ISSN: 0975 -8542

Journal of Global Pharma Technology

Available Online at www.jgpt.co.in

RESEARCH ARTICLE

Synthesis, Spectral Studies and Biological Activity of Azo dye Complexes with Some MetalIons

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Abstract

2-(2-amino-5-nitro-phenylazo) -phenol was ready by grouping the diazonium salt of 2-aminophenol with 4-nitroaniline.Thegeometry of azo ligand(HL)was resolved on the origin of (C.H.N) analysis,^{1}H and ^{13}CNMR spectra, infrared spectra and UV–vis electronic absorption spectra. Dealing with the azo ligand produced with Rh^{+3} and La^{+3}ataqueous ethanol for a 1:3 metal: ligand rate, and in perfect ph. The formation for compounds have been described by utilizing flame atomic absorption,(C.H.N) Analyses, conductivity, infrared spectra and UV–vis spectral procedures. Nature in the produced compounds have been studied obey the ratio of mole and continuous variance manners, Beer's law yielded up a concentration rate (1×10^{-4}- 3×10^{-4}M) . High molar absorbent, have been observed from compound solutions. At the origin data an octahedral geometry were assigned for the produced complexes. Biological activity of the produced compounds was assayed. In appending, the dyeing carried out of these compounds was practical above cotton fabric. The dyes were light and detergent stability.

Keywords: *Transition metals, Azo dyes, Complexes, Dyeing, Biological activity.*

Introduction

Most of azo ligands with metal complexes have a viciousness of biological, clinical and analytical, following [1]. Because of these azo ligands contain more than one active group coordinating with metal ions, they have large gravity in chemical analysis [2].Newly workers advanced a sensible way for the fixing of metal ions with azo ligands as complex metric factors by polar graphic and volt am metric mechanisms. Azo ligands reagents have obtained large deal notice as they are sensible chromogenic reagents [3].

Newly years, azo dyes and their metal complexes have been varied application in industrial and pharmaceutical, such as textile dyeing, antimicrobial, antifungal, anti-inflammatory activity, anti-hypertensive and antiviral drugs [4-8]. Metal complexes with azo dye ligand including nitrogen, oxygen and sulfur groups has been interested of biological activity [9].In this work, we produced azo ligand derived from o-aminophenol as such diazo composition as well4-nitroaniline as such linked factor.

The compound sat this ligand for lanthanides were produced also featured physic chemically.

Experimental

Instrumentation

(C. H. N) analysis was obtained, in the Al- al-Bayt, University,, Jordan, employing Euro vector, EA 3000A,Elemental Analyser,.1H-NMR spectra, were registered, at a Brucker-300, MHz Ultra, Shield spectrometer ,in the University, from Al- al- Bayt, utilizing DMSO, as such the solvent, and TMS, as such the reference.

The electronic spectra of the ligands and complexes were possessed at a Shimadzu, UV- 160A, Ultra Violet-Visible, Spectrophotometer. FT-IR spectrometer, were registered, at a Shimadzu,, FT-IR-8400S, Fourier Transform, Infrared, Spectrophotometer, on the 4000- 400,cm-1 spectral, are as for samples, produced as such KBr, discs. Atomic absorption was gained,

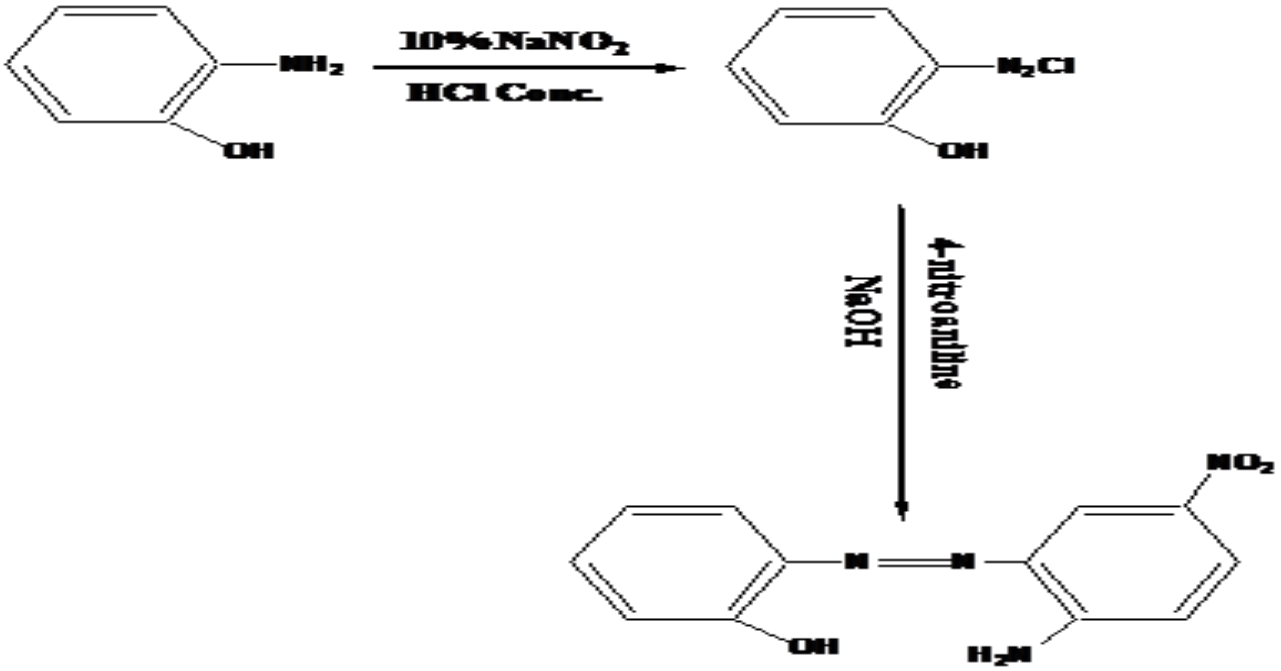
employing a Shimadzu, A.A-160A, Atomic Absorption, Flame Emission, Spectrophotometer. Conductivity was measured, to 10-3M, solutions for compounds, at ethanol in 25oC utilizing, Philips PW- Digital, Conduct meter. Other than that, melting, point's amounts were employing Stuart, Melting Point, and Apparatus.

Materials and Detectors

Obedience chemicals have been utilized, as such collected of providers: neodymium nitrate hexahydrate 99.9%, gadolinium nitrate hexahydrate 99.8%, dysprosium nitrate hydrate 98% and erbium nitrate pentahydrate 99.8%(Merck), 2-aminophenol and 4-nitroaniline(Fluka).

Preparation of the Ligand

A solution contain [10] (0. 272 gm, 1 mmole) of 2-aminophenol melted in (10ml) of Et OH including (2ml) conc. HCl which has been diluted for 10 ml H_2O, as well diazotized at 5^oC for 10%solution of$NaNO_2$. The diazotized solution was appended gradually for stirring to a cooled ethanol solution to (0.345 gm, 1mmole) from 4-nitroaniline. After that 25 ml of 1Mof sodium hydroxide solution was appended into the dark mixture and precipitation of azo ligand has been noticed. This sediment has been filtered; wash it several times for (1:1) ethanol: water, thereafter left into dry. The interaction appears sat Scheme 1.



Scheme 1: Preparation from azo ligand (HL)

Buffer Solution

(0.01M, 0.771 gm) for ammonium acetate has been melted at one liter from doubly demonized water. Adjust the pH adjustment (4-9) has beenutilizeCH_3COOH or NH_3 solution.

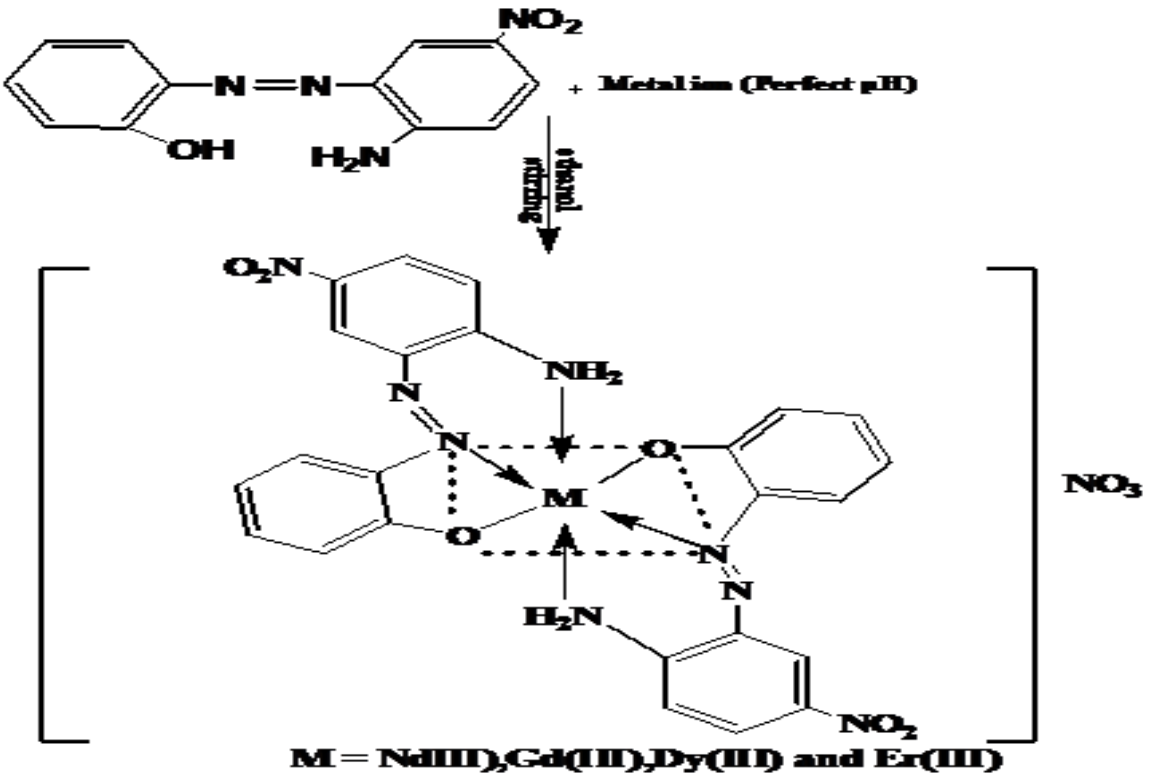
Standard Solution

A series from standard solutions of metal nitrate for [Nd^{+3}, Gd^{+3}, Dy^{+3} and Er^{+3}] were produced in (10^{-5}-10^{-3} M) variant concentration on pH adjusted (4-9).With each other a chain from ethanol solutions for ligand at the adjusted from condensation (10^{-5}-10^{-3} M) was as well produced.

Preparation from Metal Compounds (Generic Procedure)

(0.270g, 2 m mole) of the ligand dissolved in ethanol was appended progressively with stirring to the 0.131, 0.148, 0.121 and 0.146 gm (1mmole) of Nd $(NO_3)_3$. $6H_2O$, Gd $NO_3)_3$. $6H_2O$,Dy $(NO_3)_3$. XH_2O and Er $(NO_3)_3$.$5H_2O$continuously dissolved at buffer solution for wanted ph. The mixture has been cooled till dark color sediment was acquired, filtrated, and washed number ounces times for 1:1 water: ethanol mixture thereafter left to dry.

The interaction appears sat Scheme 2.



Scheme 2: The expected structure at the metal (III) compounds

Study of Biological Activity

Specific checking with antimicrobial efficiencies has been done in principle employing the disc diffusion checkup, at vitro bacterial efficiencies were metric of the diameter from obvious inhibition zones give rise to samples contra the selfsame bacteria and under the same experimental condition, into prove the constancy from new compound sat DMSO solution long- term. The antibacterial activity of the ligand and its metal complexes were examined on gram (+) and gram (-) microorganisms. Bactericidal efficiencies were estimated through gauging the growth inhibition zone versus check organisms and minimum inhibition condensation [11]. It was found to synthesize them new metal compounds showed promising bacterial efficiency versus Staphylococcus aureus, E-coli, Pseudomonas and Bacillus.

Dyeing Method

Dyeing estates of the produced compounds were examined and used to cotton fabric like (1% shade). Dyeing has been formed in fabric in (15- 20C°) at (1 hr), and in pH (10).

Results and Discussion

To prepare for ligand (HL) linkup from 4-nitroaniline for the convenient diazotized at alkaline solution was done.

The solubility to the ligand has been examined and found into be soluble at organic solvents and has been stabilized toward air and moisture. Performed ligand has been identified through ^{1}H and $^{13}CNMR$, FT-IR, (C, H, N) analysis and electronic spectral mechanisms. An aqueous-ethanol solutions were constantly completed into study the interaction to the metal ions Nd^{+3}, Gd^{+3}, Dy^{+3} and $Er^{+3}$for the produced ligand. Colors of these ones mixed solutions through the molar condensation and acidity varying perfected were varied of brown into violet.

NMR Spectrum

The $^{1}HNMR$ spectrum of the ligand (HL) at DMSO (Fig.1) displays various symbols in δ=7.001-8.413 ppm described into aromatic protons [12].Other than, the signal in δ=6.9772 ppm lead into proton of phenol [13]. The symbol in δ=3.421 ppm is appointed to proton of (NH_2) group as well the gesture in δ=2.50 ppm assigned into DMSO-d_6 [14].

The $^{13}CNMR$ spectrum of the azo ligand (Fig. 2) display signals at δ=162.342 ppm and δ=155.533 ppm assigned to carbon of phenol and carbon of amine groups. The resonance at δ=130.289 ppm due to carbon of nitro group. The various gestures at (δ=147.708, δ=145.361, δ=126.292, δ=125.492, δ=122.913 and δ=1117.036 ppm described to carbon

atoms of aromatic rings. The signal at δ=39.535 ppm due to DMSO-d6 [15].

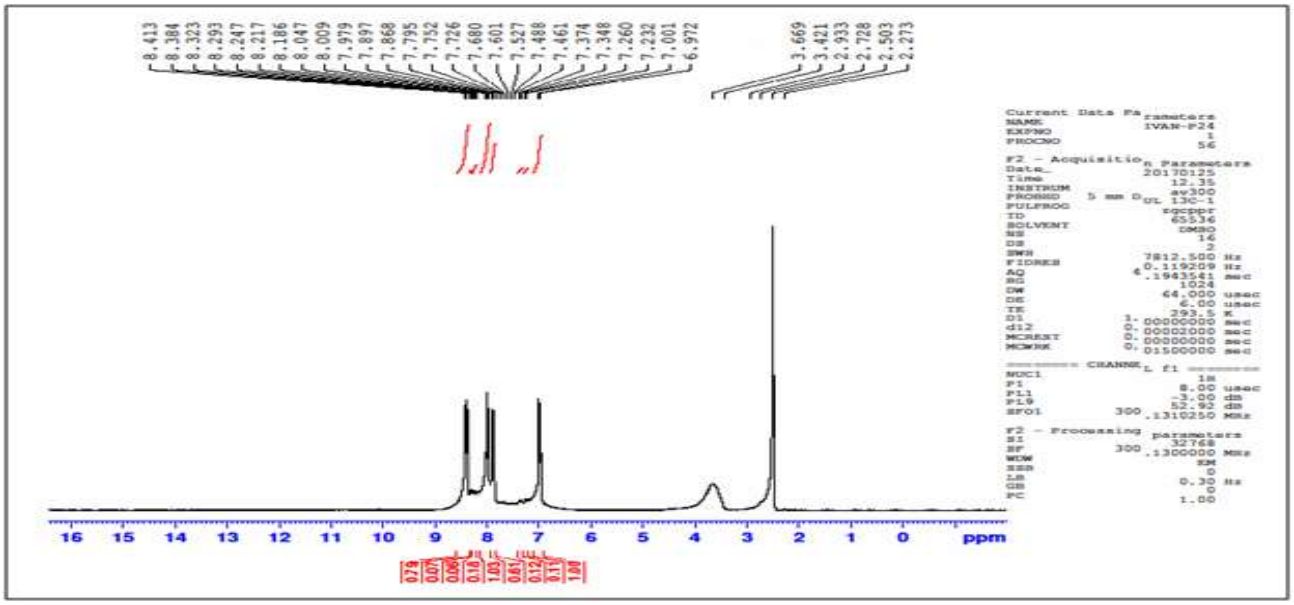


Fig. 1: 1HNMR spectral for the ligand (HL)

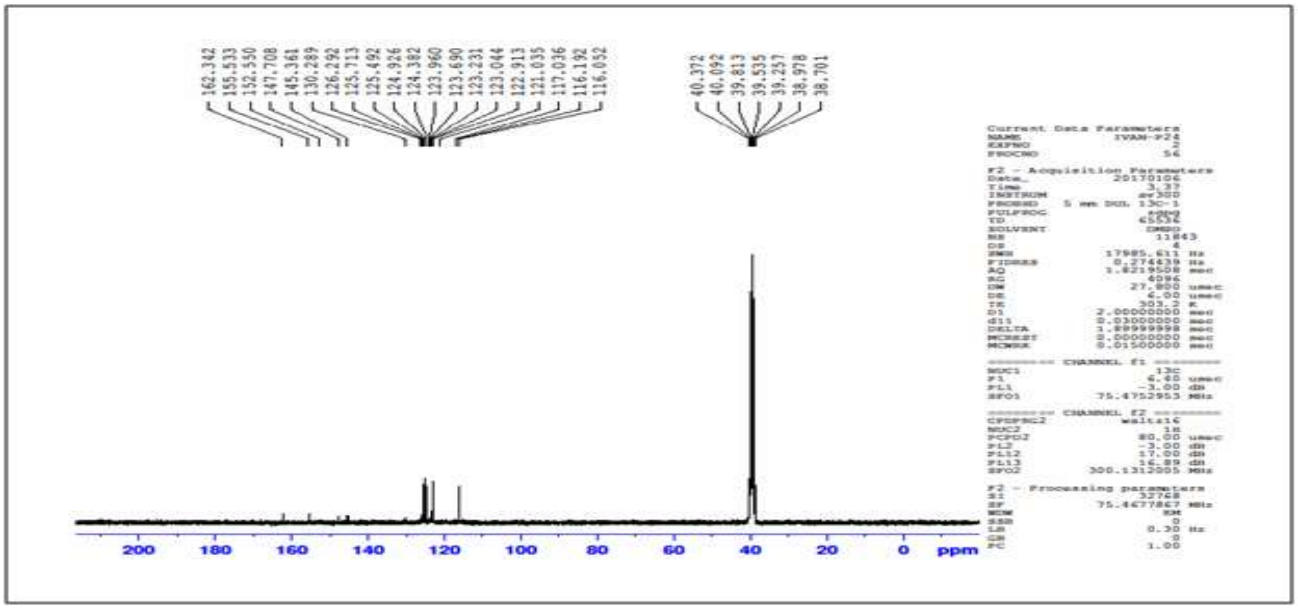


Fig. 2: 13CNMR spectral for the ligand (HL)

Physical Properties

Compounds were produced through instantaneous reaction of alcohol solution of ligand (HL) for aqueous solution of metal ions in the ideal pH and at an M: L ratio to 1:2.Analysis result (C.H.N) and the metal content for compounds were at good assents for the studied values, the data recorded in Table-1. The molar conductance for (10^{-3} M) in ethanol solutions for compounds assigned the electrolytic type ratio [16] 1:1, datumare tabulated at Table-2.

Table1: Physical properties for the ligand and compounds

Compounds	Color	M.P°C	Yield%	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand(HL)	Pal brown	136	77	-	55.81 (54.58)	3.87 (2.94)	21.70 (20.63)
$[Nd(L)_2]NO_3$	Deep brown	162	73	20.00 (19.58)	40.00 (39.69)	2.50 (2.03)	15.55 (14.77)
$[Gd(L)_2]NO_3$	brown	171	70	21.41 (20.88)	39.29 (38.93)	2.45 (1.94)	15.27 (14.84)
$[Dy(L)_2]NO_3$	Orange	177	75	22.05 (21.74)	38.97 (38.31)	2.43 (2.17)	15.15 (14.71)
$[Er(L)_2]NO_3$	Reddish brown	183	77	22.47 (21.95)	38.76 (37.69)	2.42 (1.88)	15.07 (14.86)

Table 2: Conditions of the preparation for the compounds, electronic absorption spectra and conductance menstruations datum

Compounds	Optimum pH	Optimum Molar Conc. x 10^{-4}	M:L Ratio	(λ_{max}) nm	ABS	ϵ_{max} ($L.mol^{-1}.cm^{-1}$)	Λ_m($S.cm^2.mol^{-1}$) In Absolute ethanol
Ligand(HL)	-	-	-	382	1.099	1099	-
$[Nd(L)_2]NO_3$	7	2.5	1:2	375 978	1.435 0.124	1435 124	7.47
$[Gd(L)_2]NO_3$	7	2	1:2	377 836 978	1.343 0.032 0.105	1343 32 105	6.71
$[Dy(L)_2]NO_3$	7	2	1:2	370 832 976	1.330 0.049 0.122	1330 49 122	3.83
$[Er(L)_2]NO_3$	7	2.5	1:2	378 856 978	1.325 0.028 0.104	1325 28 104	9.28

Calibration Curve

Deferent molar condensations (10-5–10-3 M) from mixed aqueous-ethanol for ligand and metal ions, just the average (1-3×10-4M) concentration succeed Beer's law and showed obvious intensive color. Best suitable up right lines were happened with correlation laborer factor R>0.9980 like shown at Fig. 3.

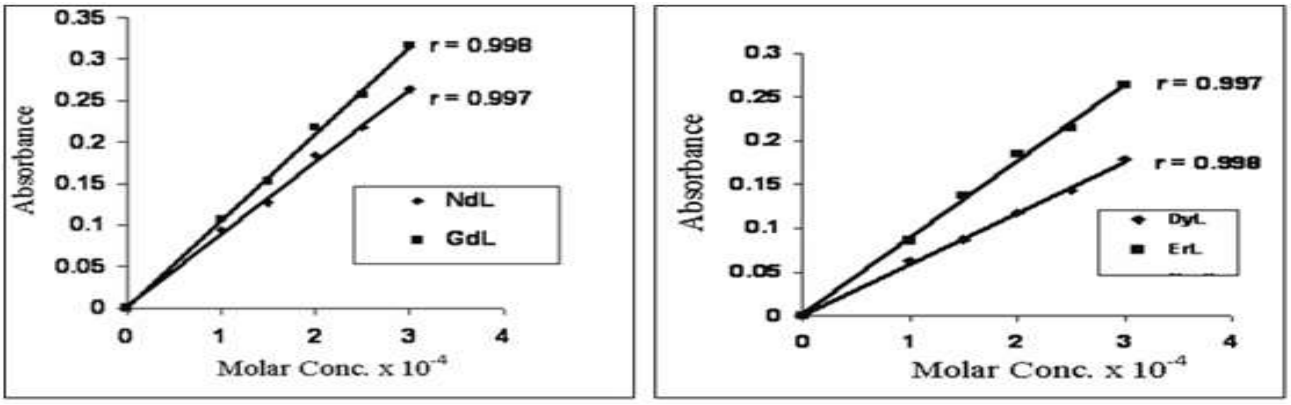


Fig.3: A linear relationship between molar condensation and absorption

Optimum Conditions

At inquire into interaction amidst the produced ligand and metal ions beneath studying to the preparation about the compounds, the spectra of combining solutions to the ligand and metal ions into obtain for optimum pH and concentration, and condensation wave length (λ_{max}) have been studied first .Another mole ratio metal into ligand (M: L) has been knew into prepare the compounds. Ideal concentration has been selected to compound solution based of which solution gives the highest absorbance in constant (λ_{max}) on various pH, and outcomes are described at Table-2.The probation outcomes proof which the absorbance for each produced compounds are extreme and steady at a buffer solution for (NH_4OOCCH_3) at the pH range (4-9).It was found which all produced compounds had ideal pH like is shown atFig.4.

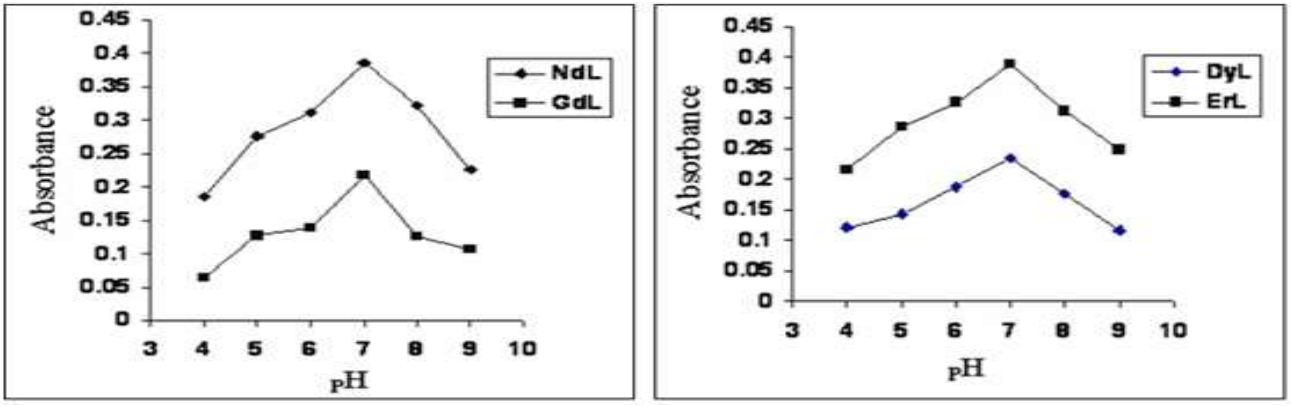


Fig. 4: Influenceat pH on absorbance (λmax) of compounds

Stoichiometry for Compounds

The writing for compounds done at solutions was permanent through mole ratio and job processes. On two locations the outcomes disclose a 1:2 metal to ligand ratio. Choice chart is represented at Fig.5. Table-2outlines the outcomes acquired, other than, stations at the preparation for the compounds.

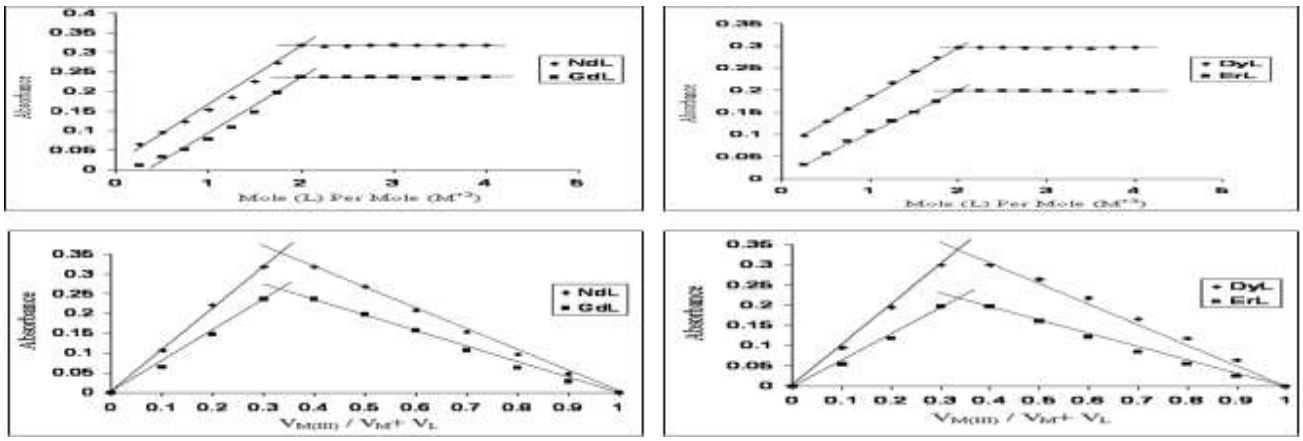


Fig.5: Mole ratio and Job manners of compounds solutions

Electronic Spectra

The electronic spectra for the produced azo ligand and compounds melted at ethanol (10^{-3} M) were studied and the datum included at Table-2.The UV- Vis spectrum for the azo ligand(Fig. 6) show peak at 382 nm due to(π-π*) electronic transition [17,18].The UV-Vis spectra of the produced complexes display peaks at the average(370-378 nm) related to ligand felid, other than, peaks at the rate(832-978 nm) due to (f-f) electronic transition [19]. Fig. 7 show the Dy^{+3} complexes.

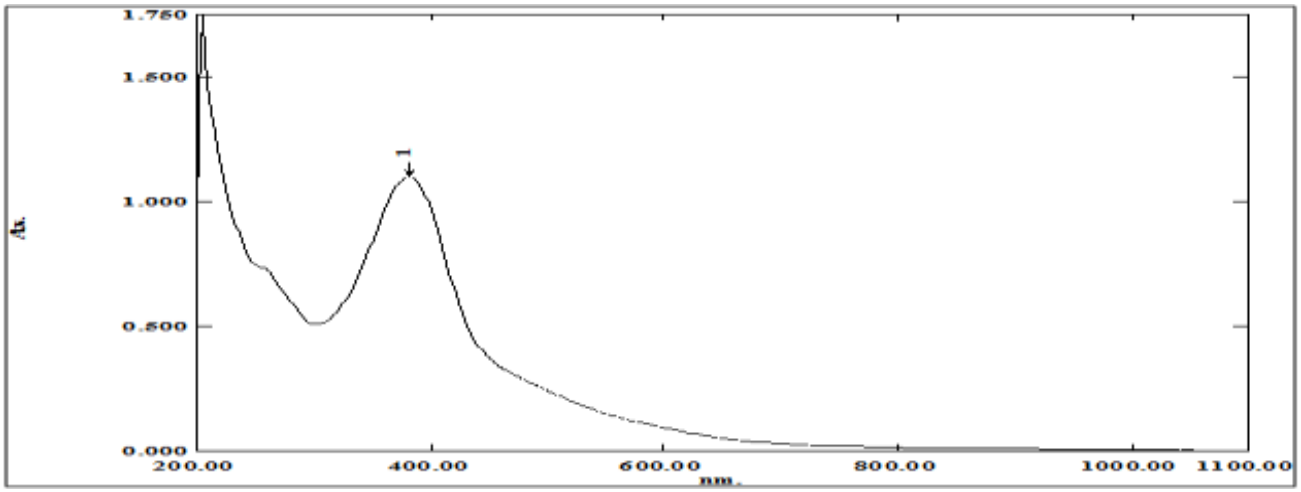


Fig. 6: Electronic absorption spectra at the ligand (HL)

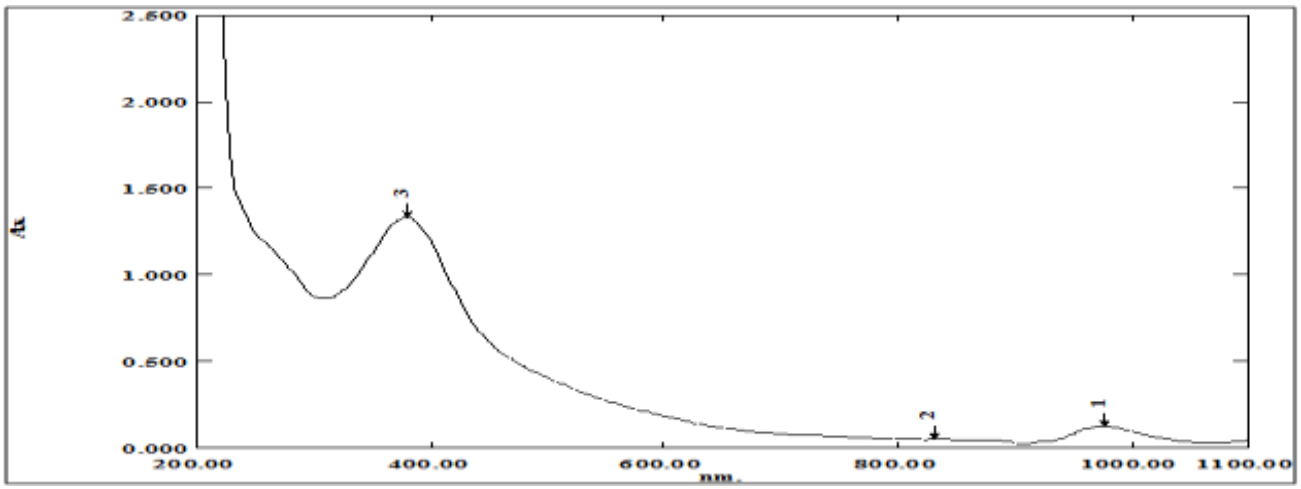


Fig.7: Electronic absorption spectra at the [Dy (L) 2] NO3 compound

IR Spectra

The infrared spectra for the produced compounds have been collated, and the data was scheduled at Table-3.The broad band atthe FT-IR spectra for the azo ligand (Fig.8) at 3477 cm^{-1}, which was related to the stretching vibration of υ(OH) phenol, the disappearance of this band at the spectrum for each produced compounds (Fig. 9) elucidated the deprotonation for phenol group to coordination with metal ion [20,21].The infrared spectra for the ligand (HL) displayed bands in 3429 and 3389 cm^{-1} ascribed to the υ(NH_2) stretching vibration [22], on complication a shiften for alteration at format have been watched of these bands, whilst growing at density were observed. Bands at 1600,1585 cm^{-1} and 1516 cm^{-1}due to frequency of (C=C) and stretching vibration of υ(NO_2) sequences [23,24].Azo group vibration in 1492 cm^{-1} shifted into lower wave number for variation at form to the spectra for compounds, indicated the engagement for that group at the coordination for the metal ion [25] . Stretching frequency bands for metal-nitrogen and metal-oxygen to the limit [26, 27] assured by the existence for the bands about 447-509 cm^{-1}. Pursuant to the results donated, an octahedral geometry has been offered for the produced complexes.

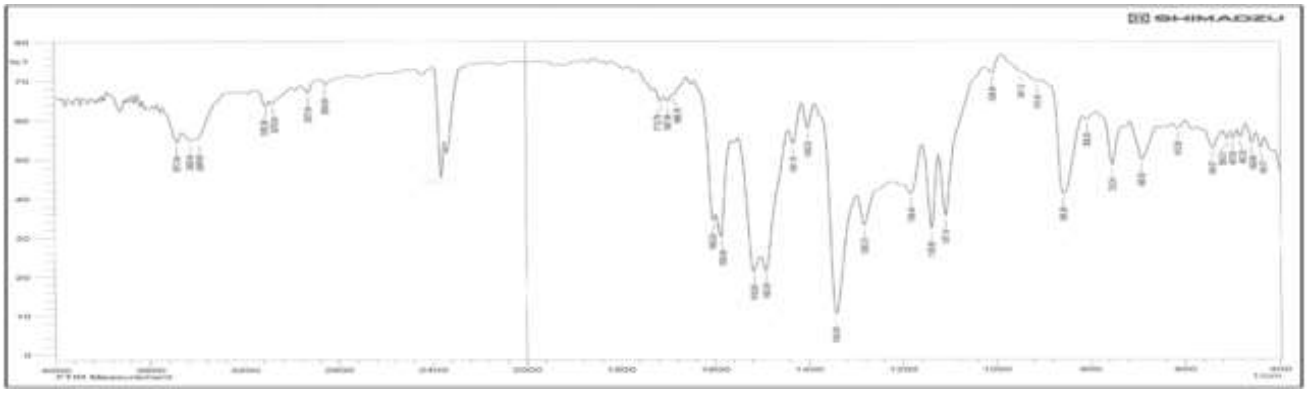


Fig.8: infrared spectra at the ligand (HL)

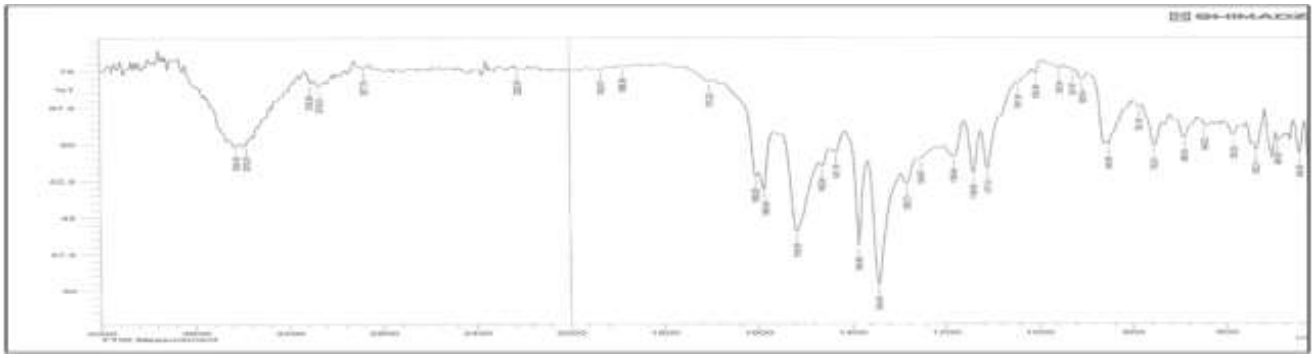


Fig.9: infrared spectra at the [Gd (L) 2] NO3compound

Table3: Major frequencies for the ligand and compounds (cm^{-1}).

Compounds	υ(NH_2) + υ(OH)	υ(C=O) + υ(C=C)	υ (N=N)	υ(M-N) + υ(M-O)
Ligand(HL)	- 3471 br.	1689 sh. 1631 s. 1585 s.	1492 sh.	443 w. 420 w.
$[Nd(L)_2]NO_3$	- 3363 br.	1685 sho. 1600 s. 1558 s.	1489 sh.	509 w. 443 w.
$[Gd(L)_2]NO_3$	- 3363 br.	1688 s. 1624 s. 1600 sho.	1481 sh.	-
$[Dy(L)_2]NO_3$	- 3452 br.	1685 sh. 1631 sho. 1600 s.	1489 s.	518 w. 474 w.
$[Er(L)_2]NO_3$	- 3407 br.	1683 sh. 1627 s. 1591 s.	1479 s.	540 w. 443 w.

br = broad, sh = sharp, s = strong, w = weak,
sho =shoulder

Biological Efficiency and Dyeing Properties

Produced compounds have been investigated with Gram-negative and Gram-positive bacteria. Table-4suggested the deactivation spread converse the bacteria specimen. Dyeing execution (Fig. 10) for the produced azo ligand and its metal compounds has been defined above cotton fabric. Dyes were essay to the light and cleanliness stability.

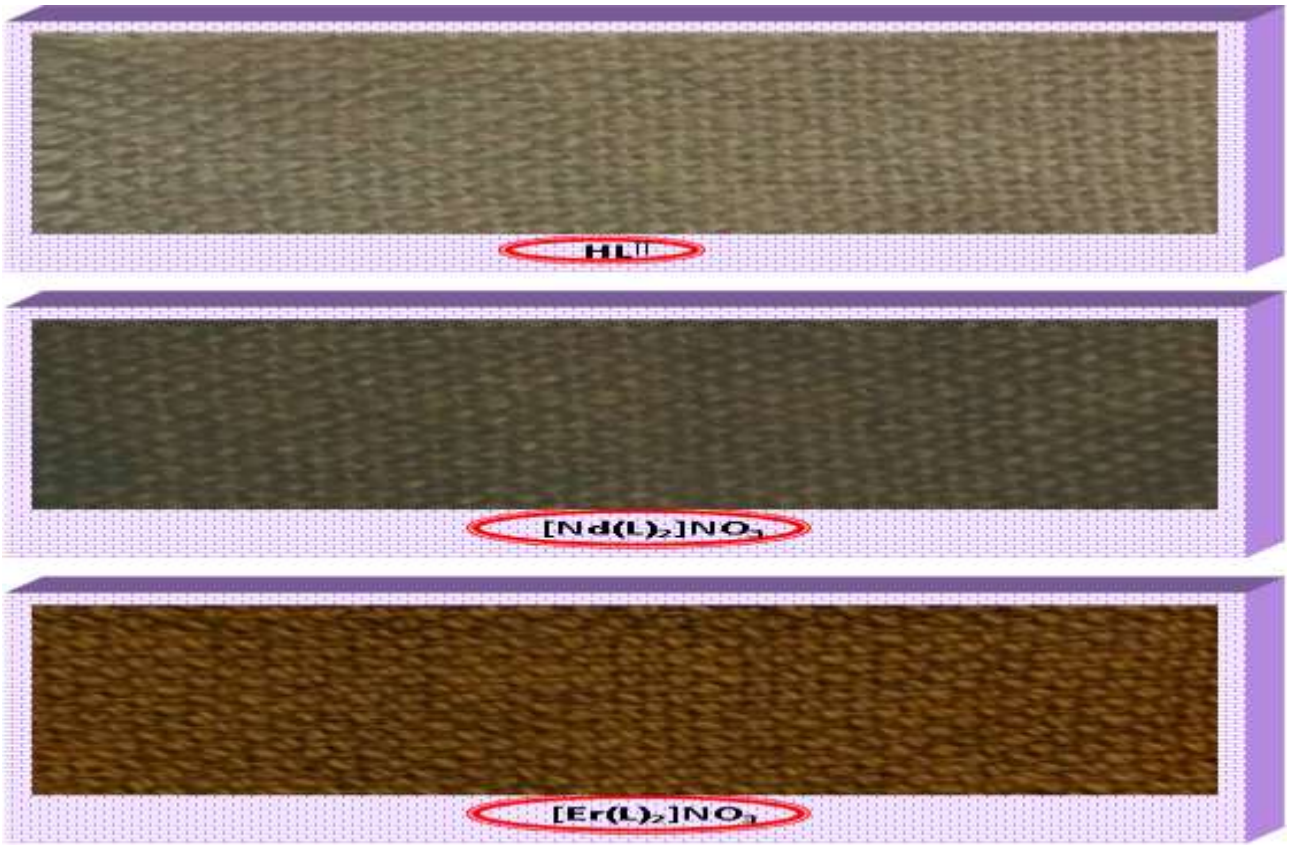


Fig.10: Samples the textiles dyeing of the ligand and their complexes.

Table 4: Diameters (mm) for suppression of bacteria for the ligand and compounds

Compounds	Bacillus	Staphylococcus aureus	E-coli	Pseudomonas
Ligand(HL)	10	20	21	12
$[Nd(L)_2]NO_3$	17	19	23	14
$[Gd(L)_2]NO_3$	8	21	15	20
$[Dy(L)_2]NO_3$	12	25	16	15
$[Er(L)_2]NO_3$	16	22	13	17

Conclusion

In this work, the metal ions complexes have been readied with the ligand (HL). The willing compounds are described by melting point, flame atomic absorption, infrared spectra and electronic absorption spectra, and conductivity quantifications. Exploration for antimicrobial activities was lifted out opposite the experimented organism. The dye as well as produced compounds has been applied above cotton fabric. According result data an octahedral structure suggested for produced complexes.

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