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RESEARCH ARTICLE

Synthesis, Characterization and Spectral Studies of Azo Dyes Ligands Complexes with Some Metal Ions and Their Industrial and Bacterial Application

Wedian Mansor Obaid

Ministry of Education/ Directorate General for the Education of Baghdad/ Rusafa First/Iraq.

Abstract

1-[4-(4-Acetyl-2-hydroxy-phenylazo)-phenyl]-ethanone (HL_1) and1-[3-Hydroxy-4(4-nitro-phenylazo)-phenyl]-ethanone (HL_2) were produced by combination the diazonium salts of amines with 3-hydroxyacetophenone. (C.H.N) analyses, FT-IR, UV-Vis, ^1H and $^{13}CNMR$ spectral are use to identified for the ligands. Complexes for Zn^{+2},Cd^{+2} and Hg^{+2} were prepared as well specified through using atomic absorption of flame, analysis of elements, spectral methods also conductivity quantification. The nature of production complexes were studied continued mole ratio as well continued variance ways, Beer's law followed over condensation scope (1×10^{-4}- 3×10^{-4})M. High molar absorption for compound solutions have been noticed. Analytical datum showed that in every the complexes offered 1:2 metal-ligand ratios. Depending physicochemical data a tetrahedral geometry were described of the metal chelates. Biological efficacy from compounds has been tested. Other than, dyeing completed of the produced compounds has been workable on fabric of cotton.

Keywords: *Complexes, azo dyes, microbial activity, dyeing*.

Introduction

Azo dyes are identified with having one or more azo group (-N=N-) in molecular geometry [1, 2]. Azo compounds are very significant class from organic dyes are synthesized due to various industrial application on many field, like textile fiber and dyeing, studies in biomedical, advanced application on organic synthesis as well high-techno. Regions like laser, liquid crystalline offers, electro-optical devise as well as inkjet printers [2-5]. Metal chelates from azo ligands are for flow attractiveness because the stunts physical, chemical, photophysical also photochemical, catalytic as well as various material characteristics [6-8].

This metal chalets have been interested electronic as well structural advantages on linkages for effecting with storage of molecular memory, non-linear visual elements as well printing system [9]. In current work, a ligands from azo functional group obtainedfor4-aminoacetophenone and 4-nitroaniline like diazo component also 3-hydroxyacetophenone like coupling agent, have been produced. Complexes from Zn^{+2}, Cd^{+2} and Hg^{+2} with these ligands were produced as well as specified through analytical and spectral studies.

Experimental

Instrumentation

Atomic absorption has been registered with employing a Shimadzu A.A-160A Atomic Absorption/Flame Emission Spectrophotometer. 13C also ^1H-NMR spectra were pointed out at a Brucker-300 MHz Ultra Shield spectrometer utilizing dimethylsulfoxide like the solvent also tetramethylsaline as internal reference. (C, H, N) analysis have been done, utilizing Euro vector EA 3000A Elemental Analyzer.

Conductivity for compounds resolved at ethyl alcohol (10-3M) has been registered at 25oC using Philips PW- Digital Conductimeter. UV-Vis spectra were registered at a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer. FT-IR spectral has been taken at a Shimadzu, FT-IR- 8400S Fourier Transform Infrared Spectrophotometer at4000- 400cm^{-1} spectra zones for specimens produced like KBr discs. Other than, melting

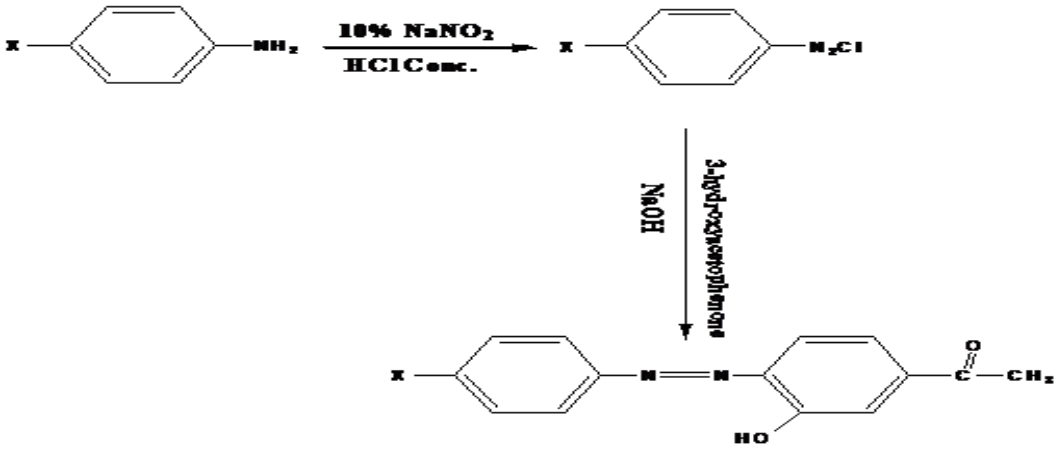
points have been performed utilizing Stuart Melting Point Apparatus.

Materials and Reagents

Obeying chemicals were employed for collected from undertakers: $ZnCl_2$, $CdCl_2.H_2O$ also $HgCl_2$ (B.D.H), 4-aminoacetophenone, 4-nitroaniline and 3-hydroxyacetophenone (fluka).

Preparation of the Ligands

A solution was produced [10] of amines (0.337gm and 0.345 gm, 1mmole) in mixture (10ml ethanol, 2ml conc. HCl), and diazotized at 5°C with 10%solution of$NaNO_2$. The diazotized solution has been added up drops age for stirring to the cooled ethyl alcohol solution for (0.340gm, 1mmole) from 3-hydroxyacetophenone. 25 ml of 1MNaOH solution has been followed into mixture of dark colored also deposition from azo ligand was observed. A precipitate was filtrated, washed number ounces for (1:1) ethyl alcohol: water, thereafter leave into dry. Reaction is according on Scheme (1).



$L_1 = X = COCH_3$, $L_2 = X = NO_2$

Scheme 1: Synthesis of the azo ligands

Buffer Solution

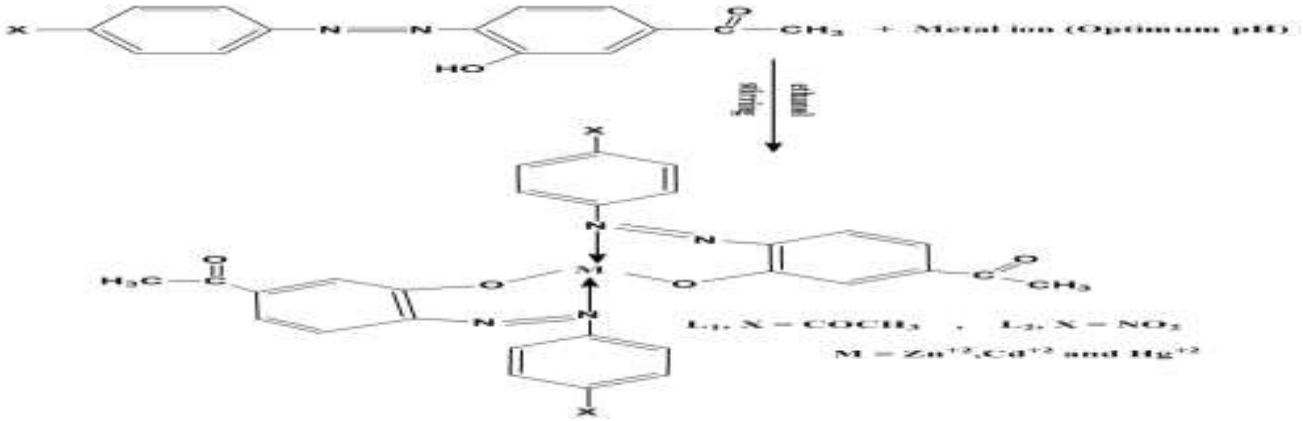
(0.01M, 0.771 gm) from CH_3COONH_4 was resolved in one liter of doubly deionized water. With only pH rate (4-9) was utilization CH_3COOH or NH_3 solution.

Standard Solution

Bulk of standard solutions for metal salt from (Zn^{+2}, Cd^{+2}also Hg^{+2}) were made in diversity resolve (10^{-5}-10^{-3} M) at pH rat (4-9). On same time a bulk from ethyl alcohol solutions from ligands during the extent from condensation (10^{-5}-10^{-3}) M has been produced.

Preparation of Metal Chelates

Ethyl alcohol solution of the ligands (0.282gm and 0.285gm, 2mmole) has been added up for stirring for 0.068,0.100 and 0.136 gm of metal chloride from (Zn^{+2}, Cd^{+2}also Hg^{+2}) resolved in pH solution with needed pH. Mixture was cooled into dark color deposition has been formed, filtrated, also washed number ounces for 1:1 H_2O: C_2H_5OHmix. The preparation method appears at scheme-2, other than the physical estates and (C.H.N) analyses are listed in Table 1.



Scheme 2: The expected geometry with metal complexes from (HL_1 and HL_2)

Table 1: Physical characteristics for ligands also its complexes

Compounds	Color	M.P°C	Yield%	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand(HL_1)	Brown	161	82	-	68.08 (67.95)	4.96 (4.78)	9.93 (8.75)
$[Zn(L_1)_2]$	Yellowish orange	235	86	10.36 (9.88)	61.24 (60.86)	4.14 (4.01)	8.93 (7.96)
$[Cd(L_2)_2]$	Yellow	220	81	16.61 (15.48)	56.97 (56.13)	3.85 (3.21)	8.30 (7.84)
$[Hg(L_2)_2]$	Orange	265	84	26.34 (25.83)	50.32 (49.77)	3.40 (2.95)	7.33 (6.83)
Ligand(HL_2)	Reddish brown	170	81	-	58.94 (57.86)	3.85 (3.27)	14.73 (13.74)
$[Zn(L_2)_2]$	Orange	232	88	10.26 (9.94)	53.08 (52.84)	3.15 (2.89)	13.27 (12.96)
$[Cd(L_2)_2]$	Brown	251	80	16.47 (15.83)	49.41 (48.92)	2.94 (3.18)	12.35 (11.78)
$[Hg(L_2)_2]$	Yellow	261	83	26.13 (25.76)	43.69 (42.98)	2.60 (2.22)	10.92 (9.84)

Microbial Properties

Azo ligand as well latterly metal chelats have been tested at vitro for antibacterial also antifungal efficacy versus: *Staphylococcus aureus, Esherichia Coli*, *Candida albicans* also *Candida tropicalis*. Zone of inhibition for ligand as well metal chelates versus growth of bacteria and fungi have been checked using agar propagation technique [11]. Organism checked were agar media have been vaccinated for check organisms as well a solution from checked compound (100µg/ml) has been placed separately at cups (10mm diameter) on agar medium.

Plates have been brood at 24 h on 37°C also the well has been full of also the check solution utilizing micropipette. Through this time, the check solution has been fulled of for prevalent as well influenced growth for vaccinated microorganisms. Efficiency has been determined through measuring diameter from zone displaying perfect inhibition(nm).Growth inhibition has been likened for control (dimethylsulfoxide), microbial efficacy outcome showed that these compounds shown a good activity.

Dyeing Technique

Dyeing techniques from produced compounds have been tested as well as apply into fabric of cotton for (1% shade).Dyeing for fabric was obtained at (15- 20C°) on (1 hr), as well in pH (10).

Results and Discussion

For the production of the ligands (HL_1 and HL_2) a joined of 3-hydroxyacetophenone with the suitable diazotized in alkaline solution was performance. Produced ligands were characterized by ^1H and ^{13}CNMR, FT-IR, UV-Vis spectroscopic technique and (C, H, N) analysis. Aqueous-ethyl alcohol solutions have been always obtained to study interaction from metal salts with the produced ligands.

NMR Spectrum

^1HNMR spectral for ligand (HL_1) in dimethylsulfoxide (Figure1) shows different signals on δ=7.073-8.206 ppm appointed into aromatic protons [12], gesture on δ=6.713 ppm due for proton from phenol [13]. Resonance at δ=2.628 ppm designated into δ (CH_3) groups also the signal on δ=2.50 ppm indicate into DMSO-d6 [14].

^{13}CNMR spectral for (HL_1) (Figure2) display symbol on δ=26.393 ppm due to carbon of (CH_3) in acetyl groups. The resonance at δ=196.070 ppm appointed into carbonyl groups. Various signals at (δ=160.000, 138.526, 133.649, 130.630, 129.440, 122.935, 120.445, 118.783 and 115.119 ppm attributed to carbon atoms from aromatic rings. Symbol on δ= 154.115 ppm because carbon of (-OH) group and signal on δ=39.536 ppm led into DMSO-d6 [15].

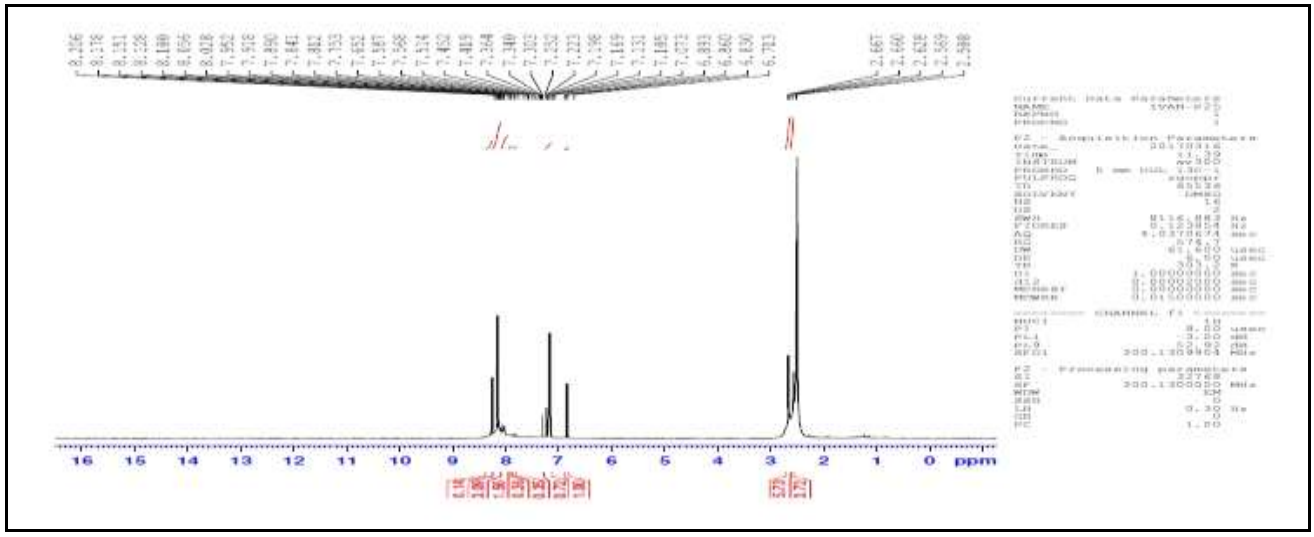


Figure1: ^{1}HNMR spectrum for ligand (HL_1)

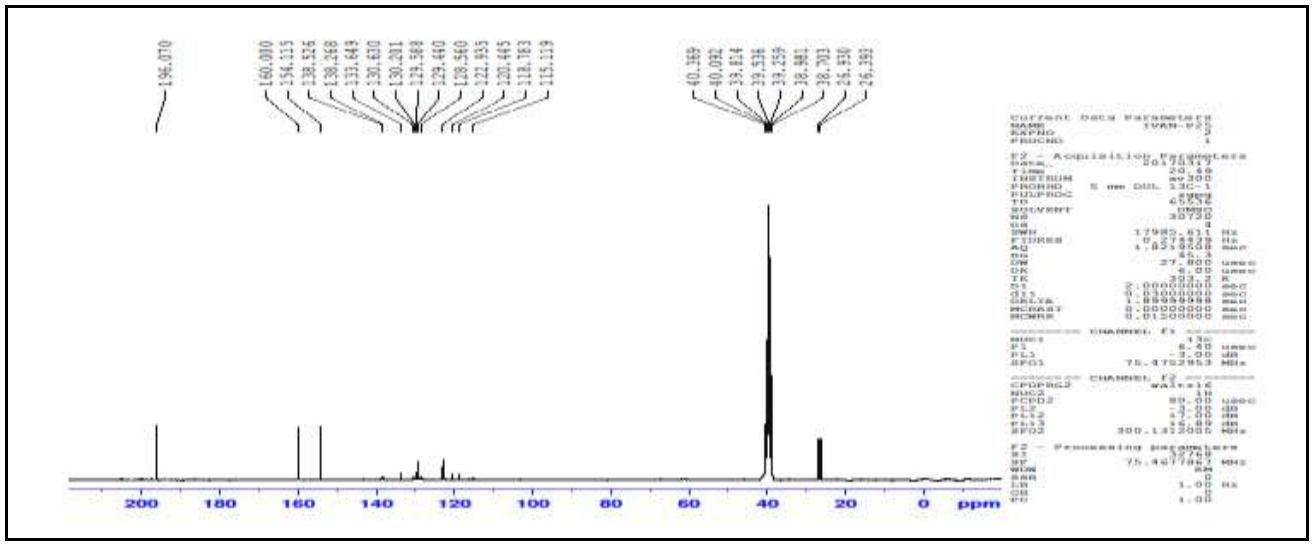


Figure 2: ^{13}CNMR spectrum for ligand (HL_1)

The^{1}HNMR spectrum of the ligand (HL_2) (Figure 3) shows diverse symbols on δ=7.028-8.258 ppm labeled for aromatic protons [16]. Symbol on δ=6.833 ppm because proton for phenol [17]. Symbol on δ=2.624 ppm due to δ (CH_3) for acetyl group as well symbol on δ=2.5 ppm reason DMSO-d6 [18]. ^{13}CNMR spectral for (L_2) (Figure 4) display various signals at (δ=160.166, 155.061, 138.594, 134.219, 130.339, 128.777, 124.918, 119.517 and 115.124) ppm described into carbon atoms from aromatic rings. Symbol on δ=148.398 ppm described to carbon from (-OH) group. Signal on δ=28.763 ppm due to carbon of (CH_3) in acetyl group. Resonance on δ=196.104 ppm assigned to carbonyl group. Gesture on δ=39.520 ppm assigned for DMSO-d6 [19].

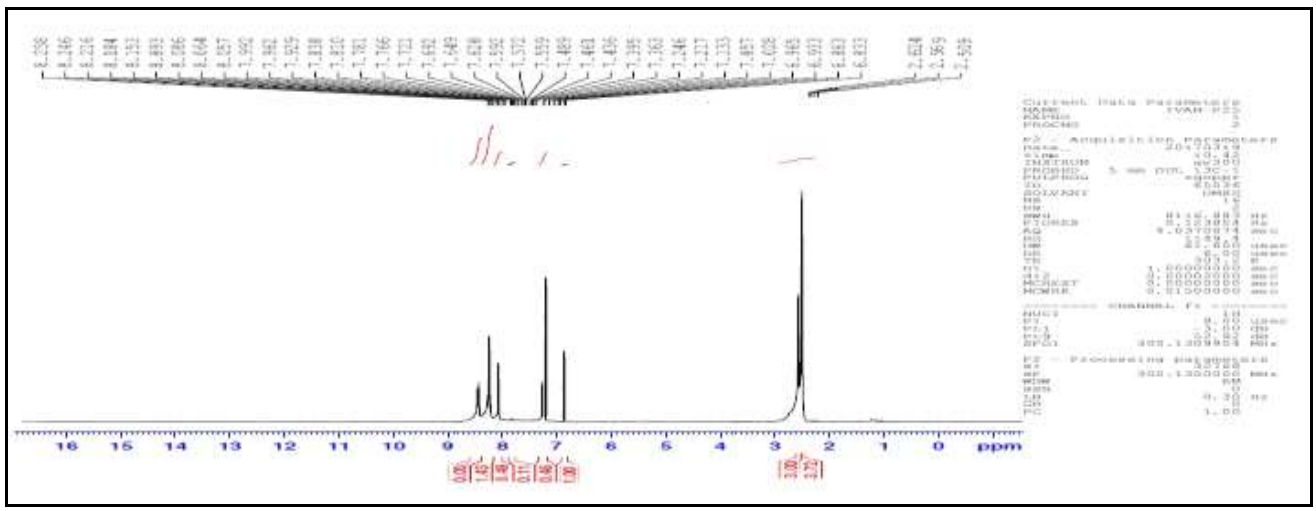


Figure 3: ^{1}HNMR spectrum for ligand (HL_2)

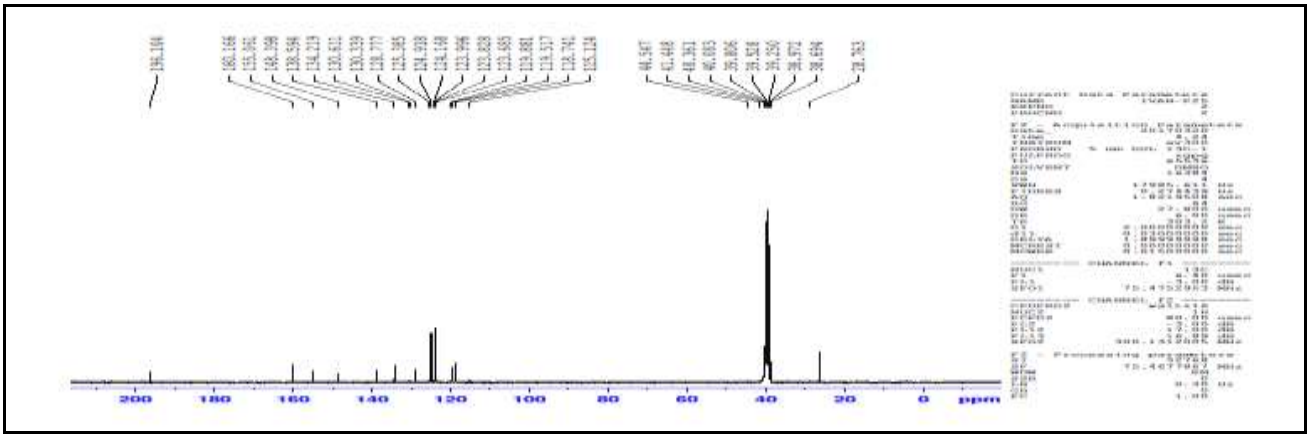


Figure 4: ^{13}CNMR spectrum for ligand (HL_2)

Calibration Curve

Mixed aqueous-ethyl alcohol of ligand and metal ions have been varied molar concentration (10^{-5}–10^{-3} M), only reach (1-3×10^{-4}M) condensation followed Beer's law as well showed clear intensive color. Better fit straight lines have been occurred for interconnected relationship factor R>0.9980 depending on the Figure 5.

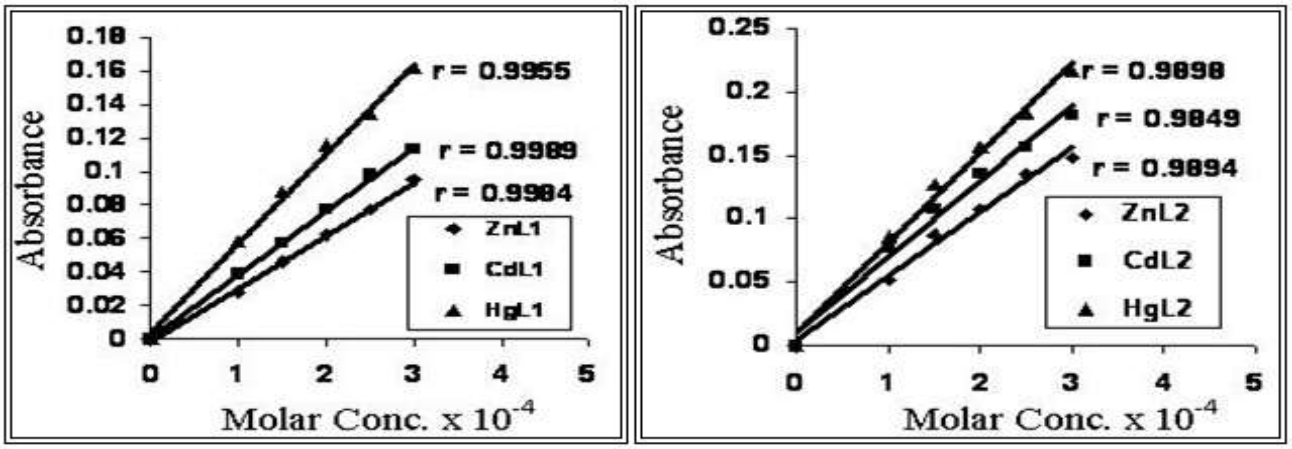


Figure 5: Linear relationship between molar concentration and absorption

Model Conditions

To find interaction between produced ligand as well metal ions under education with preparation from complexes, spectrum from combining solutions with ligand as well metal ions to achieve the perfect pH as well condensation, also firm wave length (λ_{max}) were studied the first, thereafter mole ratio metal for ligand (M:L) was defined to equip complexes. Ideal condensation has been chosen with complex solution on which basis solution gives highest absorbance at steady (λ_{max}) with different pH, as well outcomes are labeled in Table 2. Trial outcomes evidence that absorbance from every prepared complexes are maximum as well steady on buffer solution from CH_3COONH_4 on pH extent (4-9).It has been found that every prepared complexes had perfect pH according to Figure 6.

Table 2: Conditions with preparation for complexes as well UV-Vis, conductance menstruation 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_1)	-	-	-	234 274 326	0.825 1.190.1.10 6	825 1190 1106	-
[$Zn(L_1)_2$]	7	2	1:2	272 330 413	0.867 0.682 0.218	867 682 218	12.62
[$Cd(L_1)_2$]	7	2.5	1:2	285 328 421	1.651 0.866 0.146	1651 866 146	10.04
[$Hg(L_1)_2$]	7	2	1:2	243 330	1.263 0.773	1263 773	-

				406	0.104	104	
Ligand(L_2)	-	-	-	274 326 386	2.011 1.935 1.223	2011 1935 1223	-
$[Zn(L_2)_2]$	7	2.5	1:2	270333 410	1.316 1.715 0.118	1316 1715 118	18.52
$[Cd(L_2)_2]$	7	2	1:2	275 342 402	0.953 1.532 0.211	953 1532 211	13.63
$[Hg(L_2)_2]$	7	2.5	1:2	270 383 415	1.173 0.615 0.115	1173 615 115	10.43

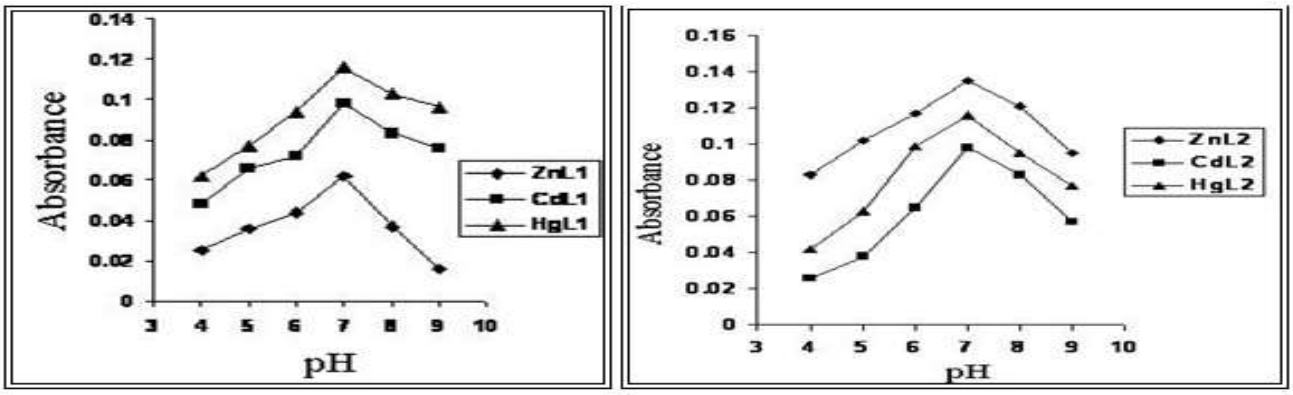


Figure 6: Effect of pH at absorption (λ_{max}) to the compounds

Metal to Ligand Ratio

Mole ratio also job techniques have been utilized to assign complexes at solutions. On both situations results spread 1:2 (metal:ligand) ratio. A chosen piece is according to Figure 7, Table2 synopsizes outcomes gated, as well as specialization with make complexes.

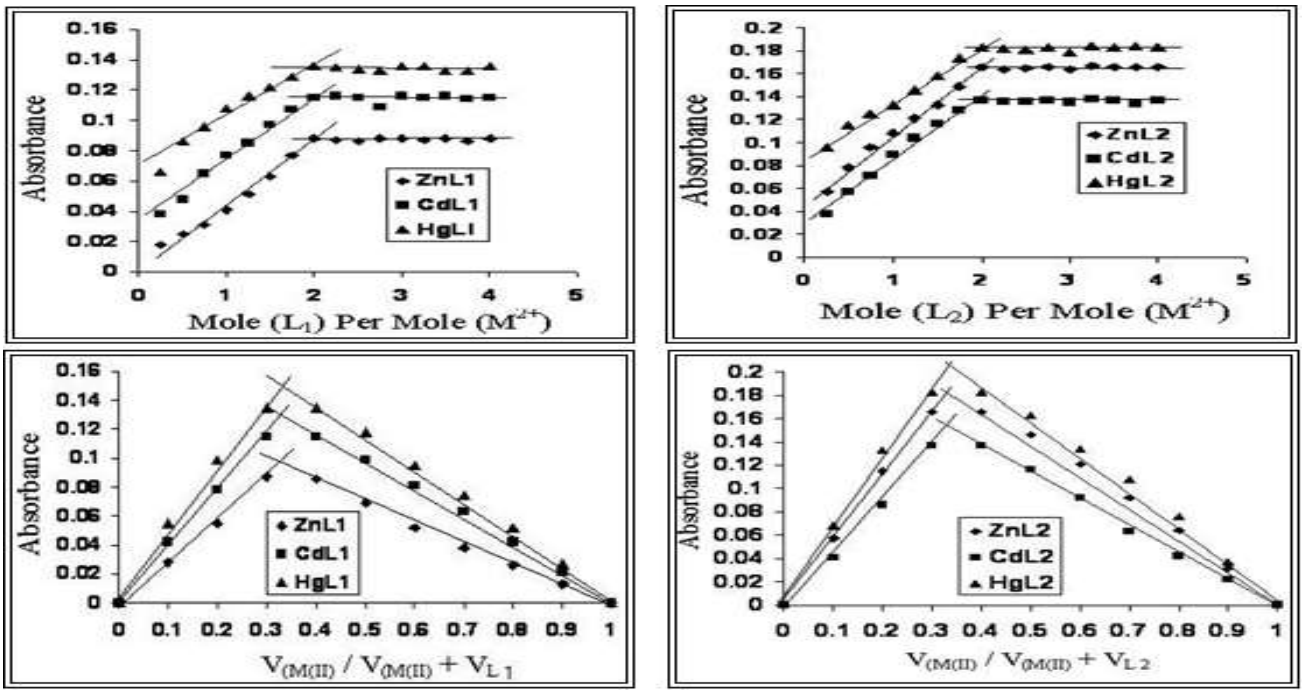


Figure7: Mole ratio as well Job manners to the compounds solutions

Physical Properties

Interaction of the ligand melted in ethanol with the metal ions melted in perfect pH and in a (Metal: Ligand) ratio of (1:2) have been produced to solid complexes.

The outcomes of elemental analyses well metal import from complexes were on real identical for calculated values. Conductivity for metal chelates melted in ethanol (10^{-3}mole/L) display non-electrolytic type [20], datum are recorded on Table2.

Determination of Stability Constant as well Free Gibbs Energy

The constant (K) of stability to (1:2) metal into ligand compound can be computed according to the equations.

$$K = \frac{1-\alpha}{4\alpha^3 C^2} \quad ; \qquad \alpha = \frac{A_m - A_s}{A_m}$$

Where *c* = condensation to the compound solution at mole/ L α = degree for fell apart, As= Absorption in solution including same amount from ligand as well metal ion also Am= absorption from solution including self same quantities for metal as well surplus for ligand. High values with (K) point out to high fastness for produced complexes [21]. Thermodynamic parameters from Gibbs free energy (ΔG) have been also studied. ΔG data have been reckoned from the equation [22].

$$\Delta G = -R\ T\ Ln\ k$$

Where; R = gas constant = 8.314 J.mol^{-1}.K, T = absolute temperature (Kelvin). Negative value from (ΔG) due to the reaction between azo dyes as well as metal ions understudy are spontaneous, see Table 3.

Table 3: Stability constant as well free Gibbs energy for metal chelates

Complexes	A_s	A_m	α	k	Lin k	ΔG kJ.mol^{-1}
$[Zn(L_1)_2]$	0.o41	0.088	0.534	19.41×10^6	16.781	- 41.648
$[Cd(L_1)_2]$	0.077	0.115	0.330	83.75×10^6	18.243	- 45.198
$[Hg(L_1)_2]$	0.108	0.136	0.205	795×10^6	20.493	- 50.772
$[Zn(L_2)_2]$	0.108	0.166	0.349	651×10^6	20.294	- 50.279
$[Cd(L_2)_2]$	0.089	0.137	0.350	10.831×10^6	14.356	-35.568
$[Hg(L_2)_2]$	0.133	0.183	0.273	145.40×10^6	18.795	-46.565

UV-Vis Spectra

UV-Vis spectra from readied compounds melted at ethyl alcohol (10^{-3} mole/L) were gauged as well data formed are listed on Table 2. UV- Vis spectra from ligands shows peaks at the range (234-326 nm) have been appointed to mild energy (π- π*) transition and peak at 386 nm in the spectrum of ligand (HL_2) due to (n- π*) transition [23].

Electronic spectra from Zn^{+2},Cd^{+2}also Hg^{+2} complexes do display charge transfer, as well magnetic susceptibility displays that three complexes have diamagnetic moments, due to d-d transition are not probable subsequently electronic spectra did not give any prolific information, reality this outcome is a good agreement for former work from geometry for octahedral [24,25].

FT-IR Spectra

FT-IR spectral from produced compounds was assembled; as well datum has been scheduled on Table 4. Broad band in the FT-IR spectra from ligands at 3437 and 3433 cm^{-1}, whom were appointed for stretching vibration from υ(OH) phenol, disappearance from this band on spectra from all outputted metal chelates specified deprotonation from phenol group into coordination for metal ion [26]. Spectra presented band on 1685 cm^{-1}because υ(C=O) vibration, since no significant change in this band was noticed, the potential that coordination occur by donating atom at this group has been precluded [27].

Bands differentiating of the azo groups at 1448 and 1546 cm^{-1} displaced for lower wave number with alter in shape on spectra from all produced complexes [28]. The bands at the range (1346-1500 cm^{-1}) because bending frequency from (δCH_3) as well stretching vibration from υ(C=C) [29]. Stretching frequency bands with metal-nitrogen also metal-oxygen moreover proven through existence from bands about 452-542 cm^{-1}. According to the outcomes preserved, a tetrahedral geometry was showed with produced metal chelates [30, 31].

Table 4: Main frequencies for ligands as well complexes (cm^{-1})

Compounds	υ(OH)	υ(C=O) + υ(C=C)	υ (N=N)	$\delta CH_{3\ as,s}$	υ(M-N) + υ(M-O)
Ligand(HL_1)	3437 br.	1685 s. 1597 s. 1500 sh.	1448 sh.	1361 sh.	-
$[Zn(L_1)_2]$	-	1683 s. 1597 s. 1500 s.	1427 s.	1368sho. 1353 sh.	542 w. 466 w.
$[Cd(L_1)_2]$	-	1685 s. 1597sh. 1500 s.	1420 s.	1381sho. 1373 sh.	534 w. 471 w.
$[Hg(L_1)_2]$	-	1683 s. 1598 s. 1501 s.	1432 sh.	1377 sh. 1366 sho.	540 w. 483 w.
Ligand(HL_2)	3402 br.	1685 sh. 1604 s.	1546 sh.	1431 sh. 1346 sh.	-
$[Zn(L_2)_2]$	-	1685 sh. 1608 s.	1533 sh.	1431 sh. 1404 sh. 1344sho.	477 w. 452 w.
$[Cu(L_2)_2]$	-	1684 sh. 1606 s.	1526 sh.	1420 sh. 1381 sho. 1345 sh.	480 w. 466 w.
$[Cu(L_2)_2]$	-	1685 s. 1605 sh.	1536 s.	1433 sh. 1355 sho. 1333 sh.	477 w. 453 w.

Microbial Efficiency and Dyeing Methods

All the produced azo ligands as well metal chelates were tested against: *Staphylococcus aureus, Esherichia Coli*, *Candida albicans* also *Candida tropicalis*, Table 5 suggests the deactivation spread converse the antibacterial and antifungal specimen. The dyeing performance of the ready compounds was defined at fabric of cotton. Dyes were essayed with light as well stability of detergents. So every dyes show very excellent dyeing holding as well depth on the fabric, see Figure 8.

Table 5: Diameters (mm) on suppression with microbial efficacy into azo ligands also metal chelates.

Compounds	Staphylococcus aureus	Esherichia coli	Candida albicans	Candida tropicalis
Ligand (HL_1)	15	11	-	-
$[Zn(L_1)_2]$	14	14	-	-
$[Cd(L_1)_2]$	10	14	15	10
$[Hg(L_1)_2]$	17	21	-	10
Ligand (L_2)	16	12	-	-
$[Zn(L_2)_2]$	20	17	12	12
$[Cd(L_2)_2]$	22	22	-	10
$[Hg(L_2)_2]$	18	15	12	14

Figure 8: Samples the textiles dyeing for azo ligands and metal chelates

Conclusion

At current work, the metal chelates were readied for ligands. Willing complexes are labeled through melting point, atomic absorption of flame, FT.IR as well UV-Vis spectral, as well as conductivity quantifications. Exploration of antimicrobial efficacies has been leaved out versus the experimented organism. Dye and produced complexes were performed on fabric of cotton .Depending the outcome datum a tetrahedral structure proposed with readied metal complexes.

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