

Synthesis and Antibacterial Activities of Mixed Ligands Complexes of Cu(II) and Zn(II) Containing Tridentate Azo Anils Ligands and Bidentate Oxalate Ion

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Mixed ligands complexes of copper(II) and zinc(II) were synthesized using azo anils ((HNPDBAB = 2-((2-hydroxy-5-[(4-nitrophenyl)diazenyl]benzylidene)amino)benzoic acid, HPIMNDP = 2-[[2-(2-hydroxyphenyl)imino]methyl]-4-[(4-nitrophenyl)diazenyl]phenol) and oxalate ion as a coordinating ligands. Elemental analysis, atomic absorption spectroscopy, FTIR, NMR, UV-visible, were used for the characterizations of synthesized azo anils ligands and their mixed ligands complexes. Distorted octahedral geometry was tentatively proposed for these new mixed ligands M(II) {Cu(II) and Zn(II)} complexes. Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative (*Enterobacter aerogenes* and *Escherichia coli*) were screened for antibacterial activities of azo anils ligands, oxalic acid, metal salts and their mixed ligands M(II) complexes. The antibacterial activities were performed to assess the extent of inhibition potential of free ligand and their mixed ligands M(II) complexes. The results revealed that antibacterial activities of azo anils became more pronounced when these were coordinated to central metal atom.

Keywords: Azo anils, Oxalate, Mixed ligands M(II) complexes, Antibacterial activity.

INTRODUCTION

Azo anils and their complexes with Cu(II) and Zn(II) had displayed antibacterial and antifungal activities¹. Azo anils ligands have been 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 of the transition metal forms stable complexes with azomethine because it has excellent π -donor character⁴⁻⁶. All at once, it is not possible for both group together to 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 more awareness in both academic and applied researches¹¹⁻¹⁶.

The complexes having bridging ligands such as oxalate ion or mixed ligands complexes with one azo Schiff base and one oxalate ligands were studied not only due to antiferromagnetic properties of oxalate group between two paramagnetic centres of binuclear homo-metallic¹⁷⁻²⁰ or hetero-metallic²¹⁻²³ 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 have reported novel mixed ligands complexes of Cu(II) and Zn(II), synthesized by the coordination of azo anils ligands and oxalate ion. The metal salt, azo anils and oxalic acid were mixed in 1:1:1 ratio and resulted to mixed ligands M(II) complexes. The objective of this study was to determine how much extent of antibacterial activities of azo anils increased when they were coordinated to central transition metal. A pronounced change in antibacterial activities have been seen from azo anils ligands to mixed ligands M(II) complexes.

EXPERIMENTAL

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 Cu(II) and Zn(II) complexes in dimethyl sulfoxide (DMSO) solvent were recorded using Perkin-Elmer Lambda 25 UV-visible spectrophotometer (800-200 nm). The IR spectra of synthesized azo anils ligands and mixed ligands complexes with KBr pellets were recorded on Jasco FTIR (4100-typeA) within (4000-400 cm^{-1}) range.

Nuclear magnetic resonance (^{13}C 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.

Reagent grade copper chloride dihydrate, zinc acetate dihydrate, 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.

Synthesis of starting materials (azo dye): An azo dye 2-hydroxy-5-[(4-nitrophenyl)diazanyl]benzaldehyde was prepared in accordance with published procedure²⁵. 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 of distilled water. The chilled diazonium solution slowly poured into salicylaldehyde solution which was prepared by 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. m.f.: $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_4$, 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-visible: $\lambda_{\text{max}} = 395; 551 \text{ nm}$.

Synthesis of azo anils ligands: Azo anils ligands were synthesized according to a reported method²⁶. 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 h.

2-((2-Hydroxy-5-[(4-nitrophenyl)diazanyl]benzylidene)-amino)benzoic acid (HNPDBAB): Dark red solid, Yield: 80 %, m.p.: 280-285 °C. m.f.: $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_5 \cdot 2\text{H}_2\text{O}$, 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}): 3250-3150 (-OH, phenolic), 3600-3500 (coordinated water), 3072 (C-H, aromatic), 2771-2638 (O-H, carboxylic acid), 1750-1704 (correspond 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-visible: $\lambda_{\text{max}} = 285, 383,$

500 nm. ^1H 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}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.

2-[[2-(2-Hydroxyphenyl)imino]methyl]-4-[(4-nitrophenyl)diazanyl]phenol (HPIMNDP): Dark brown solid, Yield: 77 %, m.p.: 287-290 °C. m.f.: $\text{C}_{19}\text{H}_{14}\text{N}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$. Anal. Calc. C: 57.28, H: 4.55, N: 14.06 %. Found: C: 57.29, H: 4.56, N: 14.15 %. FTIR spectra (KBr pellets, cm^{-1}): 3240-3150 (-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-visible: $\lambda_{\text{max}} = 280, 420, 505 \text{ nm}$. ^1H 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}C - $\{^1\text{H}\}$ NMR(DMSO) δ ppm: 113.2, 115.21, 118.22, 119.03, 119.5, 119.71, 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.

Synthesis of mixed ligands M(II) complexes: Methanolic solution of azo anils (1 mmol) and aqueous solution of oxalic acid (1 mmol) were blended and added to methanolic solution of 1 mol of metal salt [$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$]. The colour changed occurred after 2-3 min. The reaction mixture was refluxed for 3-4 h. The precipitated compounds were obtained using gooch crucible, washed with methanol and then with water to remove organic and inorganic impurities.

[(HNPDBAB)M(II)(OX)]: Orange red solid, Yield: 70 %, m.p.: 350 °C and elemental analysis results are given in Table-1. FTIR (KBr pellets, cm^{-1}): 3600-3560 cm^{-1} (coordinated water). A band at $\sim 31003150 \text{ cm}^{-1}$ indicates the coordination of phenolic group with central metal atom. The band at 2750-2640 cm^{-1} correspond coordinated (OH, Carboxylic acid) with central metal atom. Several bands were observed in the range of 1608-1450 cm^{-1} , matching to the bands of coordinated oxalate, carboxyl and azomethine group. The band at 1423 cm^{-1} correspond to (N=N, azo group), 1336 to (C-O, phenolic group) cm^{-1} . The bands at 978, 1109 cm^{-1} were assigned to $\nu_s(\text{C-C})$ and band at 754 cm^{-1} to $\nu_s(\text{OCO, carboxylic group})$. The band such as 408, 578 cm^{-1} correspond to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ band respectively. UV-visible: $\lambda_{\text{max}} = 387, 481, 558 \text{ nm}$.

[(HPIMNDP)M(II)(OX)]: Brick red solid; Yield: 72 %; m.p. above 350 °C and elemental analysis results are given in Table-1. FTIR (KBr pellets, cm^{-1}) Spectrum showed partial broad peak at 3600-3550 cm^{-1} , which correspond to coordinated water molecule. A band at 3140-3100 cm^{-1} indicates the coordination of phenolic group with central metal atom.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF LIGANDS AND THEIR M(II) COMPLEXES

Compound	Colour	Elemental analysis (%): Exp. (calcd.)				m.p. (°C)
		C	H	N	M(II)	
HNPDBAB	Dark red	56.32 (56.34)	4.25 (4.27)	13.10 (13.14)	–	280-285
HPIMNDP	Dark brown	57.29 (57.28)	4.56 (4.55)	14.05 (14.06)	–	287-290
[(HNPDBAB)Cu(II)(OX)]	Orange red	49.09 (49.08)	2.74 (2.75)	10.8 (10.9)	12.35 (12.37)	> 350
[(HNPDBAB)Zn(II)(OX)]	Orange red	48.88 (48.90)	2.75 (2.74)	10.84 (10.86)	12.69 (12.68)	> 350
[(HPIMNDP)Cu(II)(OX)]	Brick red	49.43 (49.44)	2.87 (2.9)	11.54 (11.53)	13.09 (13.08)	> 350
[(HPIMNDP)Zn(II)(OX)]	Brick red	49.20 (49.25)	2.85 (2.89)	11.50 (11.49)	13.44 (13.41)	> 350

Several bands were appeared in range of 1613-1476 matching to the bands of coordinated oxalate, 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 $\nu_s(\text{C-C})$ and band at 747 cm^{-1} as $\nu_s(\text{OCO})$, carboxylic group). The band such as 412, 589 cm^{-1} , correspond to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ band respectively. UV-visible: $\lambda_{\text{max}} = 389, 480, 560 \text{ nm}$.

Antibacterial activities measurement: Diffusion disc method²⁷⁻³² was used to determine antibacterial activities of copper chloride, zinc acetate, oxalic acid, azo anils and their mixed ligands complexes. Glass wares were sterilized at 170 °C for 1 h. 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 0.5 h and then cooled. The 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 min 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 h at 37 °C. Test compounds in measured quantities were taken and dissolved in DMSO to get required concentration of 1000 ppm. The agar media was taken in Petri dishes (9 cm in diameter). Later than solidifying it, 0.2 mL of Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative (*Enterobacter aerogenes* and *Escherichia coli*) bacteria were spread separately over agar medium using sterilized spreader in different Petri dishes and area of inhibition zone was measured and given in Table-2. The discs of Whatmann filter paper no.1 (6 mm in diameter) were soaked in test compound solutions and then placed on inoculated Petri dishes. The plates were incubated at 37 °C for 48 h. The sector of inhibition was measured in millimetres.

A measured quantity *i.e.* 0.2 mL of DMSO alone was also taken as a standard control for Gram-positive and Gram-

negative 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.

RESULTS AND DISCUSSION

FT-IR analysis: The FTIR analysis of synthesized compounds was performed over KBr pellet (4000-400 cm^{-1}). The band at 3250-3150 cm^{-1} relate to -OH (phenolic) group, shifted toward lower frequency (25-55 cm^{-1}) in complexes spectra, indicating the coordination of phenolic group with central metal atom. The new band in complexes spectra at 589-578 cm^{-1} appeared indicating presence of M-O bond. The formation of complex was showed up with increased C-O stretching vibration (1336 cm^{-1}) in complexes as compared to azo anils ligands (1280 cm^{-1}). In HNPDBAB the band at 2771-2638 correspond to -OH (carboxylic acid) which shifted toward lower frequency (23-68 cm^{-1}) in [(HNPDBAB) M(II)(OX)], which support the fact that carboxylic acid group is involved in coordination. In ligands (HNPDBAB and HPIMNDP) spectra the band at 1616-1603 cm^{-1} indicates the presence of -C=N (azomethine group) as given in literature³⁴. This band is shifted toward lower frequencies (1608-1597 cm^{-1}) upon M(II) complexes formation. This is an indication for the formation of M-N bond and it was confirmed by the results obtained from similar complexes³⁵⁻³⁷. The bands at 412-408 and 589-578 cm^{-1} could be assigned to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ stretching vibrations respectively and is in accordance with results obtained from comparable complexes³⁸. In prepared complexes the band at 754 cm^{-1} was assigned to oxalate group (OCO), which was not appeared in free ligand except HNPDBAB which contain carboxylic group. A broad band at 3600-3550 cm^{-1} shows coordinated water molecule. All other bands appeared in their customary positions and are given in Table-3.

TABLE-2
MEASUREMENT OF INHIBITION ZONE OF TEST COMPOUNDS AGAINST GRAM-POSITIVE AND GRAM-NEGATIVE BACTERIA

Compound	Volume (μL)	Diameter of inhibition zone measured (mm): Bacterial species			
		Gram-positive		Gram-negative	
		<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Enterobacter aerogenes</i>	<i>Escherichia coli</i>
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	20	4 \pm 1.0	4 \pm 1.0	4 \pm 1.0	3 \pm 1.0
$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	20	2 \pm 1.0	3 \pm 1.0	4 \pm 1.0	4 \pm 1.0
Oxalic acid	20	5 \pm 1.0	8 \pm 1.0	4 \pm 1.0	8 \pm 1.0
HNPDBAB	20	8 \pm 1.0	8 \pm 1.0	5 \pm 1.0	8 \pm 1.0
HPIMNDP	20	9 \pm 1.0	8 \pm 1.0	8 \pm 1.0	7 \pm 1.0
[(HNPDBAB)Cu(II)(OX)]	20	14 \pm 1.0	14 \pm 1.0	12 \pm 1.0	10 \pm 1.0
[(HNPDBAB)Cu(II)(OX)]	20	12 \pm 1.0	13 \pm 1.0	14 \pm 1.0	14 \pm 1.0
[(HPIMNDP)Zn(II)(OX)]	20	14 \pm 1.0	12 \pm 1.0	13 \pm 1.0	14 \pm 1.0
[(HPIMNDP)Zn(II)(OX)]	20	14 \pm 1.0	12 \pm 1.0	13 \pm 1.0	14 \pm 1.0
Streptomycin	20	5 \pm 1.0	7 \pm 1.0	8 \pm 1.0	10 \pm 1.0

These values are expressed as a mean of three replicate reading (\pm)

TABLE-3
FTIR AND ELECTRONIC SPECTRA OF AZO ANILS LIGANDS AND THEIR M(II) COMPLEXES

Azo anils/M(II) complexes	FTIR (cm^{-1})					UV-visible (nm)	
	$\nu(\text{OH})$	$\nu(\text{C-O})$	$\nu(\text{-C=N})$	$\nu(\text{OCO})$	$\nu(\text{M-O})$		$\nu(\text{M-N})$
HNPDBAB	3150-3250	1280	1704-1750	1329	-	-	285, 383, 500
HPIMNDP	3150-3240	1290	1616	-	-	-	280, 420, 505
[(HNPDBAB)M(II)(OX)]	3050-3105	1336	1580	754	578	408	387, 481, 558
[(HPIMNDP)M(II)(OX)]	3050-3100	1335	1575	747	589	412	389, 480, 560

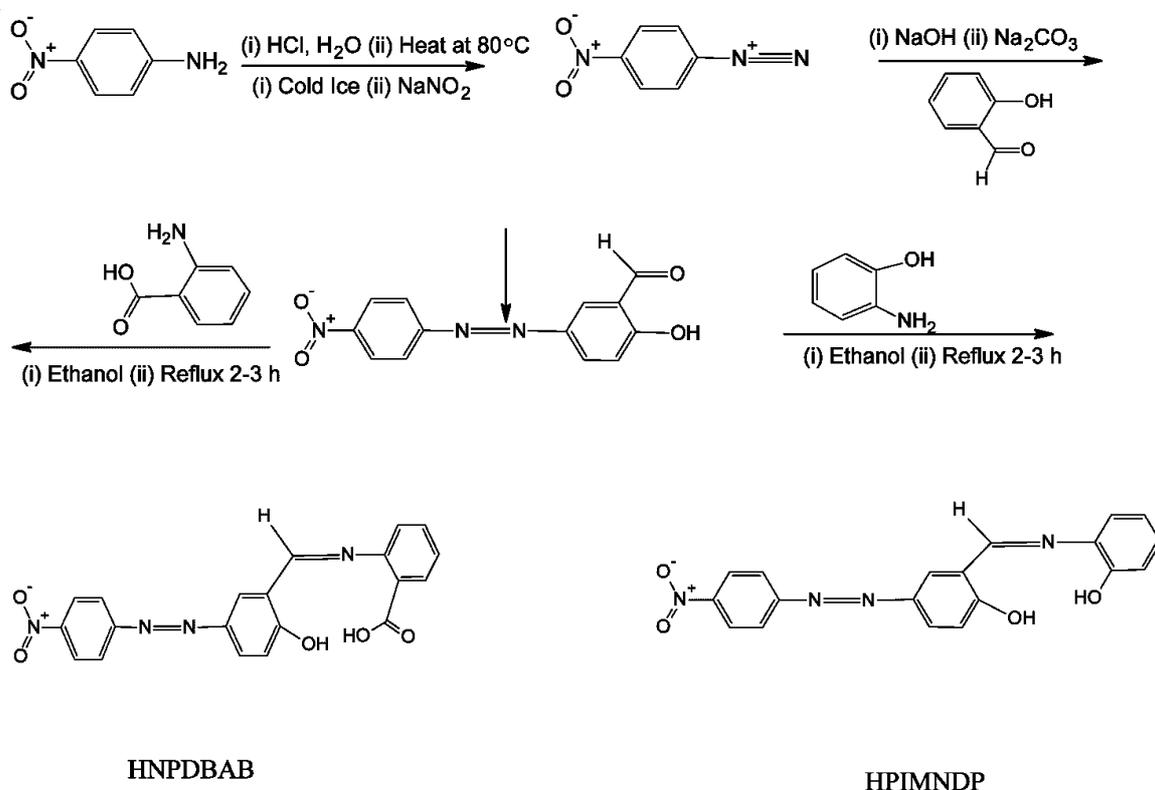
Electronic spectra of ligands and their metal complexes:

The electronic spectra of azo anils ligands (HNPDBAB and HPIMNDP), exhibited two absorption bands at 288 nm and 510 nm were assigned to $\pi \rightarrow \pi^*$ (phenyl rings) and $n \rightarrow \pi^*$ (H-C=N and azo group) transitions respectively³⁴. 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) complexes³⁹. The electronic spectra results are shown in Table-3.

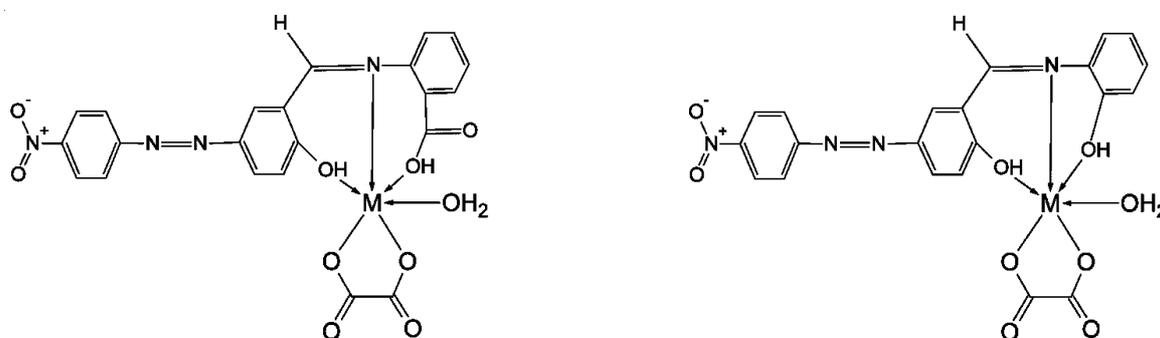
¹³C-¹H NMR spectra of azo anils: ¹³C and ¹H NMR spectroscopy of azo anils was recorded in (DMSO-*d*₆) solvent.

¹H NMR exhibited peaks at 13.50-12.80 ppm and 8.70-8.20 ppm which could be assigned to phenolic and azomethine proton respectively. In ¹³C 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 carbon.

Antibacterial activities evaluation: Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative (*Enterobacter aerogenes* and *Escherichia coli*) bacteria were used to test antibacterial activities of CuCl₂·2H₂O, Zn(CH₃COO)₂·2H₂O, 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 similar conditions. The results obtained are given in Table-4. It was concluded from these results that Cu(II) and Zn(II) complexes displayed higher antibacterial activities as compared to CuCl₂·2H₂O, oxalic acid, Zn(CH₃COO)₂·2H₂O



Scheme-I: Steps involved in the synthesis of azo anils ligands



[(HNPDBAB)M(II)(OX)] where M = Cu(II) & Zn(II)

[(HPIMNDP)M(II)(OX)] where M = Cu(II) & Zn(II)

Scheme-II: Proposed structure of distorted octahedral geometry of mixed ligands complexes containing tridentate azo anils and bidentate oxalate ion as coordinating ligands

and azo anils ligands as given in Table-4. The Tweedy's chelation theory and Searl's idea explain the reason of antibacterial activities of metal complexes increase³¹.

TABLE-4
RESULTS OF ANTIBACTERIAL STUDY OF AZO ANILS, OXALIC ACID, METAL SALT AND MIXED LIGANDS M(II) COMPLEXES

Compounds	Gram-positive		Gram-negative	
	<i>B. subtilis</i>	<i>S. aureus</i>	<i>E. aerogenes</i>	<i>E. coli</i>
CuCl ₂ ·2H ₂ O	+++	+++	+++	+++
Zn(CH ₃ COO) ₂ ·2H ₂ O	+++	+++	+++	+++
Oxalic acid	+++	+++	+++	+++
HNPDBAB	+++	++++	+++	++++
HPIMNDP	+++	++++	+++	++++
[(HNPDBAB)Cu(II)(OX)]	+++++	+++++	++++	++++
[(HPIMNDP)Cu(II)(OX)]	+++++	+++++	+++++	++++
[(HNPDBAB)Zn(II)(OX)]	+++++	+++++	++++	+++++
[(HPIMNDP)Zn(II)(OX)]	+++++	+++++	+++++	++++
Streptomycin**	++++	++++	++++	+++

*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). **Streptomycin: standard antibacterial drug.

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 mixed ligands M(II) complexes {Cu(II) and Zn(II)} were influenced due to their structural symmetry. The comparison of antibacterial activities can be seen from Table-4. 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.

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.

Conclusions

Mixed ligands complexes of Cu(II) and Zn(II) were observed more antibacterial as compared to metal salt, free ligands HNPDBAB, HPIMNDP and oxalic acid. More inhibition potential was exhibited by copper(II) and zinc(II) complexes against Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) bacteria as compared to Gram-negative (*Enterobacter aerogenes* and *Escherichia coli*). Metal complexes of Cu(II) showed higher antibacterial activities as compared to Zn(II) complexes.

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