

New Metal Complexes with AZO ligand; Synthesis, Spectral Characterisation and Biological Evaluation

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ABSTRACT

The new Azo ligand and its metal complexes have been prepared and characterized. The reaction of 4-nitroaniline and 2-hydroxy-1-naphthaldehyde in a 1:1 mole ratio resulted in the synthesis of ((E)-2-hydroxy-3-((4-nitrophenyl) diazenyl)-1-naphthaldehyde) (HL). The separation of monomeric complexes was accomplished by reacting ((E)-2-hydroxy-3-((4-nitrophenyl) diazenyl)-1-naphthaldehyde) (HL) with Cr, Mn II, Co II, Ni II, and Cu II metal ions in a mole ratio of 2:1 (L: M). Elemental microanalysis, magnetic susceptibility, conductance, FT-IR, electronic spectra, and ¹H-NMR, ¹³C-NMR, and mass spectra were among the analytical and spectroscopic techniques used to describe the products. Based on the data collected during the characterization process, six coordinates were determined. The ligand and its complexes were tested against certain bacteria and fungi. The findings acquired suggested that the metal complexes are more active against a variety of organisms have been studied as compared to the free ligand.

Keywords: ((E)-2-hydroxy-3-((4-nitrophenyl) diazenyl)-1-naphthaldehyde); Azo ligand; Candida and Rhizopus porium; 2-hydroxy-1-naphthaldehyde; Metal Complexes.

INTRODUCTION

Azo compounds or dyes are distinguished by the presence of an azo group (-N=N-) in their structure that is conjugated with two separate or identical monocyclic or polycyclic aromatic or heteroaromatic systems [1,2]. Azo dyes are synthesized in two steps, the first of which is the formation of an aromatic diazonium ion from amine derivatives. The diazonium salt is then combined with an aromatic component in the following step. Azo molecules are appropriate for the biocidal treatment of textile substances as a result of their bioactivity [3]. Azo compounds are well-known for their medicinal importance and usage as antiseptics [4], antineoplastics (Anti Cancer) [5], antibacterial [6,7] antidiabetics [8], and antitumor [9]. They participate in a variety of biological processes, including carcinogenesis inhibition, protein synthesis, and nitrogen fixation [10]. Azo compounds, which are the most widely used organic photoconductive materials, have long been employed in industries photodynamic procedures, photographic or electro-photographic systems, and so on [11]. The synthesis of azo and its complexes have recently been described [12,13]. The ligand was produced by the reaction of 4-nitroaniline with 2-hydroxy-1-naphthaldehyde. The synthesized compounds were also evaluated for anti-bacterial and anti-fungal activity.

METHODS

Materials and Methods: The ligand's NMR spectra (¹H-NMR and the ¹³C-NMR) were evaluated in DMSO-d₆ with a Bruker 400 MHz instrument (400, MHz for ¹H and 100, MHz for ¹³C), using tetra methyl silane (TMS) as an internal reference. The FT-IR spectra of potassium bromide discs were recorded using FTIR-600 Fourier Transform Infrared Spectra in the range 4000-400cm⁻¹. On a Sciex Esi mass analyzer, an electrospray (+) mass spectrophotometer was used. To determine melting points, an electrothermal Stuart apparatus, type SMP40, was employed. The electronic spectra were obtained at 25 °C using a Shimadzu UV-160 spectrophotometer with a quartz cell of (1.0) cm length and a concentration of 10⁻³ mol L⁻¹ of materials in DMSO solution.

The complexes' molar conductivities were measured at 25 °C using a Eutech Instruments Cyber scan con 510 digital conductivity meter for (10⁻³ - 10⁻⁵ M solutions) of the compounds in Dimethyl sulfoxide solution.

CHN Analysis and metal content were analysed using atomic absorption spectrophotometers from Heraeus (Vario EL

and Shimadzu (A A-7000), respectively. On a 686-Titro Processor-665 Dosim A-Metrohm/Swiss, the chloride concentration of complexes was determined using the potentiometric titration method. Differential Scanning Calorimetry (DSC) was used on an STA PT-1000 Linseis Company/Germany to conduct the thermogravimetric investigation. A magnetic moments balance on Johnson Matthey was used to quantify magnetic moments at 30°C. Compounds were tested against four different bacteria and two different species of fungus.

Synthesis: Synthesis of Azo ligand ((E)-2-hydroxy-3-((4-nitrophenyl) diazenyl)-1-naphthaldehyde) (HL) 4-nitroaniline (1.38 g, 10mm) and sodium nitrite (0.69g, 10mm) were combined in 20 mL of water, chilled to 0–5°C, and then mixed with hydrochloric acid with vigorous stirring, to prepare HL according to the literature [14,15]. The cooled solution of 2-hydroxy-1-naphthaldehyde (1.72g, 10mm) and NaOH (0.4g, 10mm) was then added to the diazonium salt solution. The precipitate formed at pH 4 was filtered and rinsed many times with cold water before being dried at pH 6-7. The orange-red precipitate was filtered out and recrystallized from ethanol, yielding 2.09g (65%) with, M.P. 255°C, Figure (1)

Synthesis of Complexes: In a mixed ethanol–benzene solution, HL (0.2g, 0.62mmol) and CrCl₃·6H₂O (0.08g, 0.312mmol) were dissolved. Drops of NaOH (0.07g, 1.24mmol) were added to the aforementioned mixture. The mixture was agitated at 80°C for 2 hours before being filtered into a covered beaker. a planning Figure (2). Yields, colors, metal salt quantities, and melting points of complexes are all included in table 1.

Microbiological Evaluation: The Kirby-Bauer technique was used to investigate the sensitivities of bacteria and fungus towards the prepared substances. The colony of organisms was mixed with an (85 percentage of Sodium Chloride) solution until the suspension was established (1/2 M.C.f). A Petri plate filled with Mueller Hinton agar was used to apply this suspension to the surface. The holes were all created at the same distance and with the same amount of focus. In the wells, the favoured concentration (100 μL) of the test sample (1 mg/mL) in dimethylsulfoxide was applied. After 24 hours of incubation at 37 °C, the zone of inhibition were measured and compared to the standard values [16]. Separate studies on the effect of dimethylsulfoxide solutions on microbiological tests indicated zero activity against any bacterial or fungal strains.

Table 1: Yields, Quantities of metal salts, colors, and melting points of HL complexes

Complex of Metal ions	Weight of metal salt(g)	The complex Weight (g)	Color	m. point .°C	Yield (%)
[Cr(L) ₂] Cl	0.08	0.13	Greenish-brown	>300*	59
[Mn(L) ₂].H ₂ O	0.06	0.17	Darkbrown	>300*	77

[Co(L) ₂].H ₂ O	0.04	0.14	Yellow	>300*	63
[Ni(L) ₂].H ₂ O	0.07	0.19	Redish-brown	>300*	90
[Cu(L) ₂].H ₂ O	0.05	0.11	Yellowish- brown	>300*	52

RESULTS AND DISCUSSION

(E)-2-hydroxy-3-((4-nitrophenyl) diazenyl)-1-naphthaldehyde is an azo ligand (HL). NaNO₂, hydrochloric Acid, and Ethanol, were utilized as catalysts and as reaction mediums, respectively, in this method. In EtOH, 4-nitroaniline and 2-hydroxy-1-naphthaldehyde are reacted in a 1:1 mole ratio. The ligand acts as a tri-dentate species, with carbonyl oxygen, OH, and the azo's nitrogen atom serving as donor atoms. The ligand was reacted with Cr II, Mn II, Co II, Ni II, and Cu II metal chlorides include a 2:1 (L: M) mole ratio, resulting in the separation of six-coordinate mono-meric compounds with the general formula [M(L)₂]Cl with Cr and [M(L)₂].H₂O Mn II, Co II, Ni II, and Cu II ions in (Figure 2). The separated mono-meric substances are air stable solids that dissolve in dimethylsulfoxide and dimethylformamide, These results (Table 2) are consistent with the formula proposed. Compound conductance measurements in dimethylsulfoxide solutions revealed whether the complexes are electrolyte or non-electrolyte. C, H, N, M (Table 2), FT-IR (Table 3), and electronic spectroscopy (Table 4) all proved Azo's occurrence.

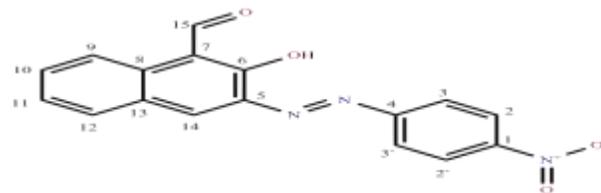


Figure 1: Chemical structure of HL.

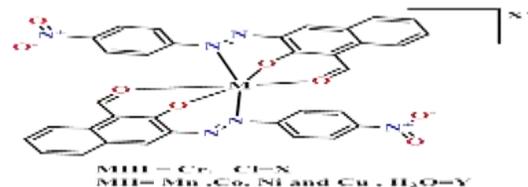


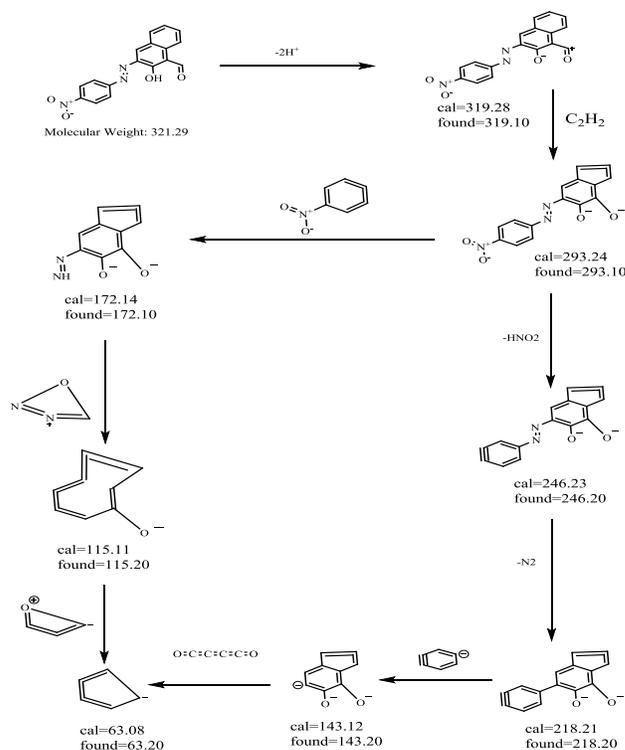
Figure 2: Chemical structure of complexes.

Table 2: Physical Properties and Microanalysis of the HL and its complexes clusters

Complexes	Molecular Formula,	M. Wt.	Microanalysis found, (calculated)%				
			C	H	N	M	Cl
[Cr(L) ₂] Cl	C ₃₄ H ₂₀ ClCrN ₆ O ₈	728.01	(56.09) 55.86	(2.77) 2.34	(11.54) 11.19	(7.14) 6.93	(4.87) 4.40
[Mn(L) ₂].H ₂ O	C ₃₄ H ₂₂ MnN ₆ O ₉	713.52	(57.23) 57.02	(3.11) 2.94	(11.78) 11.54	(7.70) 7.22	-
[Co(L) ₂].H ₂ O	C ₃₄ H ₂₂ CoN ₆ O ₉	717.52	(56.91) 56.56	(3.09) 2.88	(11.71) 11.33	(8.21) 8.06	-
[Ni(L) ₂].H ₂ O	C ₃₄ H ₂₂ NiN ₆ O ₉	717.28	(56.93) 56.30	(3.09) 2.90	(11.72) 11.55	(8.18) 8.00	-
[Cu(L) ₂].H ₂ O	C ₃₄ H ₂₂ CuN ₆ O ₉	722.13	(56.55) 56.15	(3.07) 2.87	(11.64) 11.24	(8.80) 8.18	-

FT-IR and NMR data: The major spectra of the compounds, as well as their designations, are mentioned in (Table 3) and Chemical structure Figure (1), HL spectra exhibited a peak at 3267cm⁻¹ due to the phenolic group's peak (OH). [17]. Furthermore the spectrum showed a band of spectra at 1627 cm⁻¹ attributed to ν (C=O) of the carbonyl group in the ligand was displaced to lower frequency at 1616, 1620, 1612, 1620, and 1616cm⁻¹ in complexes, respectively. The coordination of the carbonyl's oxygen atom to the metal centre may be responsible for the shifting of the carbonyl moiety [18]. The band at 1411cm⁻¹ can be attributed to (N=N) azo group[19] in ligand while in complexes at 1427, 1446, 1423 and 1400cm⁻¹ in complexes, respectively. Furthermore, the metal complexes spectra revealed additional bands, which were not seen in the ligand's spectra, approximately 690-513 cm⁻¹ attributed to ν(M-O) [18,20]. The bands observed around 499-416 cm⁻¹ are ascribed to (M-N) [18, 20]. The Azo ligand's ¹H NMR spectrum (Fig.(3)) revealed signals relating to the different protons, suggesting the ligand's synthesis. The ligand's ¹H-NMR spectra in the DMSO-d₆ solution exhibit a peak at 8.16-8.13(C9)-H (1H, d, J = 12Hz) 7.97-7.94 (C12)-H (1H, d, J=12Hz), 7.74-7.72 (C2,2')-H (2H, d, J = 8Hz), (7.65-7.61) (C10-H) (1H, t, J = 16Hz), (7.46-7.42) (C11-H) (1H,t, J = 16Hz), 7.27-7.24(C3, 3')-H (2H,d, J=12Hz),(1H,OH, s),(1H, C-H, s). The ¹³C-NMR spectrum in DMSO-d₆ solution of ligand exhibits resonance at δ=138.82,132.40,129.20(C14),(C8),(C10), 129.26,128.35,125.46 (C13), (C12), (C11),124.55,120.08 (C2,2-), (C3,3-),119.53, 110.37(C7), C9), 193.18 C=O, 161.36 (C6),159.73 (C4), 154.55(C1), 149.90(C5), Figure (4).

Mass spectrum: The electrospray (+) mass spectrum of HL, showed a band of at m/z = 319.1 amu (M-2H)⁺ calculated for C₁₇H₁₁N₃O₄⁺ requires = 321. 29 , (Fig 5), The assignment of the fragmentation species and their relative abundance is shown in Scheme 1.



Scheme 1: The fragmentation pattern and relative abundance of HL fragments.

Table 3: The FT-IR spectral data of compounds (cm⁻¹)

Compounds	v (OH)	v (H ₂ O)	v (C-H)ar	v(C=O)	v _{as} (C=C)	v N=N	sv N-O asv N-O	v C-O v C-N	v M-O	v M-N
HL	3267	-	3143, 3070,	1627	1593, 1546	1411	1500, 1361	1319 1261	-	-
[Cr(L) ₂] Cl	-	3302	3043	1616	1585	1427	1500,1365	1303,1249	655, 551	489, 451
[Mn(L) ₂].H ₂ O	-	3394	3078	1620	1585,1539	1427	1508,1365	1303, 1249	624, 513	497, 459
[Co(L) ₂].H ₂ O	-	3441	3059	1612	1593,1519	1446	1500,1361	1338, 1257	690, 586	499, 451
[Ni(L) ₂].H ₂ O	-	3414	3047	1620	1589	1423	1508,1365	1342, 1249	624, 543	497, 451
[Cu(L) ₂].H ₂ O	-	3414	3113	1616	1593	1400	1500,1373	1330, 1257	651, 613	466, 416

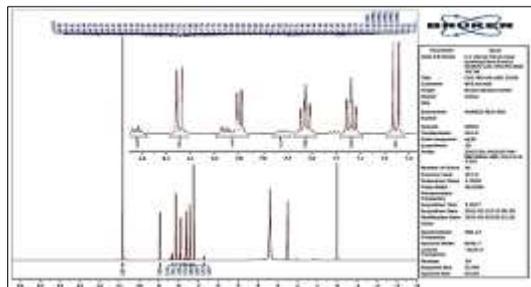


Figure 3: Spectra of ¹H-NMR in DMSO-d₆ solutions for (HL).

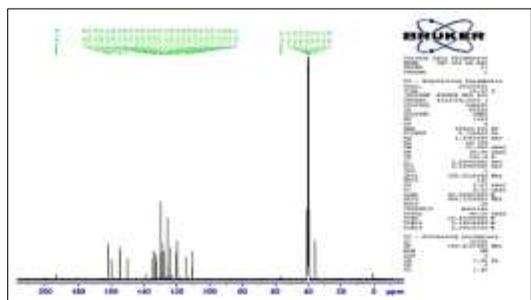


Figure 4: Spectra of ¹³C-NMR in DMSO-d₆ solutions for (HL).

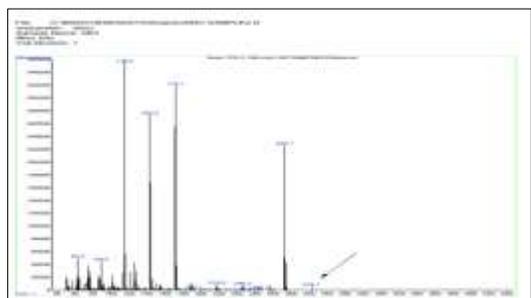


Figure 5: electrospray (+) mass spectrum of HL.

Table 4: Data on electronic spectra in DMSO solutions of HL complexes.

Complex	λ _{nm}	Wavenumber ν̄ (cm ⁻¹)	Molar extinction coefficient ε _{max} (dm ³ mol ⁻¹ cm ⁻¹)	Assignment	Suggested geometry
[Cr(L) ₂] Cl	259 327 493 807	38610 30581 20283 11025	172 359 1055 10	Intra-ligand π → π*, n → π* C.T C.T ⁴ A _{2g} → ⁴ T _{2g} (F)	Distorted octahedral
[Mn(L) ₂] H ₂ O	261 348 492 880 903	38314 28735 20325 11363 11074	315 498 1341 15 10	Intra-ligand π → π*, n → π* C.T C.T ⁶ A _{1g} → ⁴ T _{1g} (⁴ G) ⁶ A _{1g} → ⁴ E _g (⁶ D)	Distorted octahedral
[Co(L) ₂] H ₂ O	295 419 845	33898 23866 11834	2395 2084 84	Intra-ligand π → π*, n → π* C.T ⁴ T _{1g} (F) → ⁴ T _{2g} (F)	Distorted octahedral
[Ni(L) ₂] H ₂ O	276	36231	1438	Intra-ligand π → π*, n → π*	Distorted octahedral

UV-vis and the Magnetic Susceptibility measurements: The complexes' electronic spectra and magnetic moments are saved in a database (Table 4). The electronic spectra of the complexes reveal several peaks at 298-267nm, which are ascribed to π → π* and n → π*, respectively. Charge transfer (C.T) is responsible for additional peaks at 385-298nm [21,22]. At 807nm, the electronic spectra of Cr(III) display bands in the d-d region caused by 4A_{2g} → 4T_{2g}(F), suggesting a deformed octahedral structure around the Cr(III) center. The deformed octahedral shape agrees with the magnetic moment value of Cr(III). The electronic spectra of Mn(II) show d-d bands at 880 and 903nm caused by 6A_{1g} → 4T_{1g}(4G) and 6A_{1g} → 4E_g(D), respectively, showing a distorted octahedral structure around the Mn(II) center. The electronic spectrum of Co(II) displays a band in the d-d region at 845nm caused by 4T_{1g}(F) → 4T_{2g}(F), showing a deformed octahedral structure around the Co(II) center. The magnetic moment value obtained is compatible with the Co(II)-complex, which has a distorted octahedral structure around the Co atom [22,23]. At 778nm, a band in the Ni(II)-complex was found that was assigned to 3A_{2g}(F) → 3T_{1g}(F), indicating a distorted octahedral configuration around the metal center. The distorted octahedral geometry agrees with the magnetic moment value of Ni(II). The spectra of the Cu(II) complex exhibited a peak at 708nm, which was assigned to 2B_{1g} → 2B_{2g}. These transitions are characteristic of distorted octahedral Cu-complexes[22,24]. Cu(II) magnetic moment value agrees with distorted octahedral geometry.

Biological Activities: The ligand and its metal complexes were tested for microbiological activity against Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative bacteria (*Pseudomonas aeruginosa* and *Escherichia coli*). In addition to the one species of fungi studied (*Candida*). The bacteria chosen are thought to be the most dangerous and harmful types of bacteria. These bacteria have been found in many hospital operating rooms. Furthermore, two forms of fungus that influence humans, animals, and plants were examined. Table (5) shows the evolution of the diameter zone (mm) of HL-complex inhibition against the growth of various bacteria and fungus strains. The bacteria strains studied in this study were highly resistant to HL, indicating that the ligand had almost no action against all types of bacteria furthermore when compared to the free ligand, the metal complexes demonstrated antibacterial activity against various bacteria species.

	387 520 778	25839 19230 12853	840 1729 34	C.T C.T ${}^3A_2g^{(F)} \rightarrow {}^3T_1g^{(F)}$	
[Cu(L) ₂].H ₂ O	228 387 520 708	43859 25839 19230 14124	264 840 1729 66	Intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ C.T C.T ${}^2B_g \rightarrow {}^2B_g$	Distorted octahedral

The high activity of complexes, particularly Cu(II) and Ni(II) complexes, Chelation theory, and Overtone's model may be used to address this issue[25]. The complex can move and pass through an organism's cell membrane, according to the chelation theory. This might be owing to the metal ion's polarity being reduced due to partial sharing of positive charge with donor groups. As a result, the metal chelation system's lipophilic property will be strengthened, allowing the complex to pass through the cell tissue's lipid layer [26]. This might be due to the size of the metal ion and/or the complex's stability in the testing media since the

complex decomposes in the medium. According to the results, the ligand had no action against the two species of fungus. Otherwise, the complexes showed fungal organism activity. In general, the chelation concept might be used to characterize the rise in antifungal activity of complexes[27]. The delocalization of π -electrons throughout the chelate section was linked to this. This means that the ligand's and central metal atom's polarity decreases, resulting in complex penetration through the cell membrane's lipid tissue.

Table 5: The assessment of ligands and their complexes from a biological perspective

Compounds	Escherichia coli (G-)	Pseudomonas aeruginosa(G-)	Bacillus subtilis (G+)	Staphylococcus aureus (G+)	Candida
HL	18	15	20	17	22
[Cr(L) ₂]Cl	16	15	23	18	19
[Mn(L) ₂].H ₂ O	13	12	17	20	17
[Co (L) ₂].H ₂ O	24	20	27	28	18
[Ni(L) ₂].H ₂ O	15	17	25	24	15
[Cu (L) ₂].H ₂ O	10	12	19	18	18

CONCLUSION

It is reported on the synthesis and characterization of a novel azo ligand. The ligand ((E)-2-hydroxy-3-((4-nitrophenyl) diazenyl)-1-naphthaldehyde) (HL) was synthesized by a 1:1 mole ratio synthesis of 4-nitroaniline and 2-hydroxy-1-naphthaldehyde. The separation of monomeric complexes was achieved by interacting the ligand with metal ions of Manganese(II), Copper (II), Cobalt (II), Nickel (II), and Cr(III) at a mole ratio of 2:1 (L: M). To confirm the manner of bonding and overall structure of the complexes, physicochemical and spectroscopic approaches were used. These findings result in the creation of six-coordinate complexes.

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