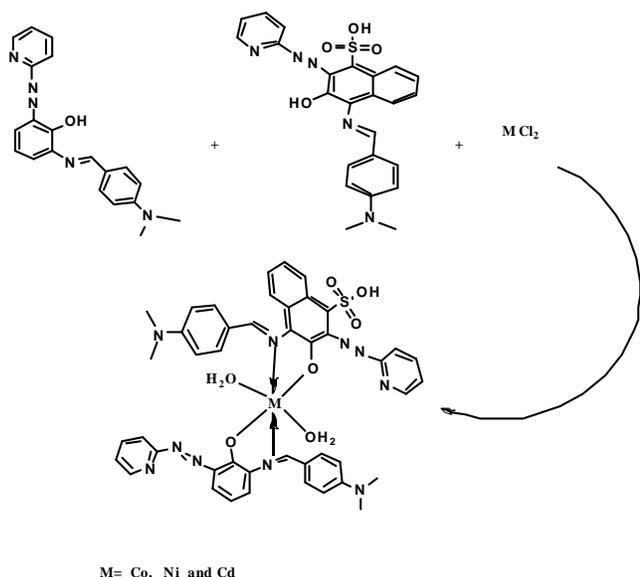
#### UV-Vis Spectral data and magnetic susceptibility for the complexes

The spectra showed peaks in the (U.V) region at (267-272) nm, can be assigned to  $\pi - \pi^*$  transition of the aromatic rings Erdem *et al.*, 2009. While the peaks at (345-396) nm are due to  $n - \pi^*$  transition of N=N group. The blue shifted behaviour observed of complexes are related to the energy change of  $\pi - \pi^*$  and  $n - \pi^*$  transitions of the conjugated chromophore, due to the chelation between metal ions and azo ligand. The complexation of the dye with the metal ion was responsible for a significant

hypochromic shift at both  $\pi - \pi^*$  and  $n - \pi^*$  transition region Kasawaki *et al.*, 1990 and may be assigned to M→L charge transfer transition for the complex. In metal chelates, the light absorption is believed to take place in the UV region as a result of absorption arising from electronic transition in a conjugated system, where a metal may or may not participate and may be assigned to M@L charge transfer transition for the complexes. Finally, the peaks in the visible region are due to d-d transitions. The Co<sup>II</sup> complex shows a peak at (810) nm assignable to  ${}^4T_1g^{(F)} \rightarrow {}^4T_2g^{(F)}$  suggesting distorted octahedral geometry around Co<sup>II</sup> ion Siddiqi *et al.*, 2006; Slddappa *et al.*, 2009. The Ni<sup>II</sup> complex shows a peaks at (660) nm and (764) nm assignable to  ${}^3T_2g \rightarrow {}^3T_1g^{(F)}$  and  ${}^3A_2g \rightarrow {}^3T_1g^{(F)}$  suggesting distorted octahedral geometry around Ni<sup>II</sup> ion Mamba *et al.*, 2010. The spectrum of the Cd<sup>II</sup> complex exhibited peaks assigned to ligand  $\pi - \pi^*$  and M@L charge transfer. The Cd<sup>II</sup> complex adopt octahedral geometry



**Scheme 1:** Synthetic route for Precursors (1 and 2).

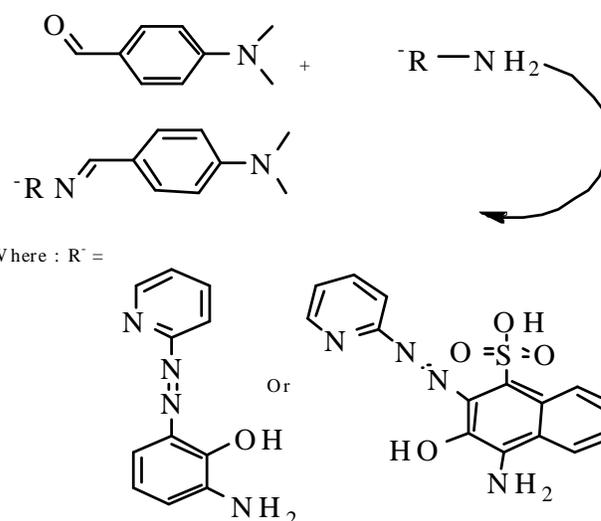


**Scheme 3:** Synthetic route of mixed ligand metal complexes (azolinked Schiff-bases).

Lever *et al.*, 1984. It is well known that the six-coordinate number is one of the most detected coordination numbers for transition metals. There are many factors that have influence on the formation of this coordination number. These related to the metal ions, ligands and type steric and electronic interaction that happened between ligands upon complex formation Al-Jeboori *et al.*, 2014. Accordingly, the isolated complexes exhibit distorted octahedral geometries around metal atoms. The U.V-Vis absorption peaks of the complexes are summarised in Table (6).

### Thermal analysis

The thermogram for [Cd(L<sup>1</sup>L<sup>2</sup>)(H<sub>2</sub>O)<sub>2</sub>] which confirmed the Cd(II) complex is stable up to 94°C. In the



**Scheme 2:** Synthetic route for Azo linked Schiff-base ligands.

TGA curve, peak detected at 235.806 °C is related to the loss of (2H<sub>2</sub>O, C<sub>6</sub>H<sub>5</sub> and CO<sub>2</sub>) portions, (det.=2.4765 mg, 17.6896 %; calc.=2.4800 mg). The second step at 582.638 °C that indicated the loss of (CH<sub>4</sub>, HCN, C<sub>5</sub>H<sub>5</sub>N and C<sub>6</sub>H<sub>6</sub>) fragment, (obs.=3.1687 mg, 22.6342%; calc. = 3.1592 mg). The final residue of the compound that is assigned to the (2C<sub>6</sub>H<sub>3</sub>, C<sub>10</sub>H<sub>7</sub>, 2CH<sub>2</sub>, HCN 3N<sub>2</sub>,Cd), (calc.=8.3402mg 59.5748 %; The DSC analysis curve verified peaks at 94, 285, 298, 325, 342,424and 520 refer to an endothermic and exothermic decomposition process. The endothermic peaks 94, 285, 325 and 424 may indicate combustion of the organic ligand in an argon atmosphere. The last at 298, 342 and 520 endothermic peak may signify the metal-ligand bond breaking Himanshu *et al.*, 2009; Qing *et al.*, 2010.

### Biological activity

The synthesized ligands and its complexes were screened for their biological activity against some bacterial strains (*Escherichia coli* and *Enterobacter(G<sup>-</sup>) Bacillus subtilis* and *Staphylococcus aureus* (G<sup>+</sup>)). 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 Rahman *et al.*, 2004. The measured size of inhibition zones against growth of different microorganisms are summarised in table7 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 (HL<sup>1</sup> and HL<sup>2</sup>) 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 theory Singh *et al.*, 2004. Therefore, the chelation decreases the

**Table 7:** Biological activity of compounds.

Gram negative (G+)		Gram negative (G-)		Compounds
Staphylococcus aureus (G+)	Bacillus subtilis (G+)	Enterobacter (G-)	Escherichia coli (G-)	
–	–	–	–	Control
15	20	–	–	HL <sup>1</sup>
-	–	–	–	HL <sup>2</sup>
10	12	7	3	[Co(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]
5	2	11	2	[Ni(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]
23	15	20	17	[Cd(L <sup>1</sup> L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> ]

polarity of the metal atom that resulted in the partial sharing of its positive charge with donor group and possible  $\pi$ -electron delocalisation over the whole ring. Cadmium complex showed almost the higher antibacterial activity, compared with other compounds. This due to their molecular weight and their electronic configuration ( $d^{10}$  system), compared with other metal complexes Singh *et al.*, 2004; Tweedy *et al.*, 1964.

### Conclusion

The preparation and characterisation of mixed ligands and their complexes are described. This was based on the preparation of two sorts of ligands; the azo-linked Schiff-base ligand that obtained by reaction of the precursor with  $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CHO}$ . The mixed ligand complexes were achieved by adding the HL<sup>1</sup> and HL<sup>2</sup> 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 six coordinate complexes.

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