

Antibacterial Activities of Newly Synthesized Azo Anils And its Oxalato-Bridged Binuclear {Cu(II) and Zn(II)} Complexes

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ABSTRACT

Novel oxalato-bridged binuclear metal {Cu(II) and Zn(II)} complexes; $[(L_1)M(II)]_2OX$ ($L_1 = 2-(2\text{-hydroxy-5-}[(4\text{-nitrophenyl)diazenyl]benzylidene\}amino)benzoic\ acid$, $OX = oxalate$) and $[(L_2)M(II)]_2OX$, ($L_2 = 2-[(2\text{-hydroxyphenyl)imino]methyl-4-}[(4\text{-nitrophenyl)diazenyl]phenol$, $OX = oxalate$) were synthesized. Azo anils and corresponding Metal {Cu(II) and Zn(II)} complexes were characterised by Elemental Combustion System, Atomic Absorption Spectroscopy (AAS), Fourier Transform Infrared (FTIR) spectroscopy, UV-Visible, Spectroscopy and ¹³C-¹H-Nuclear Magnetic Resonance spectroscopy. Elemental Analyses, FTIR and UV-Vis were used for structural characterization of metal complexes and distorted octahedral geometry for M(II) complexes came into being. The antibacterial activities of azo anils ligands, oxalate ion, $CuCl_2 \cdot 2H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$ and metal {Cu(II) and Zn(II)} complexes against gram-positive (*Bacillus subtilis*) and gram-negative (*Escherichia coli*) were evaluated. The antibacterial activities were performed to assess inhibition potential of ligand and their metal {Cu(II) and Zn(II)} complexes. The results revealed that antibacterial activities of azo anils become more pronounced when free ligands were coordinated to central metal atom.

Keywords: Azo Anils, Oxalato-bridged binuclear complexes, Antibacterial activity

1. INTRODUCTION

Azo Anils and complexes of them with Cu(II), Zn(II)} had displayed antibacterial and antifungal activities¹. Azo anils ligands are supposed as “fortunate ligands” because they can be easily synthesized by the condensation of azo dye of salicylaldehyde and aromatic amine². Azo schiff bases can coordinate through azo and azomethine group³. Most transition metal form stable complexes with azomethine because it has excellent Pi-donor character⁴⁻⁶. All at once, it is not possible for both group together take part in bonding with central metal ion because $-N=N-$ (azo group) and $-C=N$ (azomethine group) are far away from each other. So preferentially coordination take place through $-C=N$ group whereas $-N=N-$ group remain free because there is no more room for azo group to take part in coordination⁷⁻¹⁰. Azo complexes are very important compounds and have fascinated much awareness in both academic and applied research¹¹⁻¹⁶.

If we go few back years, complexes having bridging ligands such as oxalate ion were studied not only due to antiferromagnetic properties of oxalate group between two paramagnetic centres of binuclear homo-¹⁷⁻²⁰ or heterometallic²¹⁻²³ complexes but also due to their application in various fields of science (chemistry and biology). Binuclear oxalate bridged Cu(II) complexes with Schiff base have been reported²⁴.

Here we are reporting novel oxalato-bridged binuclear {Cu(II) and Zn(II)} complexes with azo anils (tridentate ligand). Oxalato-bridged binuclear Cu(II) complexes have been synthesized from (2- $[(2\text{-hydroxyphenyl)imino]methyl-4-}[(4\text{-nitrophenyl)diazenyl]phenol$) (L1) and 2- $(2\text{-hydroxy-5-}[(4\text{-nitrophenyl)diazenyl]benzylidene\}amino)benzoic\ acid$ (L2)) respectively. The structure of Cu(II) and Zn(II) complexes were determined by various spectroscopic techniques. Azo anils and metal {Cu(II) and Zn(II)} complexes were chosen for antibacterial activities against gram positive and gram negative bacteria.

2. EXPERIMENTAL SECTION

2.1 Physical Measurements

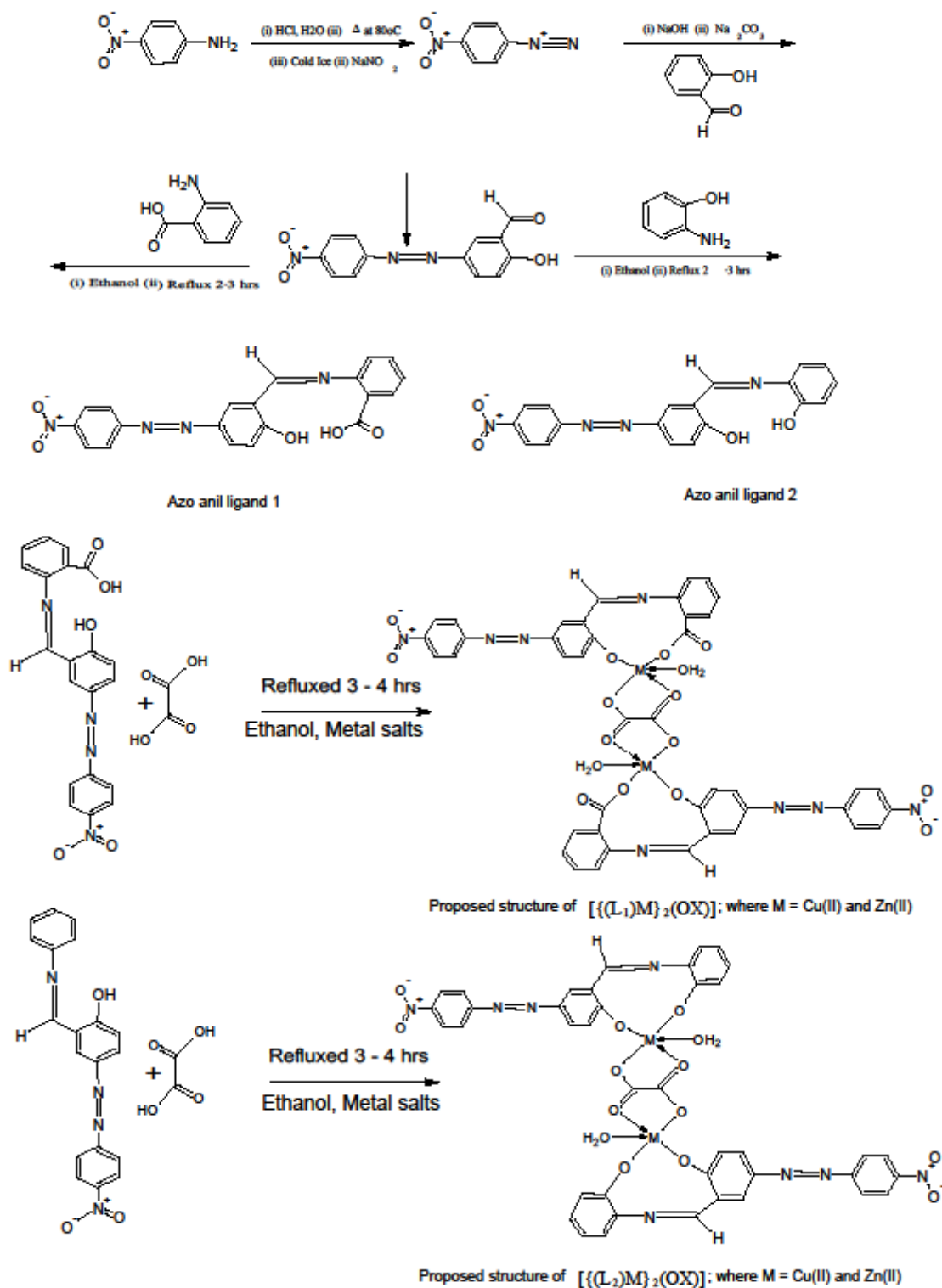
Carbon, Hydrogen and Nitrogen contents were determined using 4010-Elemental combustion system (Costech international). Atomic absorption spectroscopy (varian) was performed to determine exact Cu(II) and Zn(II) contents in synthesized complexes. Electronic spectra of oxalate-bridged binuclear {Cu(II) and Zn(II)} complexes in Dimethyl Sulfoxide (DMSO) solvent were recorded using Perkin-Elmer Lambda 25 UV-Vis spectrophotometer (800-200 nm). The IR spectra of synthesized azo anils and oxalate-bridged binuclear complexes with KBr pellets were recorded on Jasco FTIR (4100-typeA) within (4000-400 cm^{-1}) range. Nuclear Magnetic Resonance (¹³C and ¹H) spectroscopy was performed using a Bruker 300 MHz spectrometer. The antibacterial studies were carried out using diffusion disc method. The physical parameters of ligands and complexes are given in table 1.

2.2 Chemicals

Reagent grade Copper chloride dihydrate, $Zn(CH_3COO)_2 \cdot 2H_2O$, 4-nitroaniline, 2-aminophenol, 2-aminobenzoic, oxalic acid were purchased from BDH and absolute solvent (methanol and ethanol) were received from Aldrich. All chemicals were used without any further purification, except vacuum dried over silica gel.

Table-1: Physical and analytical data of ligands and M(II) complexes

Compounds	Color	Elemental Analysis Exp./Calc.				
		C	H	N	M(II)	M.P (^o C)
L1:C ₂₀ H ₁₄ N ₄ O ₅ .2H ₂ O	Dark Red	56.32/56.34	4.25/4.27	13.10/13.14	-	280–285
L2:C ₁₉ H ₁₄ N ₄ O ₄ .2H ₂ O	Dark brown	57.29/57.28	4.56/4.55	14.05/14.06	-	287–290
[{(L ₁)Cu(II)} ₂ (OX)]	Orange Red	49.09/49.08	2.74/2.75	10.8/10.9	12.35/12.37	>350
[{(L ₁)Zn(II)} ₂ (OX)]	Orange Red	48.88/48.90	2.75/2.74	10.84/10.86	12.69/12.68	>350
[{(L ₂)Cu(II)} ₂ (OX)]	Brick red	49.43/49.44	2.87/2.9	11.54/11.53	13.09/13.08	>350
[{(L ₂)Zn(II)} ₂ (OX)]	Brick red	49.20/49.25	2.85/2.89	11.50/11.49	13.44/13.41	>350

**Schem 1:** Preparation of azo anils ligands and complexes

2.3 Synthesis of starting materials (azo dye)

An azo dye 2-hydroxy-5-[(4-nitrophenyl)diazenyl]benzaldehyde was prepared in accordance with published procedure [25]. Concentrated Hydrochloric acid (40 mL) and distilled water (20 mL) were added to 4.14 g (30 mmol) of 4-nitroaniline and heated up to 80 °C until absolute dissolution occur. Diazotization occurred below 5 °C when solution of 4-nitroaniline was added to 2.1 g (30 mmol) of sodium nitrite solution in 10 mL distilled water. The chilled diazonium solution slowly poured into salicylaldehyde solution which was prepared on adding 3.2 g (30 mmol) of salicylaldehyde in 57 mL water, which also contain 11.1 g of sodium carbonate, 1.2 g of sodium hydroxide and stirred over magnetic stirrer for 40 min in ice bath. The azo dye was obtained using gooch crucible and washed with 10% sodium chloride solution. Diazonium reagent coupled to salicylaldehyde (at p-position from -OH group). The final product was extensively washed with water and ethanol to remove unreacted substance. Chemical Formula, $C_{13}H_9N_3O_4$, yellow coloured solid, yield: 85%, m.p.: 187–188 °C. The FTIR (KBr pellet cm^{-1}): 3103 (-OH), 1661 (-CHO), 1481 (N=N), 1337 (NO_2) and 1284 (C-O) cm^{-1} group. UV-Vis: λ_{max} = 395; 551 nm.

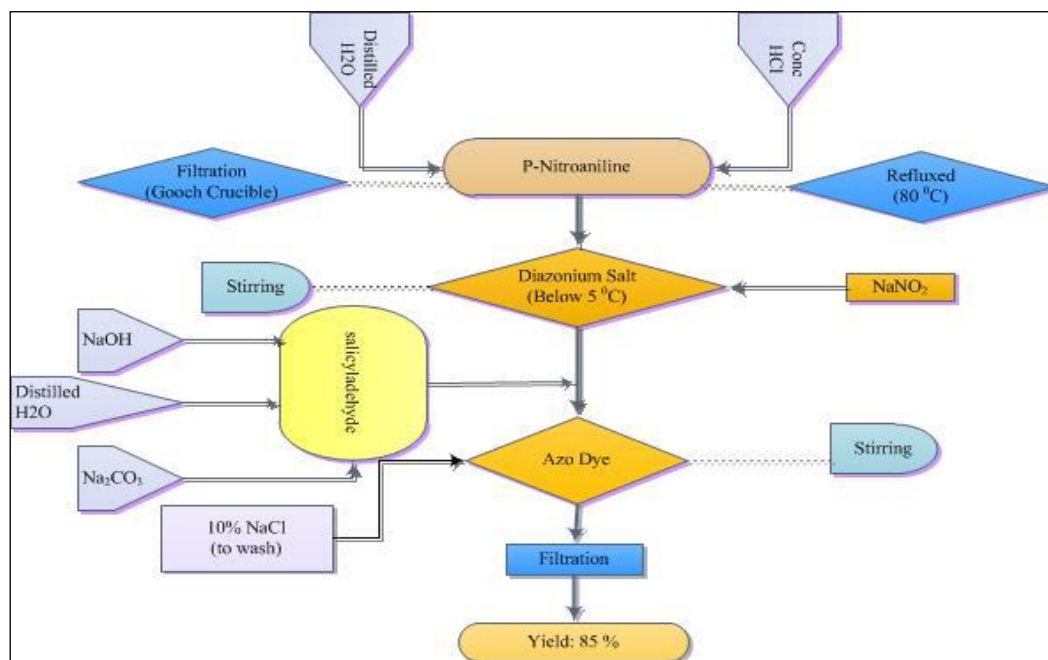


Fig-1: Flowchart indicating steps involved in the preparation of azo dye

2.4 Synthesis of Azo anils ligands

Azo anils were synthesized according to a reported method [26]. For preparation of azo anils, 50 mL of methanol was added in azo dye (4 mmol) followed by the addition of corresponding aromatic amine. Few drops of glacial acetic acid were added to catalyze the reaction mixture and refluxed for 2-3 hrs.

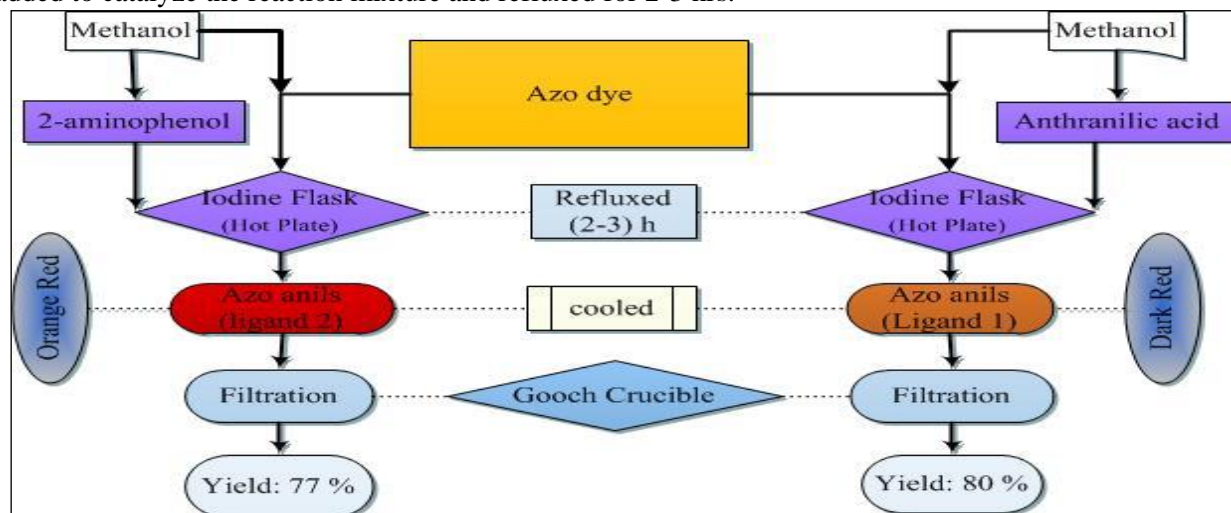


Fig-2: Flowchart indicating steps involved in the synthesis of Azo anils from azo dye.

2.4.1 2-({2-hydroxy-5-[(4-nitrophenyl)diazenyl]benzylidene}amino)benzoic acid (L1)

Dark Red solid appeared, Yield: 80%, M.p: 280–285 °C. Chemical formula: $C_{20}H_{14}N_4O_5 \cdot 2H_2O$, Anal Calc: C: 56.34, H: 4.27, N: 13.14%. Found: C: 56.32, H: 4.25, N 13.10%. FTIR spectra (KBr pellets, cm^{-1}); 3150–3250 (-OH Phenolic), 3500-3600 (coordinated water), 3072 (C-H, aromatic), 2438 – 2771 (O-H, Carboxylic acid) 1704 - 1750 (corre-

spond to -C=O and (-C=N azomethine) , 1616 (-C=C- , aromatic), 1515 (-N=N- , azo group), 1280 (C-O , phenolic), 1329 cm^{-1} (C-O carboxylic acid). UV-Vis: $\lambda_{\text{max}} = 285, 383, 460 \text{ nm}$. $^1\text{H-NMR(DMSO)}$ δ ppm: 13.50 (1H, S), 12.80 (1H, S), 8.70 (3H, S), 8.1 (1H, S), 7.90 (3H, S), 7.78 (2H, S), 7.60 (1H, S), 7.25 (1H, S), 6.90 (1H, S). $^{13}\text{C-}\{^1\text{H}\}$ NMR (DMSO) δ ppm: 113.1, 115.14, 118.21, 119.01, 123.05, 123.05, 123.50, 124.23, 124.50, 124.70, 124.75, 130.90, 136.53, 142.51, 149.40, 151.53, 152.3, 160.41, 165.34, 172.53.



Fig.3: Structure of 2-((2-hydroxy-5-[(4-nitrophenyl)diazenyl]benzylidene)amino)benzoic acid

2.4.2 2-[[2-(2-hydroxyphenyl)imino]methyl]-4-[(4-nitrophenyl)diazenyl]phenol (L2)

Dark brown solid appeared, yield: 77%, m.p.: 287–290 °C. Chemical formula: $\text{C}_{19}\text{H}_{14}\text{N}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$. Anal. Calc. C: 57.28, H: 4.55, N: 14.06 %. Found: C: 57.29, H: 4.56, N: 14.05 %. FTIR spectra (KBr pellets, cm^{-1}): 3150–3240 (-OH , Phenolic), 3500–3600 (coordinated water), 3062 (C-H , aromatic), 1616 (-C=N- , azomethine), 1604 (C=C , aromatic), 1511 (-N=N- , azo), 1290 (C-O , phenolic) cm^{-1} . UV-Vis: $\lambda_{\text{max}} = 380, 420, 515 \text{ nm}$. $^1\text{H-NMR(DMSO)}$ δ ppm: 12.90 (1H, S), 8.50 (1H, S), 8.40 (2H, S), 7.90 (2H, S), 7.81 (3H, S), 7.60 (1H, S), 7.25 (2H, S), 7.06 (1H, S), 6.91 (1H, S) ppm. $^{13}\text{C-}\{^1\text{H}\}$ NMR(DMSO) δ ppm: 113.2, 115.21, 118.22, 119.03, 119.5, 119.71, 123.11, 123.11, 124.55, 124.70, 124.75, 128, 52, 135.53, 149.50, 151.50, 151.53, 152.21, 153.06, 160.32, 170.33.

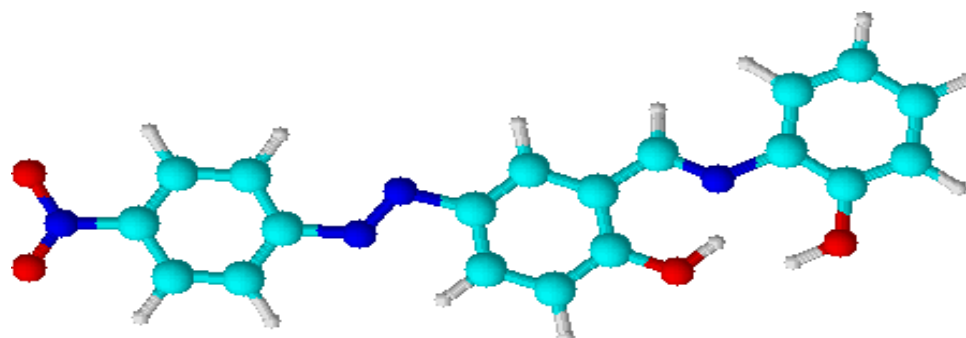


Fig.4: Structure of 2-[[2-(2-hydroxyphenyl)imino]methyl]-4-[(4-nitrophenyl)diazenyl]phenol

2.5 Synthesis of *M(II)* Complexes

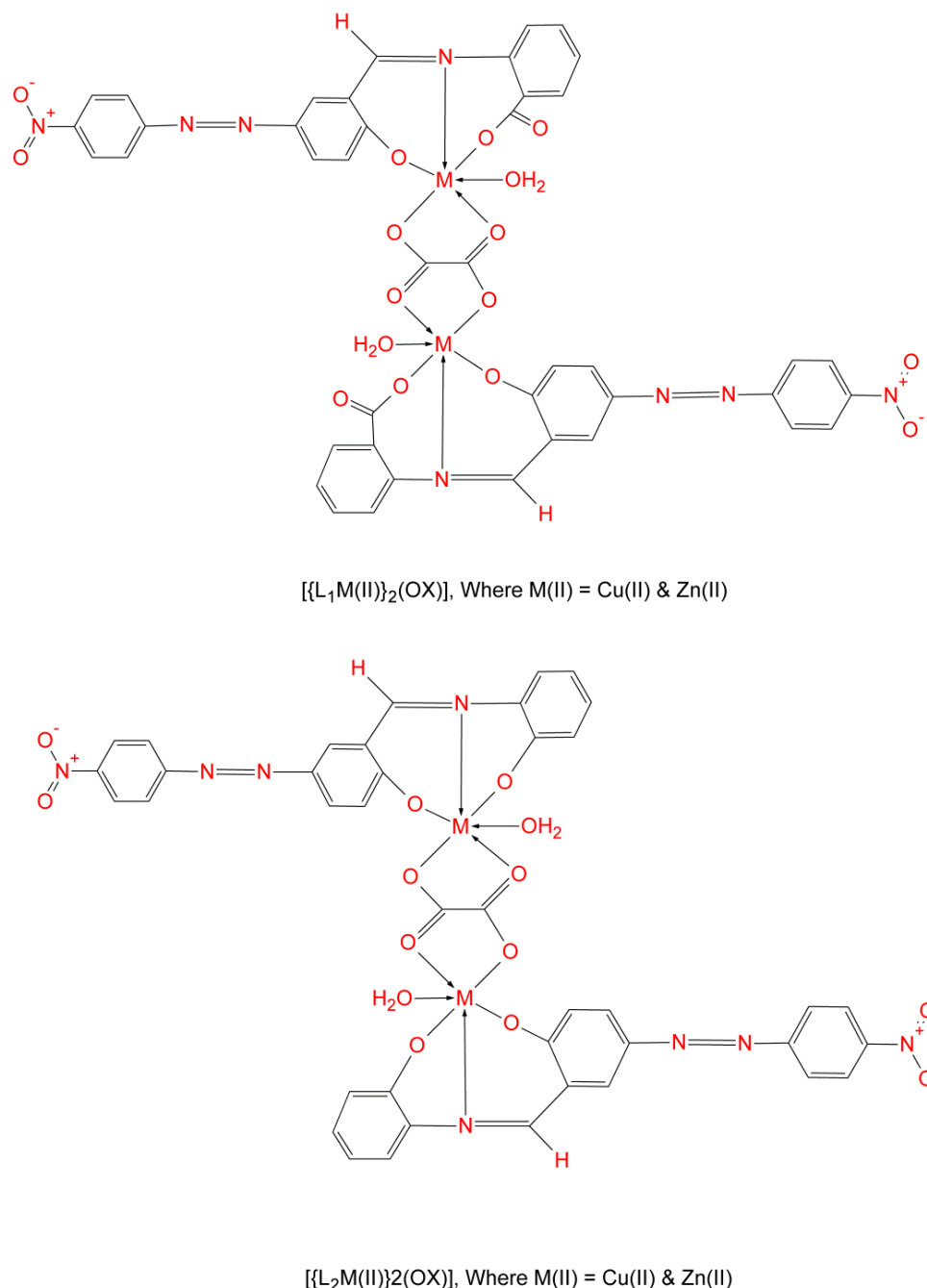
Methanolic solution of azo anils (1mmol) and oxalic acid (0.5 mmol) were blended and added to methanolic solution of 1mol of Metal salt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$). Naked eye colour change occurred after 2-3 min. The reaction mixture was refluxed for 3-4 hrs. The precipitated compound was obtained using gouch crucible, washed with methanol and then with water to remove organic and inorganic impurities.

2.5.1 Complex-1: $[(L_1)M(II)]_2(OX)$

Orange red solid appeared, Yield: 70%, m.p > 350 °C. FTIR (over KBr, cm^{-1}): 3443 cm^{-1} (coordinated water). Several bands were observed in the range of 1450–1608 cm^{-1} , matching to the bands of coordinated oxalate, carboxyl and azomethine group. The band at 1423 correspond to (N=N , azo group), 1336 to (C-O , phenolic group) cm^{-1} . The bands at 978, 1109 cm^{-1} were assigned to vs (C-C) and band at 754 cm^{-1} to vs (OCO , carboxylic group). The band such as 412, 589 cm^{-1} correspond to M-N and M-O band respectively. UV-Vis: $\lambda_{\text{max}} = 287, 328$ and 414 nm.

2.5.2 Complex-2: $[(L_2)M(II)]_2(OX)$

Brick red solid appeared; Yield 72 %; m.p above 350 °C. FTIR (over KBr, cm^{-1}) Spectrum of complex -2 showed partial broad peak at 3445 cm^{-1} , which correspond to coordinated water molecule. Several bands were appeared in range of 1476–1613 matching to the bands of coordinated oxalate, carboxyl, and azomethine group and 1420 to (N=N , azo group), 1335 to (C-O , phenolic group). The following bands such as 1030, 1109 cm^{-1} are assigned at the same time as vs (C-C) and band at 747 cm^{-1} as vs (OCO , carboxylic group). The band such as 411, 578 cm^{-1} , correspond to M-N and M-O band respectively. UV-Vis: $\lambda_{\text{max}} = 289, 324$ and 412 nm.



Scheme-2: schematic diagram of synthesized M(II) Complexes

2.6 Antibacterial activities evaluation

Diffusion disc method [27, 28-32] was used to determine antibacterial activities of copper chloride, zinc acetate, oxalic acid, azo anils and their complexes. Glass ware was sterilized at 170 °C for 1 hr. Agar medium was prepared by adding nutrient agar (2.8 g) and agar technical (1 g) in 100 mL distilled water. The mixture was boiled for half an hour and then cooled. PH of agar medium was adjusted at 7.4 with the help of dil HCl and dil NaOH solutions. The agar medium was autoclaved for 15 minutes at 121 °C (at 15 psi) [33]. Spread this autoclaved agar (20-25 mL) on Petri dishes with the help of spreader and incubated for 24 hrs at 37 °C. Test compound in measured quantities was taken and dissolved in DMSO to get required concentration of 1000 ppm. The agar media was taken in two Petri dishes (9 cm in diameter). Later than solidifying it, 0.2 mL of gram +ve and gram -ve bacteria were spread over agar medium using sterilized spreader in different Petri dishes. The discs of whatmann filter paper no.1 (6.00 mm in diameter) were soaked in test compound solution and then placed on inoculated Petri dishes. The plates were incubated at 37 °C for 48 hrs. The sector of inhibition was measured in millimetres.

A measured quantity i.e. 0.2 mL of DMSO alone was taken as a standard control for gram +ve and gram -ve bacteria under similar conditions. The thickness of inhibition zone resulting from DMSO was subtracted from the thickness of inhibition zone of test compounds and antibacterial activity was calculated as an average of three replicate.

3. RESULTS AND DISCUSSIONS

3.1 IR Spectrum

The FTIR of synthesized ligands and complexes were performed over KBr pellet (4000-400 cm^{-1}). The ligands and complexes FTIR Spectra comparison revealed that absorption band at 3250-3350 cm^{-1} related to -OH (phenolic) group, disappeared in complexes spectra, indicating loss of phenolic proton upon the formation of complex. The new band in complexes spectra at 589-578 cm^{-1} appeared indicating presence of M-O bond. The formation of complex was shored up with increased C-O stretching vibration (1336 cm^{-1}) in complexes as compared to ligands (1280 cm^{-1}). In ligands (L1 and L2) the band at 1603-1616 cm^{-1} indicated the presence of -C=N (azomethine group) as given in literature [34]. This band is shifted in the complexes toward lower frequencies (1597-1608 cm^{-1}). This is an indication for the formation of M-N bond, and it was confirmed by the results obtained from similar complexes [35-37]. The bands at 408-443 and 524-599 cm^{-1} could be assigned to M-N and M-O stretching vibrations respectively and is in accord with results got from comparable complexes [38]. In prepared complexes the band at 754 cm^{-1} was assigned to oxalate group (OCO), which was not appeared in free ligand except L₁ (an indication that complexes contain oxalate as bridging group). All the other bands appeared in their customary positions and are shown in Table 2.

Table-2: FTIR and Electronic Spectra of Azo Anils Ligands and M(II) Complexes

Azo Anils / M(II) complexes	FTIR (cm^{-1})						(UV-Vis) nm
	$\nu(\text{OH})$	$\nu(\text{C-O})$	$\nu(\text{-C=N})$	$\nu(\text{OCO})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	
(L1) C20H14N4O5.2H2O	3150- 3250	1280	1704- 1750	1329	-	-	285, 383, 460
(L2) C19H14N4O4.2H2O	3150- 3240	1290	1616	-	-	-	380, 420, 515
Complex-1 [{(L1)M(II)} ₂ (OX)]	-	1336	1580	754	412	589	287, 328, 414
Complex-2 [{(L2)M(II)} ₂ (OX)]	-	1335	1575	747	411	578	289, 324, 412

3.2 Electronic spectra of azo anils Ligands and M(II) complexes

The electronic spectra of azo anils ligands (L1 and L2), exhibited two absorption bands at 290 nm and 500 nm were assigned to $\pi \rightarrow \pi^*$ (Phenyl rings) and $n \rightarrow \pi^*$ (H-C=N and azo group) transitions respectively [39]. These transition bands were also existed in the electronic spectra of M(II) complexes with different lower intensities, which confirmed that these groups were involved in coordination. A weak band in complexes spectra at 380 nm and 480 nm was observed which correspond to charge transfer (ct). Another weak band at 480-560 nm corresponds to d-d transition, namely $2B_{1g} \rightarrow 2E_g$ and $2B_{1g} \rightarrow 2B_{2g}$. These transitions suggested distorted octahedral geometry for M(II) complexes. [40]. The electronic spectra results are shown in Table 2.

3.3 ^{13}C - ^1H NMR spectra of azo anils

^{13}C and ^1H -NMR spectroscopy of azo anils was recorded in (^6d -DMSO) solvent. ^1H -NMR exhibited peaks at 13.50 - 12.80 ppm and 8.70 - 8.20 ppm which could be assigned to phenolic proton and azomethine proton respectively. In ^{13}C -NMR, peaks emerged in the range of 113.2 - 165.34 ppm could be assigned to aromatic C and signal at 172.53 ppm to azomethine.

3.4 Antibacterial activities measurement

Gram positive (*Bacillus subtilis*) and gram negative bacteria (*Escherichia coli*) were used to test antibacterial activities of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, oxalic acid, azo anils and metal {Cu(II) and Zn(II)} complexes. Streptomycin, an antibacterial drug was used for the comparison of antibacterial activities under same conditions. The results

obtained are given in table 2. It was concluded from these results that Cu(II) and Zn(II) complexes display higher antibacterial activities as compared to $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, oxalic acid, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and azo anils. The Tweedy's chelation theory and Searl's idea explain why antibacterial activities of metal complexes increase [41].

The results revealed that antibacterial activities of azo anils become more pronounced when free ligands were coordinated to central metal atom. The antibacterial activities of these complexes (oxalate-bridged binuclear {Cu(II) and Zn(II)}) were influenced due to their structural symmetry. The enrichment in antibacterial activities may be streamlined on the basis of their structural features i.e. due to electron withdrawing group (nitro and -C=N) attached on benzene ring of azo anils.

Table-2: ^{*1}Antibacterial activities of copper chloride, oxalic acid, azo anils and Cu(II) complexes

Compounds	Gram positive	Gram negative
	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>
CuCl ₂ .2H ₂ O	++	+
Zn(CH ₃ COO) ₂ .2H ₂ O	++	++
Oxalic acid	+	+
C ₂₀ H ₁₄ N ₄ O ₅ .2H ₂ O (L1) (Ligand # L1)	++	++
C ₁₉ H ₁₄ N ₄ O ₄ .2H ₂ O (L2) (Ligand # L2)	+	++
[(L1)Cu(II)] ₂ (OX) (Complex-1)	+++	+++
[(L2)Cu(II)] ₂ (OX) (Complex-2)	+++	+++
[(L2)Zn(II)] ₂ (OX)	+++	++
[(L2)Zn(II)] ₂ (OX)	++++	+++
^{*2} Streptomycin	+++	++

^{*1}Antibacterial activity was measured using disc diffusion method: disc diameter = 6 mm; inhibition zone = 1 – 5 mm beyond control limit = + (less active); inhibition zone = 6-10 mm beyond control limit = ++ (moderately active); inhibition zone = 11-15 mm beyond control limit = +++ (highly active); inhibition zone = 0 (resistant to bacteria). ^{*2} Streptomycin: standard antibacterial agent.

It has been assumed that azo anils (or Schiff base) with nitrogen and oxygen system retard enzymatic activities of bacteria, after coordinating to central metal atom.

4. CONCLUSION

Azo anils ligands, 2-((2-hydroxy-5-[(4-nitrophenyl)diazonyl]benzylidene)amino)benzoic acid (L1) and 2-((2-hydroxyphenyl)imino)methyl-4-[(4-nitrophenyl)diazonyl]phenol (L2) were synthesized. Likewise from these ligands, novel oxalate-bridged binuclear Complex-1 [(L₁)M(II)]₂(OX) and Complex-2 [(L₂)M(II)]₂(OX) were also synthesized. Azo anils ligands and their M(II) Complexes were characterized by various spectroscopic and analytical techniques such as elemental analysis, AAS, FTIR spectroscopy, UV-Vis spectroscopy and ¹³C-¹H NMR spectroscopy. These techniques confirmed existence of distorted octahedral geometry for M(II) complexes. The antibacterial activities of azo anils ligands, oxalate ion, CuCl₂.2H₂O, Zn(CH₃COO)₂.2H₂O and metal complexes against gram-positive (*Bacillus subtilis*) and gram-negative (*Escherichia coli*) were evaluated. The antibacterial activities were performed to assess inhibition potential of ligands and their metal complexes. The results revealed that antibacterial activities of azo anils become more pronounced when free ligands were coordinated to central metal atom. The enrichment in antibacterial activities may be streamlined on the basis of their structural features. It was concluded from above mentioned results that M(II) complexes show higher antibacterial activities as compared free ligands.

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