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Synthesis And Characterization Of Metal(II) Complexes With Azo Dye Ligand And Their Industrial And Biological Applications

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Abstract

Azo ligand 4-((2-hydroxy-3,5-dimethylphenyl)diazenyl) benzoic acid was synthesized from 4-aminobenzoic acid and 2,4-dimethylphenol. Azo dye compounds have been characterized by different techniques (^{1}H-NMR, UV-Vis and FT-IR). Metal chelates of (Zn^{II}, Cd^{II} and Hg^{II}) have been synthesized with azo ligand (L). Produced compounds have been identified by using spectral studies, elemental analysis(C.H.N.) and conductivity. Produced metal chelates were studied using mole ratio as well sequences contrast types. Rate of concentration(1×10^{-4}-3×10^{-4} Mole/L) sequence Beer's law. Compound solutions have been noticed height molar absorptivity. The addendum of ligand and compounds has applied as disperse dyes on cotton fabrics for antibacterial activity of the produced compounds against various bacteria and fungi has investigated. For the gained datum, a tetrahedral geometrical structure has been suggested for each primed complex.

Keywords:-, azo dyes, metal complexes, biological activity, textile industry.

1.Introduction

Azo compounds are highly colored and analytical reagents, therefore they play important roles in different uses such as, indicators in chemical laboratories, stains in the biological estates, also because of dyeing behavior they used in industrial field for dyeing of textile(1), high-technological systems, coloring of various materials, colored plastics, biological-medical studies and advanced organic synthesis(2). Optical properties another advantage of azo compounds make them employed in optical uses including optical storage capacity, optical switching, holography and non-linear optical(3). Pharmaceutical and radiochemical another interest of of such compounds(4,5). Azo dyes metal chelates have been catch more attention in catalytic, pharmaceutical and industrial uses such as, synthetic leather, vinyl polymers, inhibition of DNA, RNA, protein synthesis, nitrogen fixation and carcinogenesis(6,7). Recently, metal chelates that obtain azo pigments have attracted more interest in the increase of electronic products as well as structural lineaments in connection for their enforcement with molecular memory storing, nonlinear visual components as well as printing structures(8,9). In this work, synthesis, identification and chelating of Zn^{II}, Cd^{II} and Hg^{II} metal complexes containing 4-aminobenzoic acid azo dye as a ligand, produced compounds have applied as disperse dyes on cotton fabrics for antibacterial activity against various bacteria and fungi has investigated.

2. Experimental

2.1 Instrumentation

UV-Vis spectrums were recorded by (UV-160 A) Shimadzu Spectrophotometer. I.R-spectra have been detrmined by Shimadzu, FTIR-8400 S measuring

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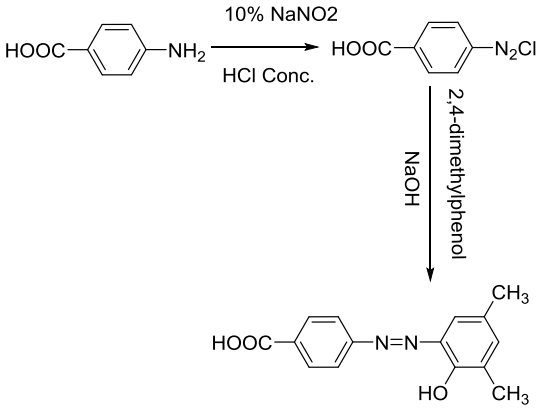
machine. Spectrophotometer (4000-400) cm-1. Atomic Absorption was attained through via Atomic Absorption / Flame Emission Spectrophotometer based on Shimadzu A.A-160A model. (C,H,N)analyses were done utilizing Euro vector EA 3000A Elemental Analyzer. The conductors of 10-3M from complexes were recorded at DMSO on 25°C via Philips PW- Digital Conductimeter. 1H-NMR spectrum was pointed out on the Brucker-300 MHz Ultra Shield spectrometer utilizing (CH3)2SO like solvent also (CH3)4Si as internal reference. Additionally, melting points have measured by Melting Point Apparatus.

2.2 Materials and reagent

The subsequent materials were received from distinguished chemical suppliers and applied; zinc chloride, cadmium chloride monohydrate and mercury chloride (Merck), 4-aminobenzoic acid and 2,4-dimethylphenol (Fluka).

2.2 Produced of azo ligand

4-aminobenzoic acid(10) (0.342gm,1mmole) meted in the combination of (10ml) of ethanol containing (2ml) conc. HCl with 10ml of water was diazotized under 5ºC with ten percent of NaNO2 solution. Diazotized solution has been inserted progressively with stirring into the cooled ethyl alcohol solution using (0.305 gm,1mmole) of 2,4-dimethylphenol. Subsequently, NaOH solution (25 ml, 1M) was inserted into the dark mix and deposited at azo ligand. The precipitate was filtrated, washed numerous intervals with ethyl alcohol until getting dry. This synthesis is explained by scheme-1.



Scheme 1: Synthesized azo ligand.

2.3 Buffer Solution

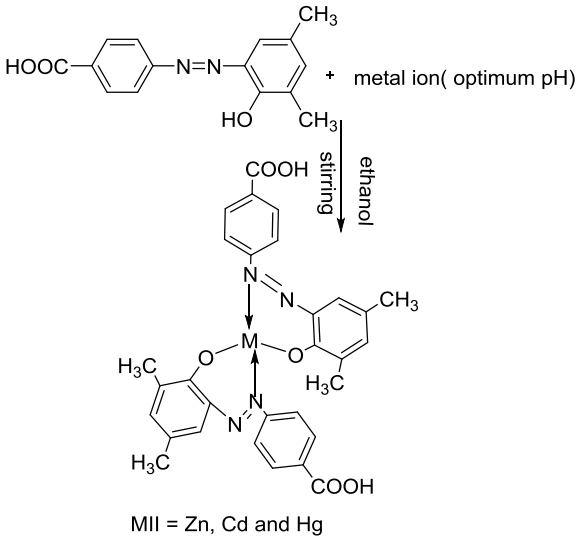
About (0.01M, 0.771 gm) of CH_3COONH_4 material has been resolved by doubly deionized water of one liter. The pH values are ranged from 4 to 9 based on CH3COOH or NH3 solution.

2.4 Standard Solution

Bulk of standard solutions based on metallic salt from (ZnII, CdII also HgII) have been made in diversity resolve (10-5-10-3 Mole/L) on pH rat (4-9). In the same time, bulk from ethyl alcohol solutions from ligand during extent from condensation (10-5-10-3)Mole/L has been produced.

2.5 Preparation of Metal Chelates

Ethyl alcohol solution from ligand (0.270 gm, 2 mmole) was added for stirring using 0.068, 0.109 and 0.136 gm of metal chloride from (ZnII, CdII also HgII) resolved n the solution with the desired pH. The mixture was cooled into dark color deposition has been formed, filtrated, also washed several times for 1:1 H2O: C2H5OHmix. The preparation method appears at scheme-2.



Scheme 2: Proposed geometry for metal chelates.

2.6 Microbial Properties

Azo ligand and newly metal chelates were checked at vitro for their antibacterial as well antifungal activity in contradiction of *Esherichia Coli*, *Staphylococcus aureus*, *Candida tropicalis* as well as *Candida albicans*, in Nutrient Agar medium using (DMSO) as solvent for controlling, focusing from compounds at solvent that are within 10^{-3}Mole/L based on disc sensitivity analysis. That pathway involves exposing from inhibition zone headed for spread from micro-organism at agar dish(11). Dishes were incubated for whole day under 37Cº.

2.7 **Dyeing Technique**

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

3. Results and Discussion

Azo ligand (L) has described by UV-Vis along with FT.IR. The solid compounds have produced by reacting ethyl alcohol solution of ligand with aqueous solution from metal ions under case of (1:2). Metal includes complexes of worthy correspondence with determined magnitudes as depicted by Table-1. This table consist physical feature details. Molar conductance from the compounds like (10-3 Mole/L) on ethyl alcohol involve electrolytic style(12). The datum have tabulated in Table- 2.

Table 1 :Physical features of ligand along with its complexes

Material	Color	M.P°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)

^{1}H-NMR Spectrum

Figure 1 states ^{1}H-NMR spectrum for (L) ligand in DMSO displaying multiplet signals on δ=6.886-8.105 ppm indicates into aromatic protons(13). On the other hand, the signal on δ=6.747 ppm because of proton from phenol(14). Whilst, the signal on δ=13.11 ppm is specified into proton of carboxylic group. Signal is on δ =2.236 ppm due to the δ (CH_3) of phenol also the signal on δ =2.50 ppm appeared in DMSO-d6(15,16).

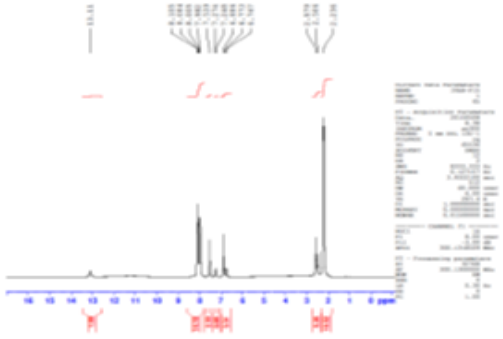


Figure 1: ^{1}H-NMR spectrum for ligand (L).

Calibration Curve

Diverse molar concentration (10^{-5}-10^{-3} Mole / L) of aqueous ethyl alcohol ligand and metal ions, only (1-3 x 10^{-4} Mole / L) followed Beer's law and showed clear intense color. Straight lines were performed more favorably for the correlation factor R> 0.9980 depending on Figure2.

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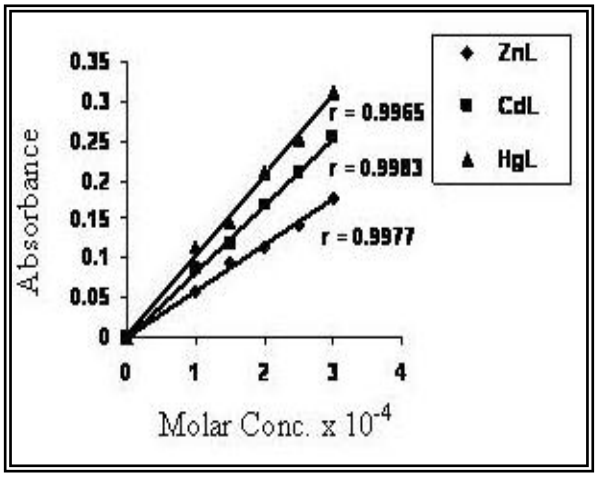

Figure 2: Linear association with molar concentration and absorption.

Model Conditions

To find interacting relation between formed ligand and metal ions under study prepared from complexes, spectrum from combining solutions with ligand as well metal ions must achieve the optimal pH based on adopted condensation. The maximum wave length (λ_{max}) was investigated firstly. Thereafter, mole ratio metal for ligand (M:L) was defined for equiped complexes. Ideal condensation has selected with complex solution using basis solution that provides maximum absorbance with steady (λ_{max}) and various pH, as well outcomes are labeled on Table 2. Trial outcomes explain that absorbance from every prepared complexes was maximum and steady on buffer solution from CH_3COONH_4 on pH extent of

(4-9). It has been found that every prepared complexes had perfect pH according to Figure 3.

Ratio for Metal to Ligand

Mole ratio measuring methods were utilized for assigning complexes at solutions. On both situations, results exhibit 1:2 (metal:ligand) ratio. A chosen piece is according to Figure 4. Table 2 synopsizes outcomes about the specified complexes.

Stability Constant as well Free Gibbs Energy Determination

Stability constant (K) based on (1:2) metal for metal chelates can be calculate 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 of a compound solution at mol / L α = degree of breakdown, As = absorption in solution including the same amount of ligand as well as a metal ion. Where Am = the absorbance from the solution including the same amounts of the metal as well as the excess of the binder. High values with (K) indicate high stability of the productive complexes (17). The thermodynamic parameters of Gibbs free energy (G) were also studied. Data for □G were calculated from equation (18).

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

Here, R is gas constant that equals to 8.314 J.mol-1.K, and T stands for absolute Kelvin temperature. Negative value from (□G) is due to the reacting among azo dyes along with metal ions understudy are spontaneous, see Table 3.

Electronic spectra

UV-Vis spectra from readied compounds melted at ethyl alcohol (10^{-3} mole/L) were gauged as well datum formed are listed on Table 2. 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(19). Electronic spectra from Zn^{II}, Cd^{II} as well as Hg^{II} complexes display charge transference along with magnetic susceptibility displays that three complexes possess diamagnetic moments, due to d-d transition aren't probable. As a result, electronic spectra didn't give any prolific information. This outcome is agreed with the former works based on tetrahedral geometry (20,21).

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

Material	Optimal pH	Optimal 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(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

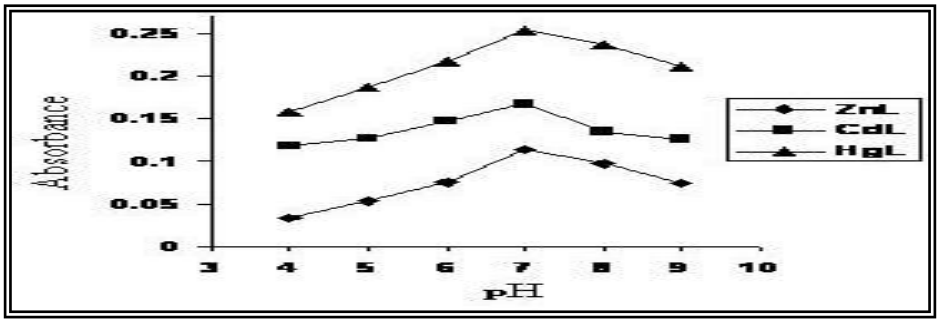

Figure 3: Effect of pH at absorption (λ_{max}) for metal chelates.

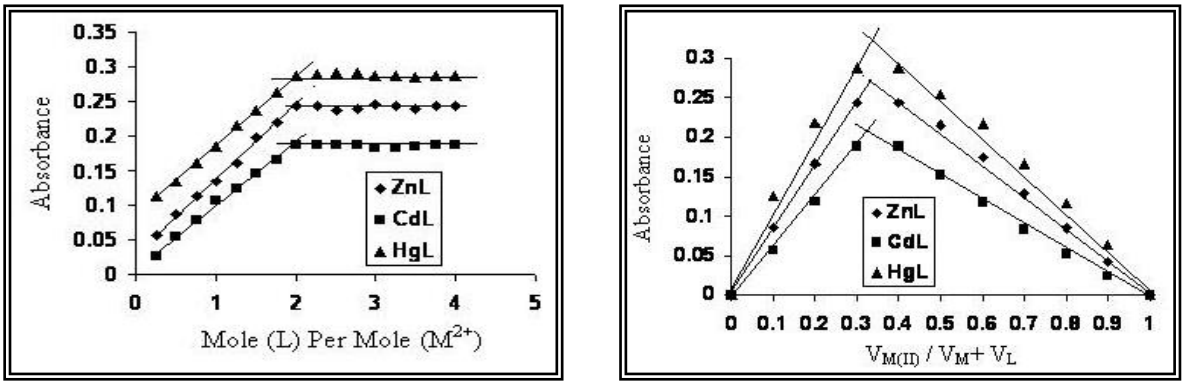

Figure 4**:** Mole ratio in accordance with compounds solutions.

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}
$[Zn(L)_2]$	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

FT-IR Spectra

At area 4000-400 cm^{-1}, relevant vibration bands for free ligands along with their compounds were recoded based on KBr. Table-4 states the characteristic bands of (FT.IR) spectrum for free azo ligand(L) and compounds. The IR spectrum for azo ligand has shown bands in 3452 and 3360 cm^{-1}, related to stretching vibration for υ(OH) carboxyl and phenol, As there is no noteworthy variation in for υ(OH) carboxyl that indicating no coordinating through this group(22). The (OH) band of phenol group has been absent at spectra from every prepared complexes, whom pointed out deprotonation and participation from enol oxygen at chelation(23). Band on 1685 cm^{-1} was assigned into stretching mode from υ(C=O). Since not significant alteration on this group has been observed, possibility that coordination occurs via the donating atom excluded(24,25). Band into IR spectrum to a ligand in 1489 cm^{-1} resulting into stretching vibration for υ(N=N)(26,27). Based on the complexation, a shift has perceived in this band in a coordination with metal ion. New bands observed in (552-443) cm^{-1} are for the time being prearranged into ν(M-N) also ν(M-O) (Metal-Ligand) stretching bands(28-.31).

Eventually, antibacterial efficiencies from ligand and their compounds were studied based on species for bacteria. Table 5 shows a suppression ability of numerous bacteria patterns for the created compounds under analysis. Ligand and compounds applied as disperse dyes at cotton fabrics. Dyes have been screened with light also detergent stability, stated on Figure 5

Table 4: Fundamental frequencies into ligand also it's compounds(cm^{-1}).

Compounds	υ(OH) carboxyl	υ(OH) phenol	υ(C=O)	υ(N=N)	υ(M-N)	υ(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.

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

Table 5: Millimeter diameter for a suppression with microbial efficacy based on azo ligand along with its compounds.

Compounds	Staphylococcus aureus	Escherichia coli	Candida albicans	Candida tropicalis
Ligand (L)	17	16	18	10
$[Zn(L)_2]$	20	19	13	16
$[Cd(L)_2]$	23	17	15	15
$[Hg(L)_2]$	26	18	12	19

Figure 5 **:** Textiles dyeing for azo ligand and metal chelates.

Conclusion

In this work, metallic chelate complexes were bonded. Desired compounds are described by melting point, atomic absorption of flame, and visible UV and IR spectra, elemental analysis(C.H.N.) as well conductivity quantifications. The addendum of ligand and compounds has applied as disperse dyes on cotton fabrics for antibacterial activity of the produced compounds against various bacteria and fungi has investigated. They are supposed to be tetrahedral along with four coordinated metal complexes.

References

[1]. Siddigua,s. and Ali,K.S. 2016. Synthesis and characterization of bisazo derivatives of 4-acetylresorcinol, J.Chem.Pharm.Res.,8(8)292-295.

[2]. Seferoglu,Z. and Ertan,N. 2008. Synthesis, characterization and spectroscopic properties of some new phenylazo-6-aminouracil, Cent.Eur.J.Chem.,6(1)81-88.

[3]. Alimmari,A.,Bozic,B.,Mijin,D.,Marinkovic,A., Valentic,N. and Uscumlic,G. 2015. Synthesis, structure and solvatochromic properties of some novel 5-arylazo-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone dyes: Hydrazone-azo tautomeric analysis, Arabian.J.Chem.,8,269-278.

[4]. Patel,B.K. and Patel,S.D. 2015. Synthesis, characterization and chelating properties of novel metal chelates derived from resacetophenone containing azo dye, J.Curr.Chem.Pharm.Sci.,5(3)116-121.

[5]. El-Ansary,A.L., Abdel-Kader,N.S., Sherif,O.E. and Sayed,A.G. 2016. Macromolecular azo dye complexes as precursors to metal oxide nanoparticles: Synthesis, characterization, biological activity and thermal studies of

sulfadimidine azo dye complexes, Inorg.Chem., 11(1)19-35.

[6]. Dahi,M.A. and Jarad,A.J. 2020. Synthesis, characterization and biological evaluation of thiazolyl azo ligand complexes with some metal ions, J.Phys.Conf.Ser.,1664,1-17.

[7].Abbas,R.A.,Abd,Almonuim,A.E.,Jarad,A,J.,Tancz os,S.K. and Constantin,P. 2020. Synthesis, characterization and biological evaluation of Cr(III),Fe(III),Co(II),Ni(II),Zn(II) and Cd(II) complexes using an azo dye as ligand, Rev.Chim.,71(6)1-8.

[8]. Dharmalingm V, Ramasamy AK, Balasuramanian V (2011) Synthesis and EPR studies of copper metal complexes of dyes derived from remazol red b,procino yellow, fast green FCF, brilliant cresyl blue with copper acetate monohydrate**,** E.J.Chem.; l., SI: S211-S224.

[9]. Jarad,A.J. and Quiasim,S.H. 2018. Synthesis and characterization of azo dyes ligands complexes with Ni(II) and Cu(II) and studies their industrial and bacterial application, Res.J.Pharm.Bio.Chem.Sci., 9(2)631-642.

[10]. Jarad,A.J. and Kadhim,Z.S. 2015. Synthesis, spectral , dyeing performance and biological activity of azo dyes complexes with some metal ions, Int.J.Human.Arts, Med.Sci., 3(10)197-210.

[11]. Iniama,G.E.,Nfor,E.N.,Okon,E.D. and Iorkpiligh,I.T. 2014. Antimicrobial activities of synthesized Zinc(II) mixed ligand complexes derived from 2-acetylpyridine-4-phenylsemicarbazone and nitrogen-sulphurmonodentate ligands, Inter.J.Sci.Techn.Res., 3(11)73-77.

[12]. Geary,W.J. 1971.Characterization of coordination ompounds, Coord.Chem.Rev., 7,81-122.

[13]. Faghihi,K. and Hagibeygi,M. 2007. New aromatic polyamide with azo and phosphine oxide groups in the main chain, Turk.J.Chem.,31,65-73.

[14]. Bashandy,M.S.,Mohamed,F.A.,El-Molla,M.M.,Sheier,M.B. and Bedair,A.H. 2016. Synthesis of novel acid dyes with coumarin moiety and their utilization for dyeing wool and silk fabrics, Open.J.Med.Chem.,6,18-35.

[15]. Khedr,A.M and Aaad,F.A. 2015. Synthesis, structural characterization and antimicrobial efficiency of sulfadiazine azo-azomethine dyes and their bi-homonuclear uranyl complexes for chemotherapeutic use,Turk.J.Chem., 39,267-280.

[16]. Vadher,G.B and Zala,R.V. 2011. synthesis and analytical studies of some dyes as ligands and their metal chelates, Int.J.Chem.Sci**.**, 9,87-94.

[17]. Cao,H.W.and Zhao,J.F. 2003. Stability constants of cobalt(II) and copper(II) with3-[(o-carboxy-p-nitrobenzene)azo]chromotropicacid and selective determination of copper(II) by competition coordination, Cro.Chem.Acta.,76,1-6.

[18]. Wtter,G., Ludwig,N. and Horst,S. 1995. Thermodynamics and statistical mechanics, Springer-Verlag, 101.

[19]. Sharma,A., Mehta,T. and Manish, K.S. 2013. Synthesis and spectral studies of transition metal complexes supported by NO-bidentate Schiff base ligand, Der.Chem.Sci., 4(1),141-146.

[20]. Al-Noor,T.H., Jarad,A.J and Abo,S.B. 2015. Synthesis, spectral and antimicrobial activity of mixed ligand complexes of Co(II),Ni(II),Cu(II) and Zn(II) with 4-aminoantipyrine and tributylphosphine, Inter.J.Curr.Res., 7(05),15605-15609.

[21]. Al-Noor,T.H., Manhel,R.A. and Al-Teboori,A.T. 2013. Synthetic, spectroscopic and antibacterial studies of Fe(II),Co(II),Ni(II),Cu(II) and Zn(II) mixed ligand complexes of nicotinamide and cephalexin antibiotics, J.Chem.Mater.Res.,3,114-124.

[22]. Maradiya,H.R and Patel,V.S. 2001. Synthesis and dyeing performance of some novel heterocyclic azo disperse dyes, J.Baraz.Chem.Soc.,12,-6.

[23]. Kumarand,H and Chandhary,R. 2010. Biological studies novel azo based heterocyclic Schiff base and its transition metal complexes, Der.Chem.Sin.,1,55-61.

[24]. Yahyazzdeh,A and Azimi,V. 2013. Synthesis of some unsymmetrical new Schiff bases from azo dyes, Eur.Chem.Bull.,2,453-455.

[25]. Saxena,A and Saxena,R. 2013. Synthesis, characterization and biological evaluation of transition and inner transition metal complexes of ligands derived Schiff base 1-phenyl-2,3-dimethyl-4-(4-iminopentan-2-one)- pyrazole-5-one and 2-aminophenol, Orient.J.Chem.,29,89-595.

[26]. Oututu,J.O. (2013) Synthesis and application of azo dyes derived from 2-amino-1,3,4-thiadiazole-2-thiol on polyester fibre, IJRRS; 15, 2, 292-296.

[27]. Canakei,D.,Saribiyik,O.Y and Serin,S. 2014. Synthesis, structural characterization of Co(II), Ni(II) and Cu(II) complexes of azo dye ligands derived from dihydroxynaphthalene, Inter.J.Sci.Res.Innov.Tech.,1,52-72.

[28]. Reddy,V.,Patil,N and S.D.Angadi,S.D. 2008. Synthesis, characterization and antimicrobial activity of Cu(II), Co(II) and Ni(II) complexes with O,N and S donor ligands, E-J.Chem., 5,577-583.

[29]. Khalil,M.M.H.,Ismail,E.H.,Mohamed,G.G.,Zayed,E.M and Badr,A. 2012. Synthesis and characterization of novel Schiff base metal complexes and their application in determination of iron in different types of natural water, Open.J.Inorg.Chem.,2,31-21.

[30]. Al-Noor,T.H.,Ali,K.F.,Jarad,A.J. and Kindeel, A.S. 2013. Synthesis, spectral and antimicrobial activity of mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with anthranillic acid and tributylphosphine, Chem.Mater.Res.,3(3)126-133.

[31]. Al-Zinkee,J.M.M. and Jarad,A.J. 2018. Synthesis, characterization and microbial efficiency of azo dye ligand complexes With some metal ions, Res.J. Pharm.Biolo.Chem.Sci.,9(6)144-155.