

## METAL COMPLEXES OF CURCUMIN AND DMB LIGAND , GEOMETRICAL AND BIOLOGICAL

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### ABSTRACT

This study was aimed to investigate synthesis and characterization of two ligands type (azo-linked Schiff-base) with its complexes. Precursor (W) obtained by reaction of diazonium salt of 1-Naphthyl amine with O-tolidin in water as a solvent *via* 2:1 mole ratio. Azo-linked Schiff-base ligands synthesized *via* the reaction of 3, 3'- dimethyl-5,5'-bis((E)-pyridin-3-yl diazenyl)-[1,1'-biphenyl]-4,4'-diamine with curcumin or dibenzyl methan for obtaining 4, 4', 4'', 4'''- ((1E, 1'E, 6E, 6'E) - ( 3, 3'- dimethyl-5, 5'-bis((E)-pyridin-3-yl diazenyl)-[1,1'-biphenyl]-4,4'-diyl) bis (azanelylidene)) bis (5-hydroxyhepta-1,6-diene-1,7-diyl-3-ylidene))tetrakis(2-methoxyphenol) ( $H_2L^1$ ) or 3,3'-((3,3'-dimethyl-5,5'-bis((E)-naphthalen-1-yl diazenyl)-[1,1'-biphenyl]-4,4'-diyl)bis(azanelylidene))bis(1,3-diphenylpropan-1-ol) ( $H_2L^2$ ). Complexes synthesis achieved *via* reaction of the metal ion salts CoII, MnII, CuII, NiII and CdII with azo-linked Schiff-base ligands within (2-1) mole ratio. Characterization of prepared ligands and complexes through spectroscopic and analytical techniques included; conductance, microanalysis, thermal analysis and magnetic susceptibility (for complexes) measurements along with NMR, UV-Vis and FTIR spectroscopies

**Keywords:** azo , curcumin , di benzylmethan, schiff base, , tolidin , 1-naphthyl amine

\* Part of Ph.D. dissertation of 1<sup>st</sup> author



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### INTRODUCTION

The functional group (-N=N-) characterizes azo compounds (Reham & Hassan , 2022), which may use as dyes and the most synthetic important colorant agent, widely applied in: paper manufacturing, printing and textile, etc. Azo compounds have the ability to have biological effectiveness (Rehab & Al-Hassani, 2016). Reaction of the azo compounds with schiff bases formed Azo-schiff base type compounds (Haider & Karam, 2022). The academic and applied researcher focused on this type of compounds, which have been used in various fields in science, medicine and technology. Azo-schiff base compounds were used in manufacturing of dyes, which belong to coloration character intensity of these ligands, this may resulted from the delocalization of pi electrons, also the containment of the azo methane and azo

moieties, enabling their uses in dyeing fabrics and polyester, acrylic and nylon threads (Bashandy *et al*, 2016, El-Sonbati *et al*, 2016). In our labs, it was reported many azo linked Schiff bases and their transition metal complexes, (Enaam *et al*, 2020, Hasan *et al*, 2013). The multiple functional groups presence in a molecule improves properties, therefore; in our research, we attempted to synthesize, characterize and bio-reactivity study of ligands type azo-Schiff base owing both imine and azo moieties along with hetero and homo aromatic rings, the ligands derived from curcumin (Zaid & Alrubeii, 2023) or dibenzyl methan with tolidine and 1-Naphthyl amine. Also transition metal complexes prepared and studied.

### MATERIALS AND METHODS

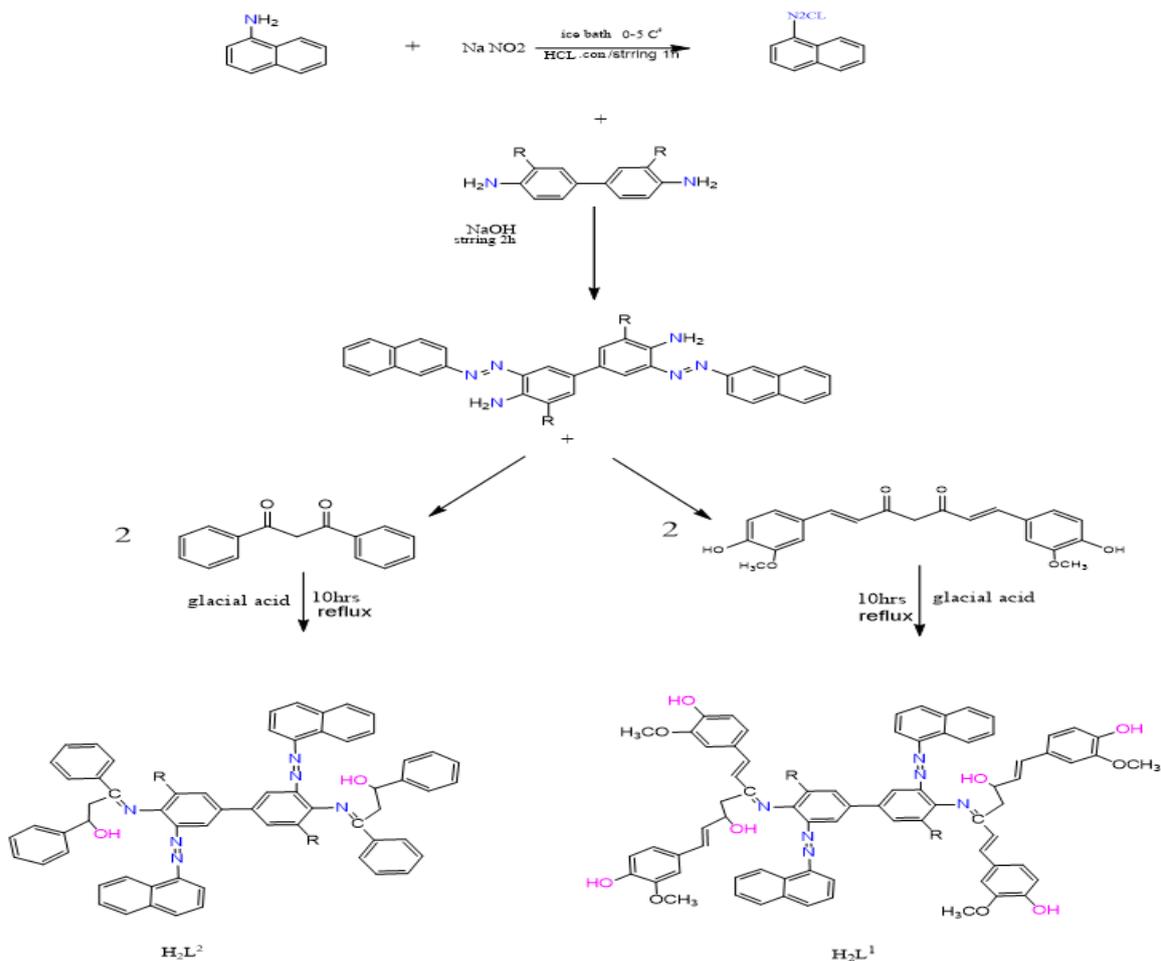
FT-IR spectral data were determined using Fourier Transform Infrared Spectra apparatus

FTIR-600, as Potassium bromide discs, in 4000-400  $\text{cm}^{-1}$  range. An internal reference, tetra methyl silane (TMS), in  $\text{DMSO-d}_6$  solvent to assess some synthesized compounds  $^1\text{H}$  and  $^{13}\text{C}$ - NMR spectra using a Bruker 400 MHz instrument (100 MHz for  $^{13}\text{C}$  and 400 MHz for  $^1\text{H}$ ). The electronic (U.V-Vis) spectral data were obtained with a quartz cell of (1.0), at 25 °C, with Shimadzu UV-160 spectrophotometer using  $\text{DMSO-d}_6$  as a solvent. Electrospray (+) mass spectrophotometer type a Sciex Esi mass analyzer to obtain mass spectra, Euro EA 3000 apparatus were used for the ligands' elemental analysis (C.H.N.) and Shimadzu (A.A) 680G atomic absorption spectrophotometer for metal content determinations. Stuart apparatus of type SMP40 electro-thermal was used to estimate melting points of prepared compound.

### Synthesis of azo ligands

Figuer (1) shows precursor compound (W) were synthesized by dissolving 1-naphthyl amain (0.5g, 3.49 mmol) in water (10 ml) and

3 ml of hydrochloric acid, this mixture was agitated until a clear solution obtained, and it was then stored at a temperature of 0 to 5 °C. Then, a drop wise addition of a sodium nitrite aqueous solution (1g, 14.49mmol) in 5ml of water was made while maintaining a pH of about (Eman *et al*,2020) and a temperature below 5°C. Tolidine (( 0.37g, 1.74 mmol) solutions, and an equivalent volume of NaOH was added to the diazonium salt solution, before being dried at pH 6-7, the precipitate was filtered and repeatedly rinsed with cold water. After that curcumin or dibenzayl methan solution was added (0.74g, 2.01mmol ) or (0.43g,1.92mmol) respect to azo derivative (0.5g, 0.96mmol) W with a few drops of glacial acetic acid as a catalyst, refluxed 10 hrs., before the precipitate compound was obtained by filtration, the solution leaved at room temperature for about 15 minutes.(Said *et al*,2017) Table (1): displays the physical properties of the synthesised precursors and ligands



Figuer 1. Synthetic route for Precursors and ligands

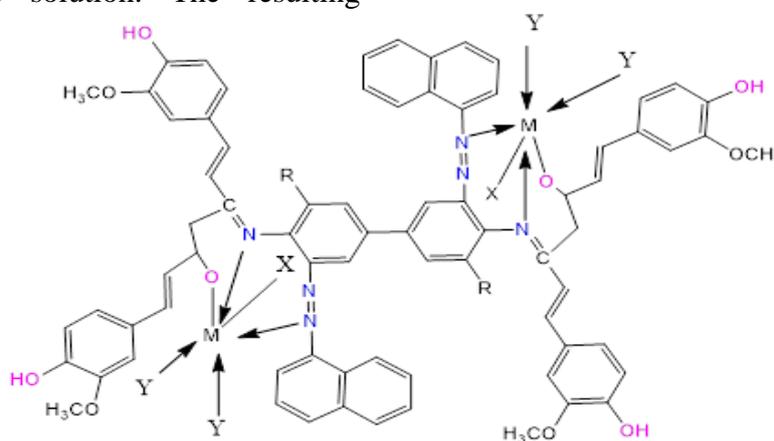
**Table 1. colours, melting points, Weight and yields of the precursor and ligand**

m.p.	Color	Yield (%)	Weight of azo (g)	Weight of amine (g)	Precursor °C
Dark Purpl	165	85%	1.54	0.5	W
109	Violat	94%	1.11	0.5	H <sub>2</sub> L <sup>1</sup>
79	Violat	95%	0.85	0.5	H <sub>2</sub> L <sup>2</sup>

### Synthesis of complexes

Figure (2) shows synthesis of complexes achieved through adding an ethanolic potassium hydroxide solution equivalent amount (10 ml with heating and stirring to a solution of (0.5 g, 0.40 mmol) or (0.5g, 0.53mmol ) from the ligands [H<sub>2</sub>L<sup>1</sup>] or [H<sub>2</sub>L<sup>2</sup>] dissolved in (40 ml) of ethanol. Equivalent amount of each metal salt [CdII, MnII, CoII, NiII and Cu II dissolved in 10 ml ethanol was added to ligands solution. The resulting

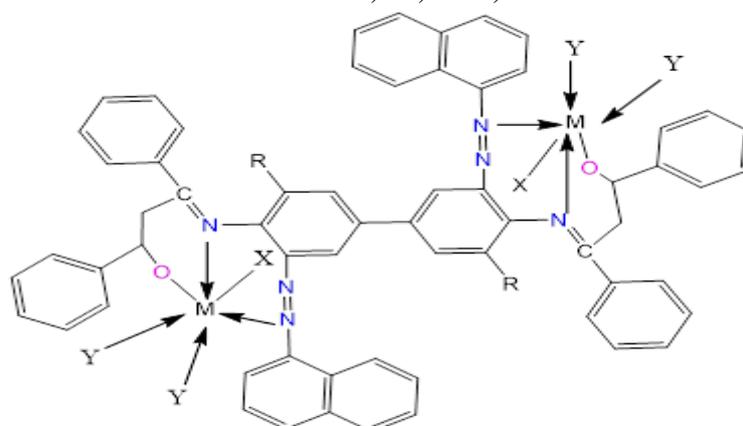
mixture was refluxed for 2 hrs., then washed with ethanol and recrystallized. Analysis of microelements and calculated values include: practically C (72%) H (5.5%) N (7.2%); theoretical C (73%) H (5.3%) N (7.9%); [H<sub>2</sub>L<sup>2</sup>]: practically C (71%) H (5.5%) N (9.9%) theoretical: C (72%) H (5.8%) N (9.7%). (Hasan &Fluorescence, 2017). Table (2)and (3): displays the physical properties of the synthesised complexes.



H<sub>2</sub>L<sup>1</sup>

Were M=Mn, Ni, Co , Y=H<sub>2</sub>O X=Cl

Were M= Cu , Cd, X=Cl, Y=0



H<sub>2</sub>L<sup>2</sup>

Were M=Mn, Ni, Co ,X=Cl, Y=H<sub>2</sub>O

Were M= Cu , Cd, X=Cl, Y=0

**Figurer 2. Synthetic route of complexes**

**Table 2. Some physical properties for complexes of [H<sub>2</sub>L<sup>1</sup>]**

Complex of Metal ions	Molecular Formula	M.Wt	Weight of metal salt(g)	The complex Weight(g)	color	m.p.C	Yield
[Co <sub>2</sub> (H <sub>2</sub> L <sup>1</sup> )(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]	C <sub>76</sub> H <sub>74</sub> C <sub>02</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>14</sub>	1475.76		0.3 0.33	green	>300*	91
[Ni <sub>2</sub> (H <sub>2</sub> L <sup>1</sup> )(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]	C <sub>76</sub> H <sub>74</sub> Ni <sub>2</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>14</sub>	1467.76		0.5 0.31	red	>300*	86
[Cu <sub>2</sub> (H <sub>2</sub> L <sup>1</sup> ) Cl <sub>2</sub> ]	C <sub>68</sub> H <sub>60</sub> Cu <sub>2</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>10</sub>	1417.76		0.2 0.20	Brown	>300*	86
[Cd <sub>2</sub> (H <sub>2</sub> L <sup>1</sup> ) Cl <sub>2</sub> ]	C <sub>68</sub> H <sub>60</sub> Cd <sub>2</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>10</sub>	1515.76		0.3 0.32	Yellow	>300*	86
[Mn <sub>2</sub> (H <sub>2</sub> L <sup>1</sup> )(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]	C <sub>76</sub> H <sub>74</sub> Mn <sub>2</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>14</sub>	1473.76		0.3 0.32	red	>300*	88

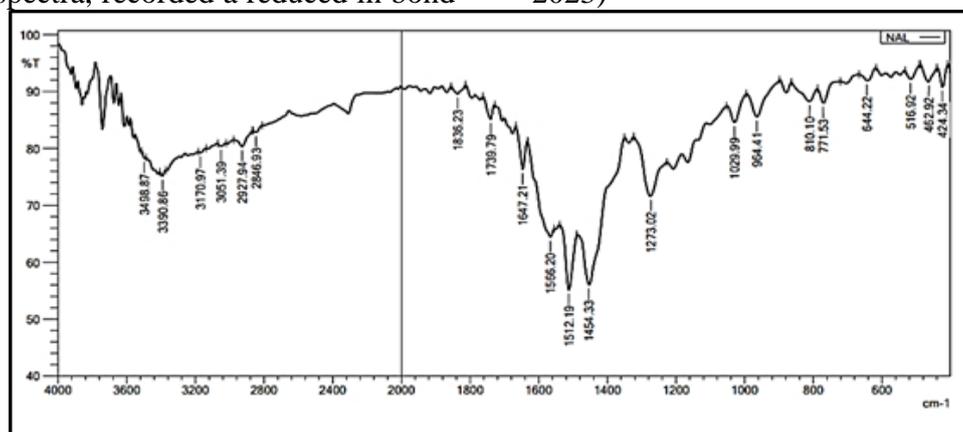
**Table 3. Some physical properties for complexes of [H<sub>2</sub>L<sup>2</sup>]**

Complex of Metal ions	Molecular Formula	M.Wt	Weight of metal salt(g)	The complex Weight(g)	color	m.p.C	Yield
[Mn <sub>2</sub> (H <sub>2</sub> L <sup>2</sup> )(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]	C <sub>64</sub> H <sub>54</sub> Mn <sub>2</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	1188.75		0.5 0.32	red	159	88
[Co <sub>2</sub> (H <sub>2</sub> L <sup>2</sup> )(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]	C <sub>64</sub> H <sub>54</sub> Co <sub>2</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	1189.5		0.2 0.21	Green	175	84
[Ni <sub>2</sub> (H <sub>2</sub> L <sup>2</sup> )(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]	C <sub>64</sub> H <sub>54</sub> Ni <sub>2</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	1182.5		0.5 0.57	Orange	197	90
[Cu <sub>2</sub> (H <sub>2</sub> L <sup>2</sup> ) Cl <sub>2</sub> ]	C <sub>68</sub> H <sub>60</sub> Cu <sub>2</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>2</sub>	1132.5		0.3 0.31	Green	194	86
[Cd <sub>2</sub> (H <sub>2</sub> L <sup>2</sup> ) Cl <sub>2</sub> ]	C <sub>68</sub> H <sub>60</sub> Cd <sub>2</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>2</sub>	1230.5		0.3 0.33	Yellow		

## RESULTS AND DISCUSSION

The precursors produced using a conventional azo dye method. The 2:1 mole ratio reaction between 1-Naphthyl amine diazonium salt and O-Tolidine. Look at Scheme 1. precursors W reacted with curcumin or di benzyl methan to produce [H<sub>2</sub>L<sup>1</sup>] and [H<sub>2</sub>L<sup>2</sup>], which were then used as the ligands of azo-linked Schiff bases. (Scheme 1 and Scheme 2). The complexes created by reacting the metal salts of Cd II, Mn II, Co II, Ni II, and Cu II in a 2:1 mole ratio with the azo-linked Schiff base ligands. Elemental analyses, electronic spectra, FT-IR data and magnetic susceptibility measurements, all supported the novel compounds' existence. The suggested structures supported by the analytical results in Table 4. The complexes' molar conductance in DMSO solvents is indicative of electrolyte and non-electrolyte behavior. As a result of complex formation, the  $\nu(\text{C}=\text{N})$  at ca. (1647, 1639) cm<sup>-1</sup> in the free ligands were shifted and appeared at lower frequencies in the complexes spectra, recorded a reduced in bond

order, and appeared at (1620-1624) cm<sup>-1</sup>. Bands in the (1400–1454) cm<sup>-1</sup> range were categorized as belonging to the (N=N) azo group. This shift in the two groups insured the involvement and coordination of the C=N and N=N moieties to the metallic center. (Baidaa *et al*, 2021). The delocalization of the metal electron density into the ligand -system, which reveals the participation of the azo and imine groups in the coordination, may be the cause of the shift in frequency in these bands. (HOMO-LUMO), where HOMO is the highest Lowest Unoccupied Molecular Orbital, or HOMO, is the highest occupied molecular orbital and. (Mustafa *et al*, 2021) The complexes exhibited at lower frequencies bands around (401–497) and (501– 578) cm<sup>-1</sup> which may referred to (M–O) and (M– N) stretching vibration respectively. The (M–O) band noticed at higher frequency ranges compared to (M–N), this could belong to the change in (dipole moment) value for M–O when compared to M–N. (Dhekra & Mahdi, 2023)



**Figure 3. FT-IR spectrum of H<sub>2</sub>L<sup>1</sup>**

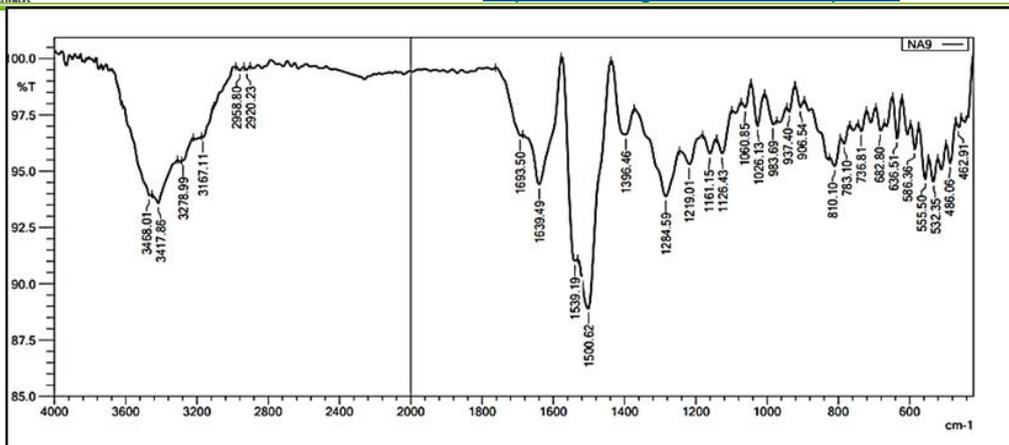


Figure 4. FT-IR spectrum of  $H_2L^2$

### Mass spectrometer

Mass spectra of the Schiff base ligand,  $[H_2L^1]$  spectrum in Figure (5) exhibits a distinct molecular ion peak at  $m/z = 1222.76$ amu, which coincides ( $M + 1$ ) with the molecular composition of the Schiff base ligand ( $C_{76}H_{68}N_6O_{10}$ ). The fragments are shown by a series of peaks in the  $[H_2L^1]$  ligand's spectrum at  $m/z$  650, 574, 524, 433, 496, 212, 369, 195,

247, 144, and 128 amu. These peaks' intensity reveals the stability of the parts. in Figure (6) A peak in the mass spectrum of  $[H_2L^2]$  at  $m/z = 937$  amu, attributable to  $[M+1]$  of the ligands' chemical formula ( $C_{64}H_{52}N_6O_2$ ), Also observed at the same time peaks at 863, 786, 639, 485, 383, 225, 212, 156, 149, 160, 110, 136, 88, 78, and 56 amu, which the fragments. (Ali *et al*,2007).

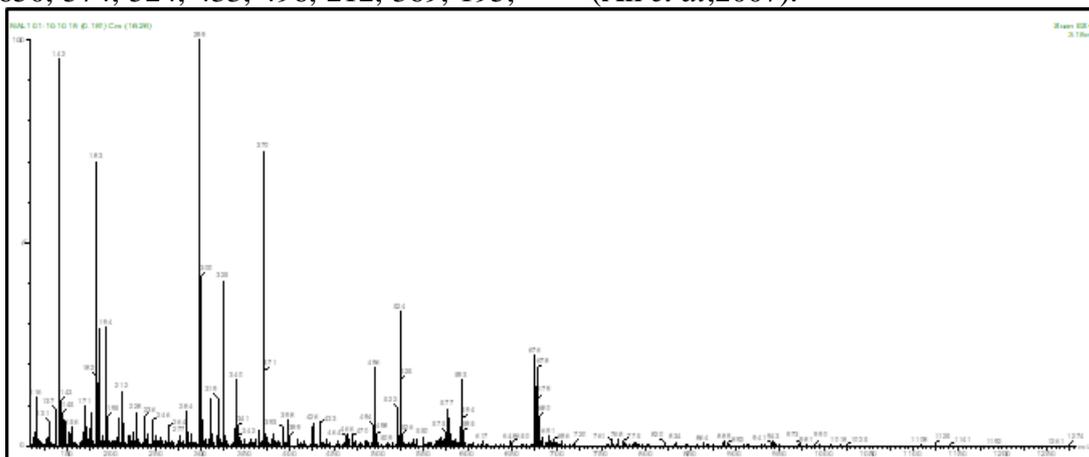


Figure 5. mas spectrum of

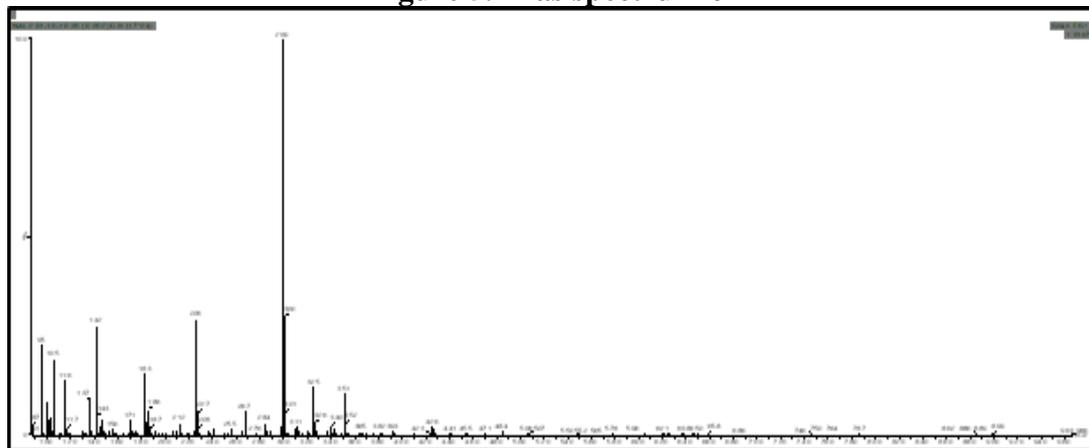


Figure 6. mas spectrum of  $H_2L^2$

**Electronic spectral data for the ligand and complexes:** The chelation between metal ions

and the azo linked Schiff base ligand causes the  $\pi-\pi^*$  and  $n-\pi^*$  transitions of the conjugated

chromophore to change in energy, which is connected to the blue shift behavior of complexes. It is possible to attribute the considerable hypochromic shift in the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transition regions caused by the dye's complexation with the metal ion to the complex's M-L charge transfer transition. An electronic transition in a conjugated system, in which a metal may or may not participate and may be assigned to M-L charge transfer transition for the complexes, is thought to be the cause of the light absorption in metal chelates, which is thought to occur in the UV area. (Mohammad *et al.*, 2010)

The absorption peaks for  $H_2L^1$  and  $H_2L^2$  are (213, 213), (212, 345) nm, respectively, relating to overlaps of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  are caused and (422, 424) Due to the transition of the N=N group (24). The Mn(II) complex  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  transition assigned by peak at (819), (717) nm indicates a deformed octahedral geometry around the Mn(II) ion for  $H_2L^1$  and  $H_2L^2$  respectively. Due to the C.T and  ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  transitions, the Co(II) complex exhibits additional peaks in the d-d region at 422, 618, and 776 nm, and 424, 745 nm in  $[H_2L^1]$  and  $[H_2L^2]$  respectively. The octahedral geometries around the Co atom in Co(II) complexes with this spectrum are deformed. (Shaima & Salih, 2022) A deformed octahedral geometry around the Ni atom was corroborated by peaks in the Ni(II) complex at

445 and 777 nm and 359, 709 nm that were attributed to C.T and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  transitions, for  $[H_2L^1]$  and  $[H_2L^2]$  respectively (Muntaha & Majeed, 2023, Said *et al.*, 2020). The  $H_2L^1$  and  $H_2L^2$  Cu(II) complex spectrum has shown peaks in the regions (420, 772) nm and (364, 748) nm due to C.T and d-d transitions type  ${}^2B_{1g}(F) \rightarrow {}^2B_{2g}(F)$  respectively. The spectrum of the  $[H_2L^1]$  and  $[H_2L^2]$  Cd(II) complex exhibited peaks at (267, 345) and (268, 421) assigned to ligand  $\pi$ - $\pi^*$  and M  $\rightarrow$  L charge transfer. (Naureen *et al.*, 2021)

#### ${}^1H$ AND ${}^{13}C$ -NMR spectra of azo

The NMR spectra were recorded in DMSO- $d_6$  (dimethyl sulfoxide) using tetramethylsilane (TMS) as standard. Table 4 shows the spectral data of  ${}^1H$ NMR of the azo compound W, as displayed in Figure (7) The resonance at ( $\delta$ =8.00-9.00) ppm referred for four ( $NH_2$ ) protons, the (C-H) aromatic protons showed signals at ( $\delta$ =7.51-7.94) ppm, while the signals referring to the aliphatic  $CH_3, CH_2$  appeared at ( $\delta$ =1.98, 2.37) ppm (7) The  ${}^{13}C$ -NMR spectral data for (W) shown in Table (4), the spectrum revealed aromatic carbon atoms are located at ( $\delta$ =123.52-129.80) ppm, while the carbon of the imine ( $C=N$ ) group signal appeared at ( $\delta$ =185) ppm. The chemical shift at ( $\delta$ =123.58-129.88) ppm may referring to the (C-N, C-O and C-C) In Figure (8). The difference in signals results from the difference in the electronic environment surrounding the groups.

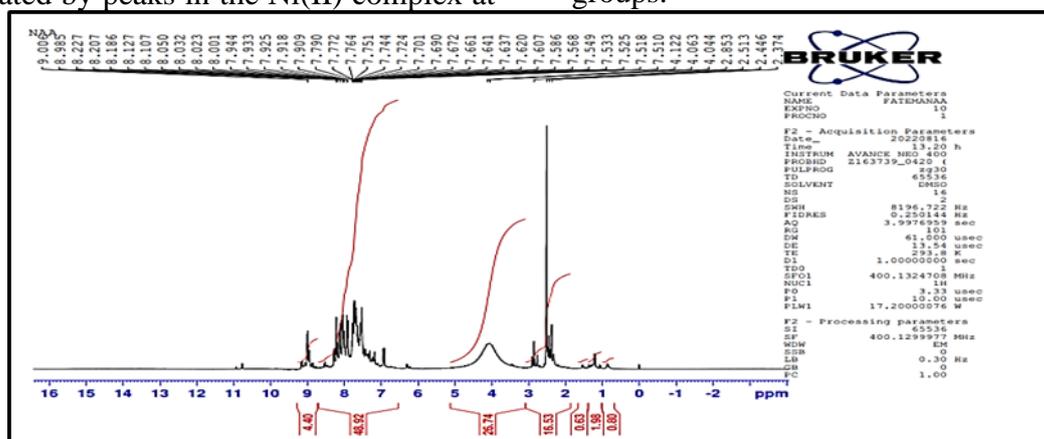


Figure 7. Spectrum of  ${}^1H$ -NMR for (W)

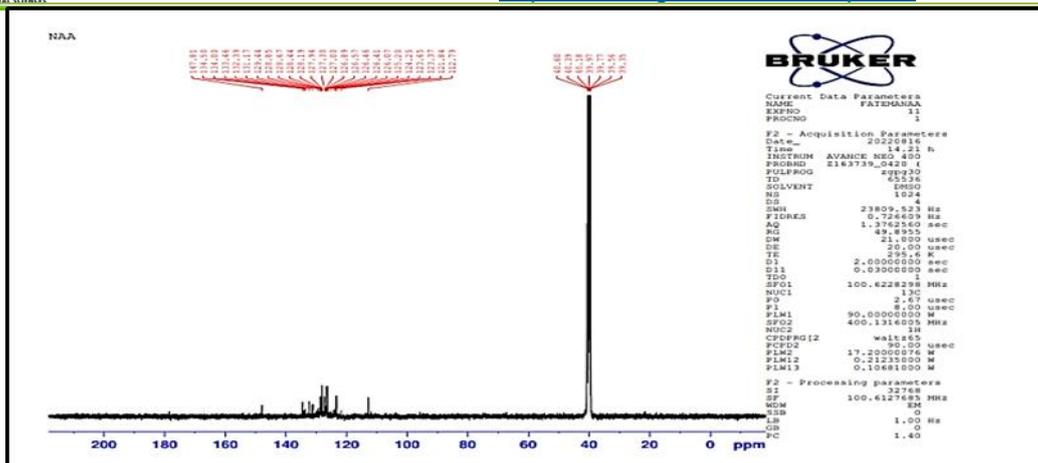


Figure 8. Spectrum of <sup>13</sup>C-NMR for (W)

Table 4. <sup>13</sup>CNMR –H-NMR and spectral data of the W

Funct. Group	H-NMR (ppm)	<sup>13</sup> C NMR (ppm)
C=N	—	185
-NH <sub>2</sub>	8.00-9.00	—
-CH <sub>3</sub>	1.98	2.37-2.85
-CH <sub>2</sub>	2.37-2.85	40.18-49.87
-CH arom	7.51-7.54	123.52-129.80
-C-N ,C-O and	—	132.16-136.70
-C-C-	—	—
C=C	—	93.72
DMSO-d <sub>6</sub>	4.04-4.12	—

### Schiff base ligands [H<sub>2</sub>L<sup>1</sup>], [H<sub>2</sub>L<sup>2</sup>] <sup>1</sup>H-nmr and <sup>13</sup>C –nmr spectra

In Figure (9) and (11), the OH groups (resulted from tautomerization of the curcumiin and dibenzyl methan moiety resonances shifted to the upper field and appeared at (6.05), and (6.89) for [H<sub>2</sub>L<sup>1</sup>] and [H<sub>2</sub>L<sup>2</sup>] respectively. This may attributed to the intramolecular hydrogen bonding (OH...N=C). (Muna & Kareem, 2020) While (CH<sub>3</sub>) protons were given the chemical shift between (1.21) and (1.07) ppm. The (-CH<sub>2</sub>) was attributed to the strong peaks at (2.51) and (2.50) ppm. The aromatic protons of [H<sub>2</sub>L<sup>1</sup>] and [H<sub>2</sub>L<sup>2</sup>] may be attributed to the numerous chemical shifts around (7.17-8.98) and (7.36-8.97) ppm, respectively. The chemical shift caused by the DMSO-d<sub>6</sub> protons was lastly seen in the spectra at (3.80-40.62) and (3.42- 4.89) ppm (Aemed & Enaam, 2022; Wasan *et al*, 2019). <sup>13</sup>C-NMR in

Figure(10) and (12) the [H<sub>2</sub>L<sup>1</sup>] and [H<sub>2</sub>L<sup>2</sup>] regions with ppm values between (δ=111.81–130.80) and (δ=111.69–129.32) can be assigned to the C-O, C-N, and C-C groups in the two ligands respectively. Aromatic (C=C) for [H<sub>2</sub>L<sup>1</sup>] and [H<sub>2</sub>L<sup>2</sup>] is responsible for the chemical shift at the ranges of (δ=131.17-141.18) and (δ= 133.50-147.80) ppm. While the carbon atom (C=N) azomethine groups in the [H<sub>2</sub>L<sup>1</sup>] and [H<sub>2</sub>L<sup>2</sup>] are responsible for the chemical shifts at (δ=148.46) and (δ=185.80) ppm, respectively. signals at (δ=93.72) and (δ=93.72) refers to (C-OH) alif for [H<sub>2</sub>L<sup>1</sup>] and [H<sub>2</sub>L<sup>2</sup>], respectively. In the azo-linked Schiff base compounds, the carbonyl group C=O that was produced by the tautomerization of the dipnzeyl methan moiety was lastly observed at about (δ=183.68) and (δ=196.20) ppm for [H<sub>2</sub>L<sup>1</sup>] and [H<sub>2</sub>L<sup>2</sup>] respectively. (Kheirkhahi *et al*, 2021)



### Thermal analysis

Three peaks in Figure (13) could be seen on the  $[\text{Ni}_2(\text{H}_2\text{L}^2)(\text{H}_2\text{O})_2\text{Cl}_2]$  TGA curve. The first peak was discovered between (58.03 - 102.70 °C) and it was accompanied with a mass loss calculation of 8.08% that was attributed to the mass loss of  $(\text{C}_6\text{H}_{12})$  molecules. The second peak, which was discovered between (339.05-

411.61°C), was accompanied by an 7.18% calculated mass loss due to the breakdown of  $(\text{N}, \text{H}_2\text{O}, 2\text{Cl})$  molecules. The third peak was found between (428.87 – 535.46 °C) with a mass loss of 6.970% calculated that was attributed to the mass loss of  $(\text{N}, \text{H}_2\text{O}, 2\text{Cl})$  molecules. (Ali *et al*,2007).

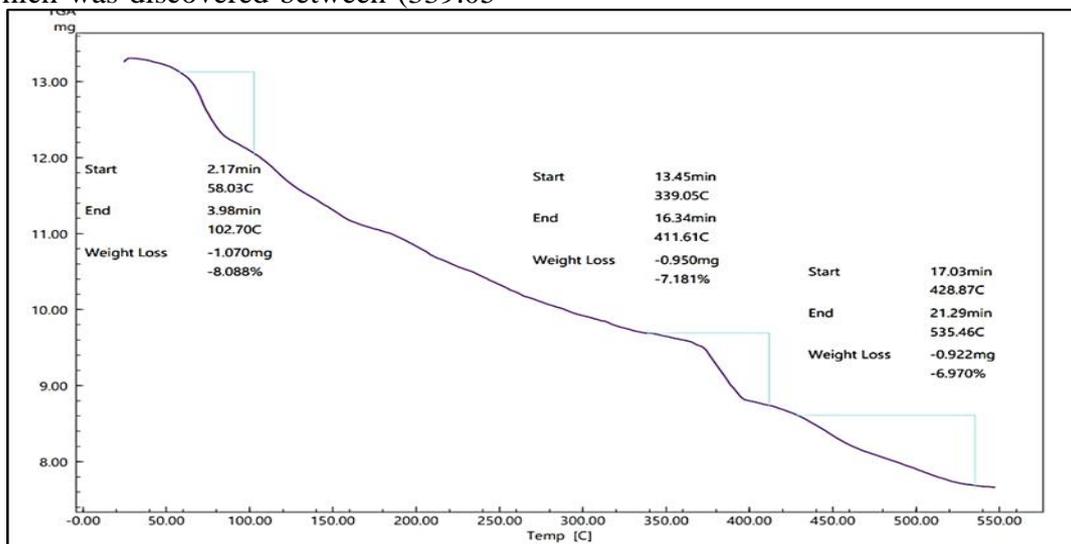


Figure 13. TGA curves of the  $[\text{Ni}_2(\text{H}_2\text{L}^2)(\text{H}_2\text{O})_4 \text{Cl}_2]$

**Molar conductivity measurement for the complex:** Molar conductivity measurement for the complexes A compound's conductance can be calculated using its measurement of conductivity nonelectrolyte with concentrate  $(1 \times 10^{-3})$  nature of the of the  $(\text{H}_2\text{L}^1)$  and  $(\text{H}_2\text{L}^2)$  complexes . The molar nonelectroconductivity of complexes listed in Table (5) and (6) in (DMSO) solvent

Table 5. The molar conductivity of the  $(\text{H}_2\text{L}^1)$  complexes

Compound	No Compound m S.cm <sup>2</sup> molar <sup>-1</sup> Ratio
$[\text{Mn}_2(\text{H}_2\text{L}^1)(\text{H}_2\text{O})_4 \text{Cl}_2]$	19.5
$[\text{Co}_2(\text{H}_2\text{L}^1)(\text{H}_2\text{O})_4 \text{Cl}_2]$	16.7
$[\text{Ni}_2(\text{H}_2\text{L}^1)(\text{H}_2\text{O})_4 \text{Cl}_2]$	23.2
$[\text{Cu}_2(\text{H}_2\text{L}^1)\text{Cl}_2]$	18.9
$[\text{Cd}_2(\text{H}_2\text{L}^1)\text{Cl}_2]$	17.8

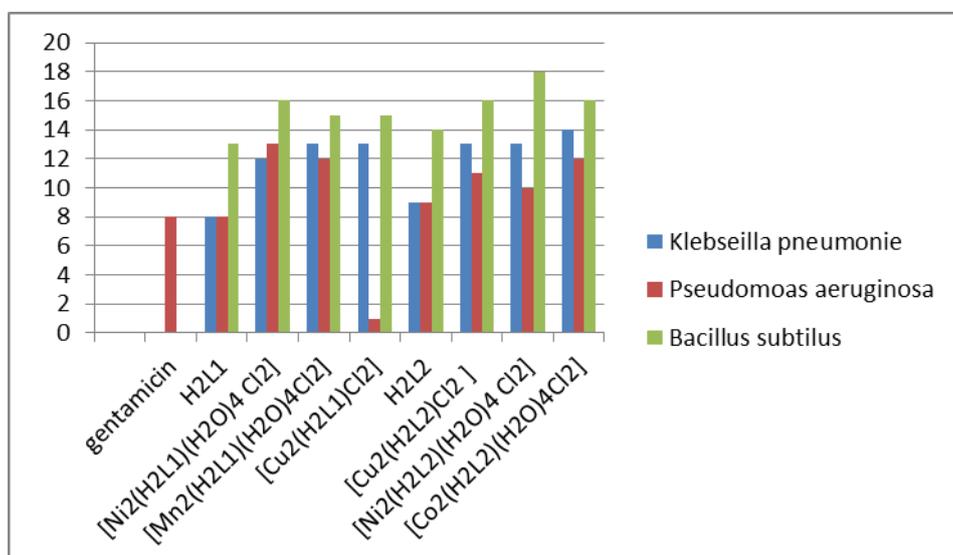
Table 6. The molar conductivity of the  $(\text{H}_2\text{L}^2)$  complexes

Compound	No Compound m S.cm <sup>2</sup> molar <sup>-1</sup> Ratio
$[\text{Mn}_2(\text{H}_2\text{L}^2)(\text{H}_2\text{O})_4 \text{Cl}_2]$	20.4
$[\text{Co}_2(\text{H}_2\text{L}^2)(\text{H}_2\text{O})_4 \text{Cl}_2]$	21.2
$[\text{Ni}_2(\text{H}_2\text{L}^2)(\text{H}_2\text{O})_4 \text{Cl}_2]$	21.6
$[\text{Cu}_2(\text{H}_2\text{L}^2)\text{Cl}_2]$	20.7
$[\text{Cd}_2(\text{H}_2\text{L}^2)\text{Cl}_2]$	19.3

**Biological activity complexes and ligands:** In addition to the one species of fungi studied (*Candida*), microbiological activity against Gram-positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*) and Gram-negative bacteria (*Klebsiella pneumonia* and *Pseudomonas aeruginosa*) (Zaid & Alrubei, 2023) for the ligands and their metal complexes were tested in Table(7). Alone solution of DMSO studied and showed no activity against organisms. The test organisms inoculated with agar media, and (100 µg/ml) a solution of the tested compound was separately, placed in a 6 mm diameter plates in the agar medium. The inhibition zones were measured after 24 hours' incubation,. The bacteria and fungi were chosen because of their well-known effects on a range of diseases; they also show different levels of resistance to drugs and drug compounds. The zone of inhibition for the ligand and its complexes was effective. ( Khadij & Hassan, 2022)

**Table 7. inhibition zone ligands and complexes against pathogenic bacteria and fungi**  
**Inhibition zone mm ligands and complexes**

Complexes	<i>Klebsiella pneumoniae</i>	<i>Pseudomonas aeruginosa</i>	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Candida albicans</i>
gentamicin	-	8	-	20	20
H <sub>2</sub> L <sup>1</sup>	8	8	13	16	18
[Ni <sub>2</sub> (H <sub>2</sub> L <sup>1</sup> )(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]	12	13	16	15	20
[Mn <sub>2</sub> (H <sub>2</sub> L <sup>1</sup> )(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]	13	12	15	16	16
[Cu <sub>2</sub> (H <sub>2</sub> L <sup>1</sup> )Cl <sub>2</sub> ]	13	1	15	17	20
H <sub>2</sub> L <sup>2</sup>	9	9	14	15	16
[Cu <sub>2</sub> (H <sub>2</sub> L <sup>2</sup> )Cl <sub>2</sub> ]	13	11	16	15	16
[Ni <sub>2</sub> (H <sub>2</sub> L <sup>2</sup> )(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]	13	10	18	16	18
[Co <sub>2</sub> (H <sub>2</sub> L <sup>2</sup> )(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]	14	12	16	15	18



**Figure 14. The inhibition zones diameter (mm) against (*K. pneumoniae* , *P. aeruginosa*, *S. aureus*, *B. Subtilis*, and *Candida***

### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

### DECLARATION OF FUND

The authors declare that they have not received a fund.

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المعقدات الفلزية لليكنيدات الكركمين وثنائي بنزيل ميثان ، الشكل الهندسي، ودراسة الفعالية البيولوجية

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المستخلص

هدفت هذه الدراسة إلى بحث تخليق وتوصيف نوعين من الروابط (azo-linked Schiff-base) مع مركباتها. تم الحصول على المركب الأولي (W) من خلال تفاعل Naphthyl amine-1 مع O-tolidin في الماء كمذيب بنسبة مولية 2:1. يتم تصنيع روابط Azo-linked Schiff-base عن طريق تفاعل 3,3'-dimethyl-5,5'-bis((E)-pyridin-3-ylidiazanyl)-[1,1'-biphenyl]-4,4'-diamine with curcumin or dibenzyl methan for obtaining 4, 4', 4'', 4'''- ((1E, 1'E, 6E, 6'E) - (3, 3'- dimethyl-5, 5'-bis((E)-pyridin-3-ylidiazanyl)-[1,1'-biphenyl]-4,4'-diyl) bis (azaneylylidene)) bis(5-hydroxyhepta-1,6-diene-1,7-diyl-3-ylidene)) tetrakis (2-methoxyphenol) (H2L1) or 3,3'-((3,3'-dimethyl-5,5'-bis((E)-naphthalen-1-ylidiazanyl)- [1,1'-biphenyl]- 4,4'-diyl) bis (azaneylylidene)) bis (1,3-diphenylpropan-1-ol) (H2L2). تم تحضير هذه المركبات المعقدة عن طريق تفاعل أملاح أيونات المعادن Coll و MnII و CuII و NiII مع روابط azo-linked Schiff-base المرتبطة برابطة azo-linked بنسبة مولية (2:1). شملت تقنيات التحليل الطيفي والتحليلي توصيف الروابط والمركبات المحضرة، بما في ذلك قياسات التوصيلية، والتحليل الدقيق، والتحليل الحراري، والحساسية المغناطيسية (للمركبات المعقدة)، بالإضافة إلى مطيافية الرنين النووي المغناطيسي، ومطيافية UV-Vis، NMR، والتحليل الطيفي FTIR.

الكلمات المفتاحية : قواعد كشف ,ازو,نفثايل امين, تولودين,كركمين, داي بنزا امين

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