

Synthesis, Characterization, Dyeing Performance and Biological Evaluation of Zn(II), Cd(II) and Hg(II) Complexes with Azo Dye Ligand

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Abstract: Azo ligand 4-((2-hydroxy-3, 5-dimethylphenyl)diazenyl) benzoic acid was derived from 4-aminobenzoic acid and 2, 4-dimethylphenol. Azo dye was identified by (CHN) analysis and (UV-Vis, FT-IR and ¹H-NMR). Attended compounds have been identified by utilizing atomic absorption flame, FTIR also UV-Vis spectrum manners and conductivity ministrations.

INTRODUCTION

Many applications of azo dyes such as chemistry, pharmaceutical and radiochemical industry, these azo dyes are used complexing and pharmaceutical agent for many of metal ions^[1,2]. Metal chelates for azo ligands are widely important type for dyeing the wool, nylon and silks into higher fastness for washing and light^[3]. Recently metal chelates obtaining azo dyes have attracted increasing attention into increasing structural and electronic properties depending on their uses for molecular systems^[4,5]. In this research, synthesis of azo dye by react for 4-aminobenzoic acid with 2, 4 dimethylphenol, complex of azo dye have been identified and produced via. different analysis.

MATERIALS AND METHODS

Instrumentation: Shimadzu UV-160 a has been used to study the UV-Vis spectrum. IR-spectrum have been

possessed at a (Shimadzu, FTIR-8400 S) Fourier transform infrared. Spectrophotometer (4000-400 cm⁻¹) as well patterns attended like KBr discs. Atomic absorption was studied via. using Shimadzu A.A-160A. elements analysis have been done, utilizing Euro vector EA 3000A Elemental Analyzer. The conductors of 10⁻³ M from complexes measured at DMSO on 25°C through employing (Philips PW-Digital Conductimeter). ¹H-NMR spectrum was pointed out at a like the solvent also tetramethylsaline as internal reference. Moreover, melting points were gained through employing (Melting Point Apparatus).

Materials and reagent: All chemicals used as purchased including ZnCl₂, CdCl₂.H₂O and HgCl₂ (Merck), 4-aminobenzoic acid and 2, 4-dimethylphenol (Fluka).

Produced of azo ligand: 4-aminobenzoic acid (Jarad and Kadhim, 2015) (0.342 g, 1mmole) meted in a mixture of (10 mL) of ethanol including (2 mL) conc. HCl and

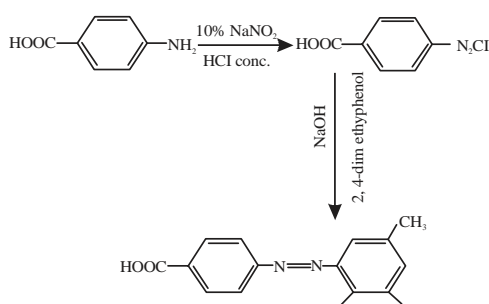


Fig. 1: Produced of azo ligand

(10 mL) water and diazotized at 5°C with 10% solution of NaNO_2 to the a cooling ethyl alcohol solution at (0.305 g, 1 mmole) of 2, 4-dimethylphenol. After that 25 mL at 1M of NaOH solution has been added up into mix the dark color as well deposition at azo ligand was observed. This precipitate was filtrated, washed several times with ethyl alcohol, then leave to the dry. The interaction seems at Fig. 1.

Preparation of buffer: $\text{CH}_3\text{COONH}_4$ (0.77 g, 0.01 mol) was resolved in 1000 ML Dw. With only pH rate (4-9) was utilization CH_3COOH .

Solution: Bulk of standard solutions for metal salt from (Zn^{II} , Cd^{II} also Hg^{II}) were made in diversity resolve (10^{-5} - 10^{-3} Mol L^{-1}) at pH rat On same time a bulk from ethyl alcohol solutions from substrate during the extent from condensation (10^{-5} - 10^{-3} Mol L^{-1}) has been produced.

Preparation of metal chelates: Ligand solution (0.270 g, 2 mmol) added up for stirring for 0.068, 0.109 and 0.136 g of metal chloride from (Zn^{II} , Cd^{II} also Hg^{II}) 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 : $\text{C}_2\text{H}_5\text{OH}$ mix. The preparation method appears at Fig. 2.

Microbial properties: Nutrient agar medium, utilized (DMSO) like as solvent also like as control, focus from compounds at solvent has been 10^{-3} Mol L^{-1} , utilized disc sensitivity exam. That path includes exposition from zone for inhibition towards spread from micro-organism at agar dish. Dishes have been brood into 24 h at 37°C.

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 (15-20°C) on (1 h) as well in $\text{pH}^{[6]}$.

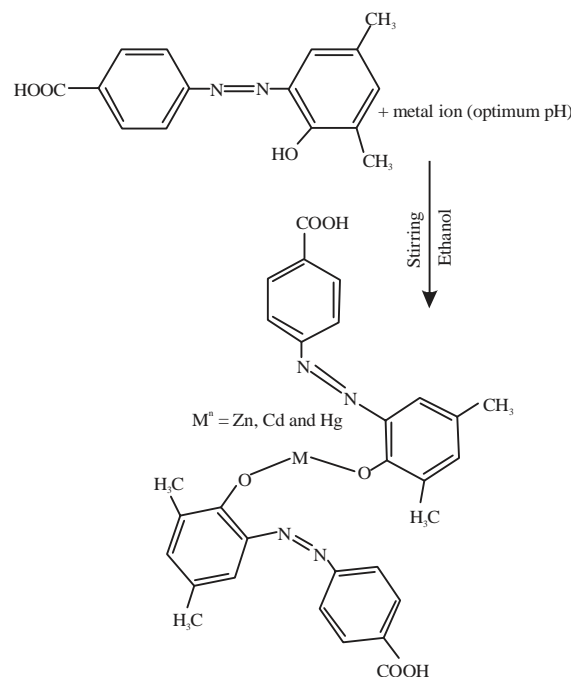


Fig. 2: Proposed geometry of the metal (II) complexes

RESULTS AND DISCUSSION

Azo Ligand (L) was characterized by FTIR and UV-Vis. The solid compounds were generated through reaction from ethyl from metal ions at (1:2). Metal includes from complexes have been into good correspondence for calculated values (Table 1) consist physical characteristics. Molar conductance from the compounds like (10^{-3} Mol L^{-1}) on ethyl alcohol consist electrolytic style^[7], the datum were tabulated in Table 2.

¹H-NMR spectrum: ¹H-NMR spectrum of the Ligand (L) in DMSO (Fig. 3) shows multiplet signals at $\delta = 6.886$ - 8.105 ppm refers to aromatic protons. On the other hand, the signal at $\delta = 6.747$ ppm due to proton of phenol. Whereas, the signal at $\delta = 13.11$ ppm is assigned to proton of carboxylic group. $\delta = 2.50$ ppm referred to DMSO-d₆^[8, 9].

Calibration curve: Mixed aqueous-ethyl alcohol of ligand and metal ions have been varied molar concentration (10^{-5} - 10^{-3} Mol L^{-1}), only reach (1.3×10^{-4} Mol L^{-1}) 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 Fig. 4.

Model conditions: To find interaction between ligand as well under education with preparation from complexes,

Table 1: Physical characteristics for ligand also its complexes

Compounds	Colors	MP°C	Yield (%)	Analysis calc (Found)			
				M (%)	C (%)	H (%)	N (%)
Ligand(L)	Orange	264	81	-	66.66 (65.79)	5.18 (4.93)	10.37 (9.82)
[Zn(L) ₂]	Brown	287	82	10.78 (9.85)	59.70 (58.92)	4.31 (4.01)	9.28 (8.96)
[Cd(L) ₂]	Reddish brown	295	86	17.23 (16.75)	55.38 (54.22)	4.00 (3.98)	8.61 (7.85)
[Hg(L) ₂]	Yellow	293	80	27.19 (26.87)	48.71 (47.77)	3.51 (2.88)	7.57 (6.77)

Table 2: Conditions with preparation for complexes as well UV-Vis, conductance menstruation datum

Compounds	Optimum pH	Optimum molar Conc .×10 ⁻⁴	M:L ratio	λ _{max} (nm)	ABS	ε _{max} (Lmol ⁻¹ cm ⁻¹)	Λ _m (S _{cm} ² mol ⁻¹) in absolute ethanol
Ligand(L)	-	-	-	250 338 402	0.630 1.520 0.710	630 1520 710	-
[Zn(L) ₂]	7	2.5	1:2	237 340 475	0.325 0.740 0.438	325 740 438	10.62
[Cd(L) ₂]	7	2.0	1:2	264 363 480	0.932 0.867 0.559	932 867 559	12.11
[Hg(L) ₂]	7	2.5	1:2	277 358 466	1.036 0.877 0.661	1036 877 661	15.23

spectrum from combining solutions with ligand as well metal ions to achieve the perfect pH as well condensation also firm wave length (λ_{max}) n 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 CH₃COONH₄ on has been found that every prepared complexes had perfect pH according to Fig. 5.

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 Fig. 6 and Table 2 synopsis outcomes gated as well as specialization with make complexes.

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 (Fig. 7).

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

Where:

C : Condensation to the compound solution (mol L⁻¹)

α : Degree for fell apart

A_s : Absorption in solution including same amount from ligand as well metal ion also

A_m: 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^[6]. Thermodynamic parameters from Gibbs free energy (DG) have been also studied. DG data have been reckoned from the equation^[10].

$$\Delta G = -RT \ln K$$

Electronic spectra: UV-Vis spectra from readied compounds melted at ethyl alcohol (10⁻³ mol L⁻¹) were gauged as well datum formed are listed on Table 3. UV-Vis spectra from Ligand (L) shows peaks at 250 and 338 nm have been appointed to mild energy (π-π*) transition and peak at 402 nm due to (n-π*) transition^[11].

Electronic spectra from Zn^{II}, Cd^{II} also Hg^{II} 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 tetrahedral^[12, 13].

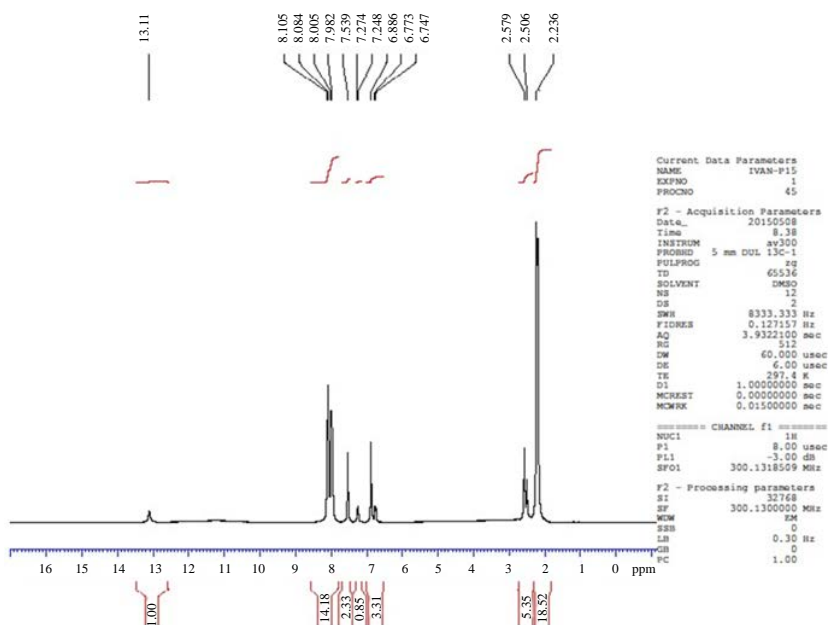


Fig. 3: ¹H-NMR spectrum for Ligabd (L)

Table 3: UV-UIS spectra from readied compounds melted at ethyl alcohol

Complexes	A _s	A _m	α	k	Lin k	ΔG kJmol ⁻¹
[Zn(L) ₂]	0.135	0.244	0.446	25.18×10 ⁶	17.041	-42.220
[Cd(L) ₂]	0.105	0.188	0.441	43.00×10 ⁶	17.576	-43.545
[Hg(L) ₂]	0.185	0.288	0.357	58.45×10 ⁶	17.883	-44.306

Table 4: Fundamental frequencies to the ligand and it's compounds (cm⁻¹)

Compounds	ν(OH) carboxyl	ν(OH) phenol	ν(C = O)	ν(N = N)	ν(M-N)	ν(M-O)
Ligand (L)	3452 br.	3360 sho.	1685 sh.	1489 s.	-	-
[Zn(L) ₂]	3450 br.	-	1682 sh.	1470 sh.	552 w.	470 w.
[Cd(L) ₂]	3452 br.	-	1681 s.	1472 s.	530 w.	463 w.
[Hg(L) ₂]	3450 br.	-	1685 sh.	1475 s.	482 w.	442 w.

Table 5: Suspension capability boist various the bectria pattern

Compounds	<i>Staphylococcus aureus</i>	<i>Esherichia coli</i>	<i>Candida albicans</i>	<i>Candida tropicalis</i>
Ligand (L)	17	16	18	10
[Co(L) ₂].H ₂ O	-20	19	13	16
[Ni(L) ₂].H ₂ O	23	17	15	15
[Cu(L) ₂].H ₂ O	26	18	12	19

FT-IR spectra: Pertinent vibration bands for free ligands as well their compounds have been registered into KBr at area 4000-400 cm⁻¹. Assignments into distinctive bands (FT-IR) spectrum to free azo Ligand (L) and compounds are abbreviate at Table 4. The IR spectrum for the azo ligand offer bands in 3452 and 3360 cm⁻¹, whom were qualified into stretching vibration for ν(OH) carboxyl and phenol, Since no significant change in for ν(OH) Since, no significant change in this group was noticed, the possibility that coordination occurs via. the donating atom excluded^[14]. Band into IR spectrum to the ligand in 1489 cm⁻¹ consequent into stretching vibration for ν(N = N)^[15]

on complexation a shifting for alteration into from was noticed of this band whereas growing into density were observe, specified can be an outcome from coordination for metal ion. New bands watched in (552-443 cm⁻¹) are temporarily appointed into ν(M-N) and ν(M-O) (Metal-Ligand) stretching bands^[16, 17].

Table 5 shows the suppression capability oboist various the bacteria pattern for the generated compounds beneath study. Lgand and compounds are application as disperse dyes on cottonfabrics, the dyes were tested for light and detergent fastness, showed on Fig. 5.

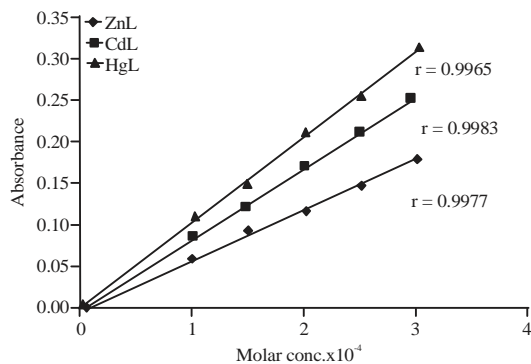


Fig. 4: Mixed aqueous-ethyl alcohol of ligand and metal ions

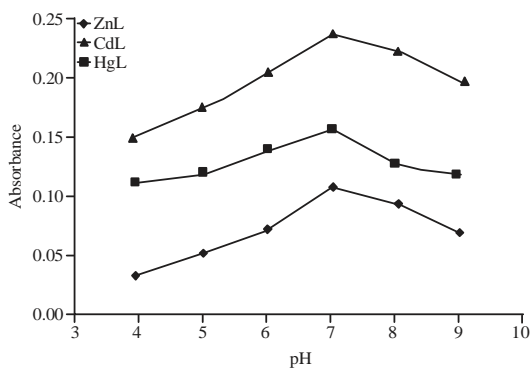


Fig. 5: Effect of pH at absorption (λ_{\max}) to the compounds

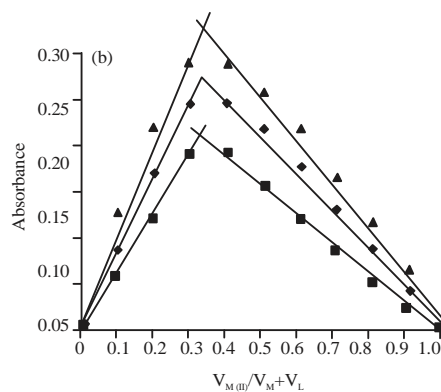
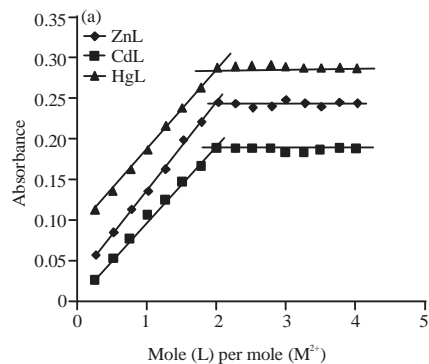


Fig. 6(a-b): Mole ratio as well job manners to compounds solutions



Fig. 7: Gand and compounds are application as disperse dyes on cotton fabrics

CONCLUSION

At addendum from ligand and compounds are application as disperse dyes on cotton fabrics as well antibacterial activity of the produced compounds against various bacteria and fungi investigated. Of the gained datum a tetrahedral geometry was proposed into whole prepared complexes.

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