

**SYNTHESIS & SPECTROSCOPIC INVESTIGATION OF CU(II), CO(II)
AND ZN(II) COMPLEXES OF AZO DYE DERIVED FROM
CALIX[4]RESORCINARENE AND THEIR BIOLOGICAL SCREENING**

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ABSTRACT

The chemistry of metal complexation containing azo group has been a subject of greater interest in the 21st century. Novel azo dye derived from o-amino phenol and calix[4] resorcinarene having a conjugated chromophoric azo (-N=N-) group in upper-rim was synthesized by microwave irradiation technique. This compound in the solid and solution form is elucidated by FT-IR, ¹H-NMR, ¹³C-NMR, as well as

elemental analysis technique. Bivalent metal [Copper, Cobalt, and Zinc] complexes of azo-calix[4] resorcinarene were synthesized in different molar ratio of metal and ligand in alcoholic medium under different pH condition if required. The chemistry of all these complexes is presented here with special attention given to their synthesis, structure, spectral and various other properties. These complexes were studied by UV, IR, TGA, DTA, and ESR techniques. AAS of metal ions reviewed that 4:1 (M:L) complex is established. The stoichiometry of the azo-metal chelates was also determined by the spectroscopic titration method. These complexes have shown slightly increased biological activity on S.aureus and E.coli respectively compared to ligand.

KEYWORDS: Azo Dye, Calix[4] resorcinarene, Metal complexes, Biological study.

1. INTRODUCTION

Calixarenes are often described as “macrocycles with unlimited possibility” because of their versatility and utility as host molecules which most comes from the ease in the synthesis of

the basic platform and ready functionalization at lower and upper rim to construct variously modified three dimensional structure.^[1,2] In recent years an increasing interest and attention was highlighted on investigation on molecular and or ionic recognition by calixarenes and their derivatives as synthetic receptors because of their potential to serve as molecular devices and functional materials.^[1,3-6] Calix[4]resorcinarenes structurally similar to calixarenes show interesting receptor properties, performs as building blocks for large supramolecular assemblies of fascinating architecture.^[7,8] The calixresorcinarenes belong to a class of metacyclophanes in which resorcinol units are linked by methylene bridges, having unique three dimensional cyclic tetramers and hexamers. Chemistry of Calix[4]resorcinarenes started in late 19th century by its synthesis by Baeyer et al.^[9-11] Synthesis of Calix[4]resorcinarenes was done by acid catalyzed cyclocondensation of resorcinol with various aliphatic and aromatic aldehydes.^[12-16] Calixresorcinarenes possess properties which continue to draw research interests due to its prospective relevance as macrocyclic receptors^[17], as dendrimers in biological systems^[18], nano-capsule, nanoparticles^[19], optical chemosensors^[20], supramolecular tectons^[21], host molecules^[22], as components in liquid crystals^[23], photoresists^[24], selective membranes^[25], surface reforming agents^[26], HPLC stationary phases^[27], as ion channel mimics^[28], and metal ion extraction agents.^[29] Our earlier publications showed synthesis of four new azo dyes by coupling diazonium salts of amino compounds like sulphanilic acid, anthranilic acid, *o*-aminophenol, and *p*-aminobenzoic acid with Calix[4]resorcinarene.^[30] Azo dyes consisting atleast one conjugated chromophore azo (-N=N-) group plays a significant role as organic colorants and are considered most versatile and largest among all classes of dyes.^[31] Of the synthesized dyes, *p*-aminobenzoic acid dye was further functionalized to get various Schiff bases by breaking the azo group in basic medium to get the free amino functional group and further condensation with various aldehydes resulted in novel Schiff bases.^[32] In this article we are presenting some new azo-metal chelates using *p*-(2-hydroxyphenylazo) calix[4]resorcinarene dye derived by coupling calix[4]resorcinarene with *o*-amino phenol, with transition metal ions like Copper, Zinc and Cobalt in solid state. Furthermore these type dyes and their complexes have been most widely used in field such as biomedical studies, advanced applications in organic synthesis and high technology areas like lasers, liquid crystalline displays, electro-optical devices, ink-jet printers, catalysts, fluorescence properties.^[33-37] Besides the characterization of complexes by physico chemical techniques like IR, ¹H NMR, elemental analysis, EPR and TG –DTA analysis the biological activities of the synthesized complexes have also been examined

against pathogenic bacterial strains namely *Staphyococcus aureus*, *E. Coli* possessed good activity against these bacteria.

2. EXPERIMENTAL

2.1 Materials and Methodology

All the chemicals used in this study were of analytical grade and were used as procured. Solvents used in this study were of analytical grade and were purified by standard procedures. Melting points were taken in single capillary tube using a Veego (Model: VMP-DS, India) melting point apparatus and were uncorrected. Elemental analysis was done on Perkin Elmer, Series II, 2400 elemental analyzer. Their IR spectra were recorded in Bruker Tensor 27 spectrophotometer as KBr pallets and expressed in cm^{-1} . Metal Content was estimated on a Chemito flame atomic absorption spectrophotometer in solution prepared by decomposing the respective complex in hot concentrated HNO_3 . ^1H NMR spectra of the ligand were recorded on Bruker ARX 500 Mhz operating for proton in DMSO-d_6 with tetramethylsilane as internal standard. The UV-Vis spectra were recorded in DMSO on a JASCO 570 spectrophotometer with a quartz cell of 1 cm path length. EPR spectra were recorded on a Varian E-112 spectrometer with a variable temperature liquid nitrogen cryostat (the error in g value is ± 0.001). Perkin Elmer Model Diamond TG-DTA was used for simultaneous recording of TG-DTA curves at a heating rate of 10°min^{-1} . For TG, the instrument was calibrated using calcium oxalate while for DTA, calibration was done using indium metal, both of which were supplied along with the instrument. A flat bed type aluminium crucible was used with alpha – alumina (99% pure) as the reference material for DTA. The numbers of decomposition steps were identified using TG. The activation energy and Arrhenius constant of the degradation process was obtained by Coats and Redfern method.^[38] For determining the stoichiometry and formation constant of the azo metal complex, the absorbance of a series of metal salts + ligand [in ethyl alcohol] mixtures, which were prepared from their 10^{-5} moles/lit solution were measured. The data were analyzed using Job's method.^[39,40]

2.2 Synthesis of Ligand [Diazotization and Coupling]

The diazotization of 2-amino phenol and coupling with Calix[4]resorcinarene was carried according to the published methods.^[13,41]

A mixture of 2-amino phenol (4.36gm, 40.0mmol), water (20cm^3), and concentrated hydrochloric acid (2.5cm^3 , 30mmol) was stirred until clear solution was obtained. The

resulting clear solution was cooled to 0-5°C and a solution of sodium nitrite (3.04g, 44mmol) in 5ml of water was then added dropwise, maintaining the temperature below 5°C.

Calix[4] resorcinarene (5.44gm, 10mmol) was dissolved in sodium hydroxide(40mmol) and cooled to 0-5°C in an ice bath. This solution was then gradually added to the solution of the cooled diazonium salt of 2-amino phenol and the resulting mixture was continually stirred at 0-5°C for 2 hrs. The resulting crude precipitate was filtered and washed several times with cold water and dried under vacuum. The progress of reaction was followed by TLC using a mixture of hexane and ethyl acetate in the ratio 8:2 v/v as the developing solvent and silica gel Kieselgel 60 HF₂₅₄ TLC plates as stationary phase. The crude material was made soluble in hot solution of sodium bicarbonate and then reprecipitated by addition of concentrated hydrochloric acid dropwise. The mixture was stirred for at least 7 hours at room temperature, filtered and washed with water followed by methanol and dried under vacuum (Fig. 1).

Reddish brown powder; mp > 300° C; λ_{\max} 440 nm in DMF; IR (KBr) 3429.78 (Ar-OH), 1607.38 (-N=N-) cm⁻¹; ¹H NMR (DMSO-d₆) δ 1.65 ppm (d, 12H, CHCH₃), δ 4.88 ppm (q, CHCH₃), δ 7.1-8.0 ppm (m, ArH), δ 10.12 ppm (s, 12H OH). Anal. calcd. for C₅₆H₄₈O₁₂N₈: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.42; H, 4.71; N, 10.89.

2.3 Synthesis of Azo-metal Chelates.

Metal Complexes were synthesized by addition of a hot ethanolic solution of metal salts (acetates, chlorides, sulphates, nitrates) for Copper, (acetates and nitrates) for Cobalt(nitrates and acetates) and Zinc(sulphates and acetates) to hot ethanolic solution of calix[4] resorcinarene dye. The resulting mixture was stirred under reflux for 4 hrs and left to cool, complexes were precipitated in case of Copper salts while in case of Zinc and Cobalt complexes, complexes were precipitated by increasing the pH up to 5.5 for Zinc and 6.5pH for Cobalt Complexes. The complexes precipitated were filtered, washed with ethanol and dried in vacuum desiccators over anhydrous calcium chloride.^[42-44](Fig. 2)

3. RESULTS AND DISCUSSIONS

(o-amino phenol)- Calix[4] resorcinarene dyes [OAPCRD](Fig. 1) were synthesized by azo-coupling reactions of diazonium salt of o-amino phenol with Calix[4] resorcinarene. The ¹H-NMR (DMSO-d₆) spectrum showed a doublet at 1.65 ppm for (-CH₃), a quartet at 4.6 ppm (-CH), a multiplet from 7.25-7.9 ppm for aromatic protons (ArH), a singlet at 8.8-9.9 ppm for (-OH). Dye showed a singlet at 9.8 ppm for (-OH).

The ^{13}C NMR (DMSO-d_6) spectrum of ligand displayed singlet at 123-125 and 140-150 ppm for aromatic carbons. In addition ligand displayed one quartet at 21.0 ppm for methyl group at the bridge and one doublet at 28.1 ppm for bridged methane group.

Metal(II)Chelates $[\text{M-OAPCRD}]$ of these azo compound were isolated by refluxing metal (II) salts like chlorides, sulphates, nitrates, acetates and buffer solutions in some cases for 4 hrs in ethanol medium. The stoichiometry of azo metal chelates was described having the metal: ligand ratio of 4:1 by spectroscopic titration method.(Fig.3) For more verification stoichiometry was also done by AAS analysis. Through this analysis also the metal : ligand ratio was found to be 4:1 as same found in spectroscopic titration method.^[45](Fig. 4) The physical properties and analysis of metal cations for the dyes and metal chelates have been represented in Table 1.

3.1 IR spectra and UV-VIS study

The IR data of azo dyes and their metal chelates have been mentioned in the Table-2. Absorption in the region of $4000\text{-}2500\text{ cm}^{-1}$ involves the bands of $-\text{OH}$, $-\text{NH}$ as well as those of the C-H phenyl and C-H aliphatic and associated water molecules in the compounds. The band at $3450\text{-}3400\text{ cm}^{-1}$ in the IR spectra of the ligand can be attributed to the $-\text{OH}\cdots\text{N}$ intramolecular hydrogen bonding, while there is absence of this band in the spectr as of the metal chelates indicating deprotonation of phenolic $-\text{OH}$ groups, by this means showing its coordination to the metal ions.^[46] The band at $3450\text{-}3400\text{ cm}^{-1}$ is assigned to $-\text{OH}$ weakly while $3400\text{-}3300\text{ cm}^{-1}$ stands for strongly bonded $-\text{OH}$ stretching frequency of coordinated water molecules in azo-metal chelates.

In the region of $2500\text{-}1400\text{ cm}^{-1}$ bands for C-O, $-\text{N}=\text{N}-$ and $-\text{C}=\text{C}-$ are present. $1450\text{-}1400\text{ cm}^{-1}$ and $1600\text{-}1650\text{ cm}^{-1}$ are assigned to phenolic $-\text{C}-\text{O}$ vibrations and $-\text{N}=\text{N}-$ vibrations, respectively in the ligand.^[39] A bathochromic shift is observed for the above vibrations to $1400\text{-}1350\text{ cm}^{-1}$ and $1550\text{-}1500\text{ cm}^{-1}$ for respective $-\text{C}-\text{O}$ and $-\text{N}=\text{N}-$ vibrations, indicating the bonding of ligand with metal ion through azo nitrogen.^[47] 1400 cm^{-1} to 1000 cm^{-1} region consists of bands for aromatic C-H in the plane deformation vibration, C-N stretching vibration and C-C stretching vibration. Two bands were seen in region of $1200\text{-}1210\text{ cm}^{-1}$ which changed to $1990\text{-}1200\text{ cm}^{-1}$. In the region of $1000\text{-}400\text{ cm}^{-1}$, out of plane deformation frequencies of aromatic C-H band are received, observed at 810 cm^{-1} in case of ligand while 803 cm^{-1} for the complex. Some new bands are seen in this region for the azo metal chelates ,

755cm^{-1} assigned for ring_{def} and M-OH_2 – a water molecule coordinated in the complex molecule, 497cm^{-1} assigned for M-N and 455cm^{-1} assigned for M-O .^[32]

The UV–VIS spectral behavior of the p-(2-hydroxyphenylazo) calix[4]resorcinarene dye ligand and their metal chelates were investigated in DMSO and the compared dates of the UV–VIS spectra are shown in Fig.4. It was found that all of the spectra show a strong absorption maximal in the 560–480 nm ranges with high extinction coefficients. As show, the absorption maximum of the azo-metal chelates demonstrated a bathochromic shift between ca. 100 nm in comparison with 2-hydroxyphenylazo) calix[4] resorcinarene dye.

3.2 Antibacterial Study on Azo-Metal Chelates

The antibacterial activity of the metal chelates against *E.coli* and *S.aureus* were carried out using Muller Hinton Agar media (Hi media). Paper disc method was used for carrying out the antibacterial activity. The activity for antibacterial study is reported in the Table 3. Base plates were arranged by transferring 10ml of autoclaved Muller-Hinton agar into sterilized Petri dish and allowed them to settle. Molten autoclaved Muller Hinton that had been kept at $48\text{ }^\circ\text{C}$ was incubated with a broth culture of the *E.coli* or *S.aureus* and then poured over the base plate. The discs were air dried and placed on the top of agar layer. The solutions of all compounds were prepared at two different concentrations and chloramphenicol was used as a reference. The plates were then incubated for 18 h at room temperature. Among the various azo-metal chelates, No 3 and No 7 have been found out to be most effective against these microbes showing maximum clarity of zones, its antibacterial activity was found maximum against *E.coli*. while No 4 was found out to be most effective against *S.aureus*.(Fig. 6)

3.3 Electron spin Resonance

The X-Band ESR spectra of Cu(II) were obtained in the solid state at 300K in order to confirm the geometries around Cu(II) . Complex shows symmetrical one line spectra with peak line of 375 gauss. The single g value has been interpreted to arrive from a complex containing grossly miss aligned tetragonal axis. This situation is probably for most common reason for observation of isotopic EPR spectra. The azo complex in solid state shows weak resolution of g parallel component. Therefore further high resolution EPR is needed to provide further evidence regarding its geometry.(Fig. 5)

The samples were heated in the temperature ranges room temperature- $1000\text{ }^\circ\text{C}$. The thermo gram of complex shows weight loss corresponding to one water molecule in the range from

room temperature to 240 °C. The loss of water in this temperature range indicates the presence of water molecule, from this analysis the complex are endothermic.

Captions

Fig. 1. Structure of 2-aminophenol dye of Calix[4]resorcinarene

Fig. 2. Chemical Structure of Azo Metal(II) Chelates

Fig. 3. Job's Diagram for the azo-Copper Chelate ($\lambda = 505\text{nm}$)

Fig. 4. Electronic Spectra of the Azo ligand and its metal chelates.

Fig. 5. ESR spectra of $[(L)(CuCl_2)_4].3H_2O$

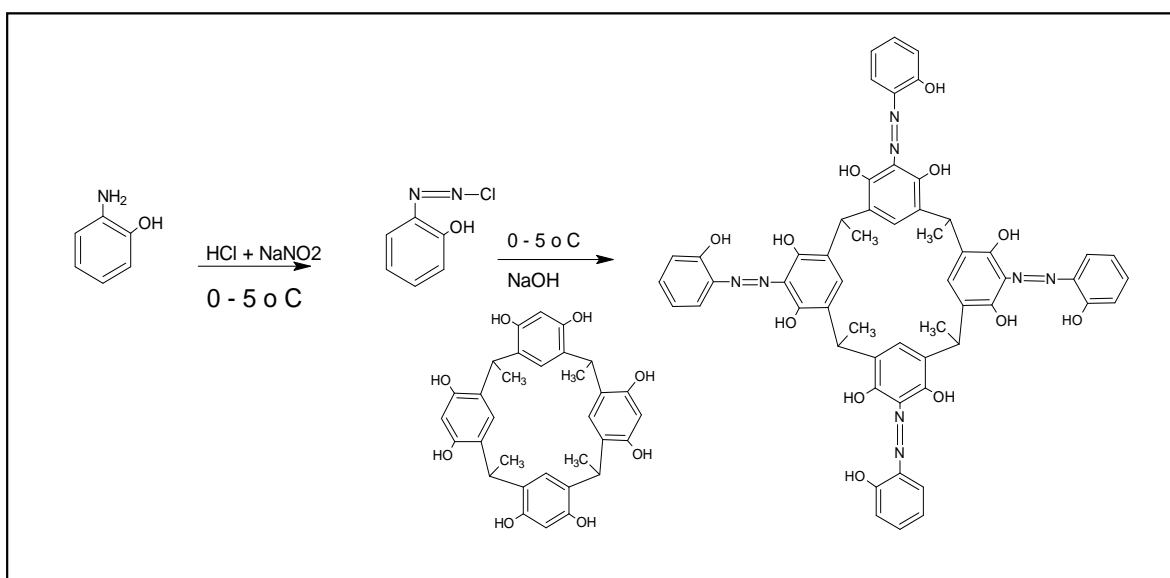


Fig. 1: Structure of 2-aminophenol dye of Calix[4]resorcinarene

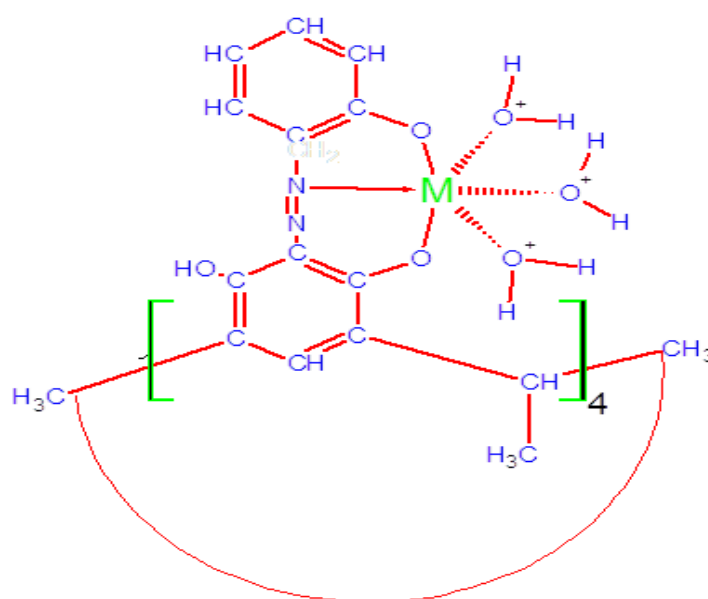


Fig. 2: Chemical Structure of Azo Metal(II) Chelates.

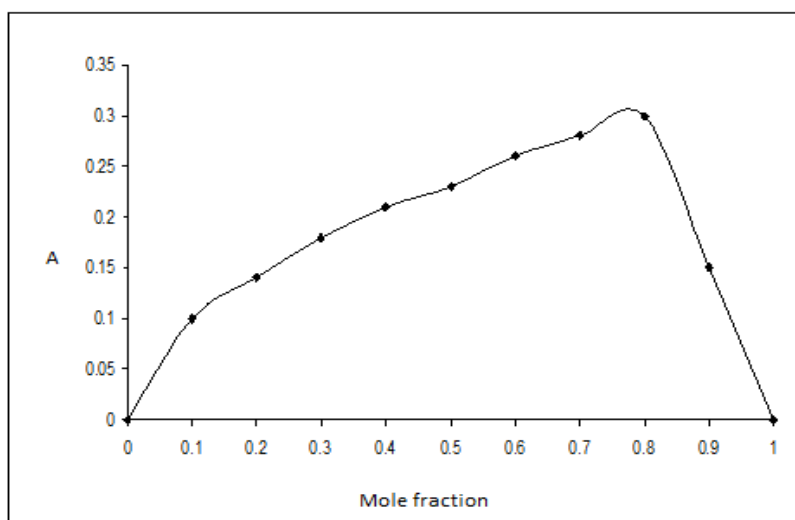


Fig. 3: Job's Diagram for the azo-Copper Chelate ($\lambda = 505\text{nm}$).

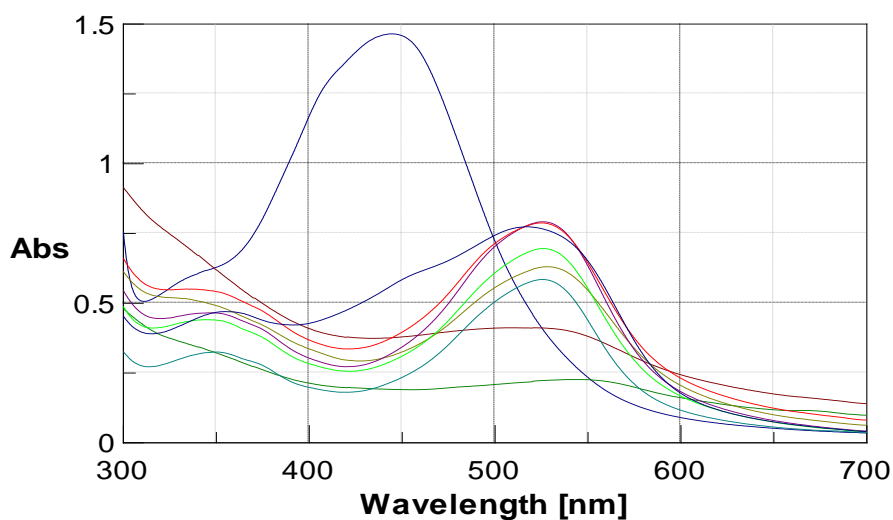


Fig. 4: Electronic Spectra of the Azo ligand and its metal chelates.

Ligand

- [(L)(ZnSO₄)₄].3H₂O
- [(L)(CuCl₂)₄].3H₂O
- [(L)(CuNO₃)₄].3H₂O
- [(L)(CuAc₂)₄].3H₂O
- [(L)(CuSO₄)₄].3H₂O
- [(L)(ZnAc₂)₄].3H₂O
- [(L)(CoNO₃)₄].3H₂O
- [(L)(CoAc₂)₄].3H₂O

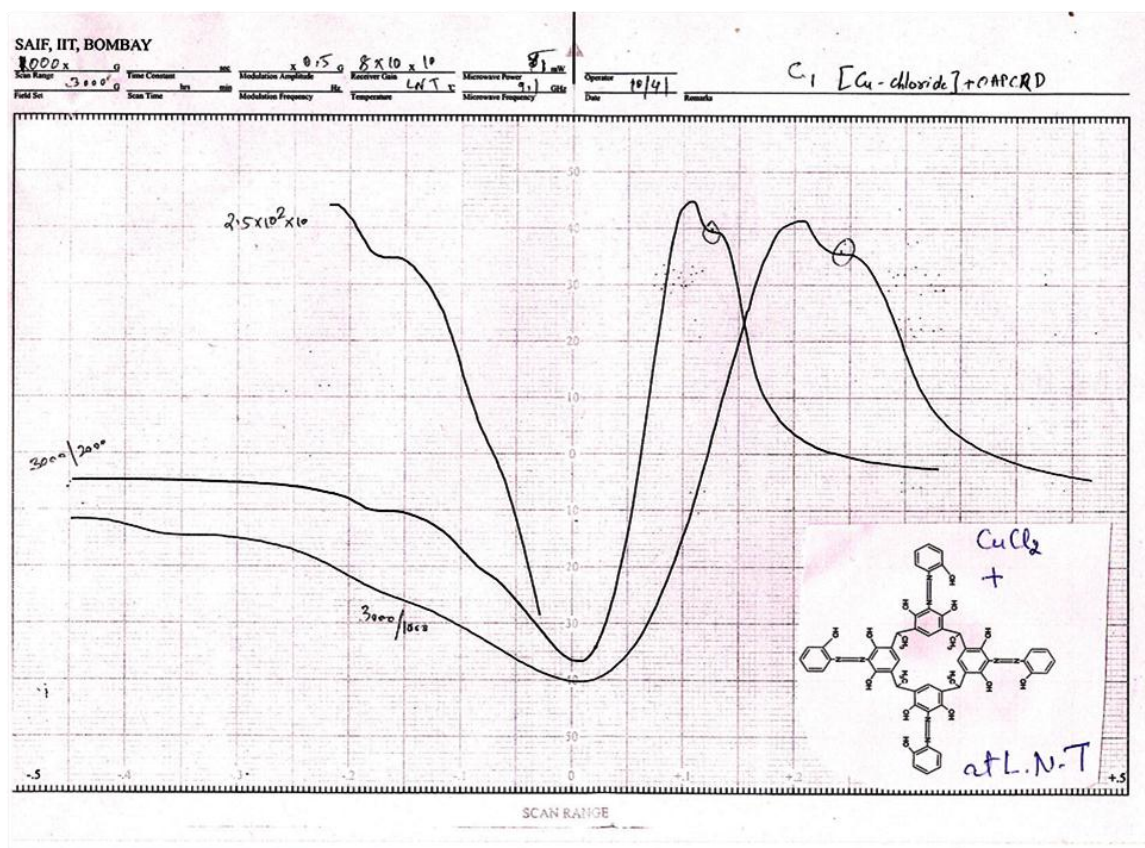


Fig. 5: ESR spectra of $[(L)(CuCl_2)_4].3H_2O$.

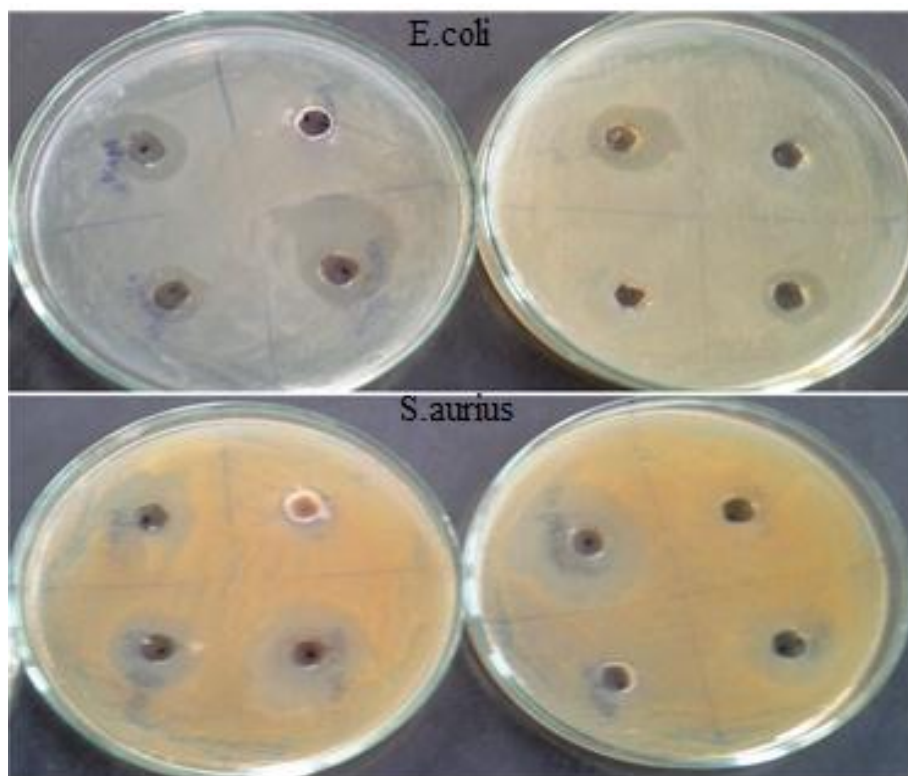


Fig. 6: Antibacterial Activity of Azo-metal Chelates.

Table 1: Formula weight, Colours, Yields, Decomposition point and Metal Cation analysis results of the azo ligand and their azo-metal chelates.

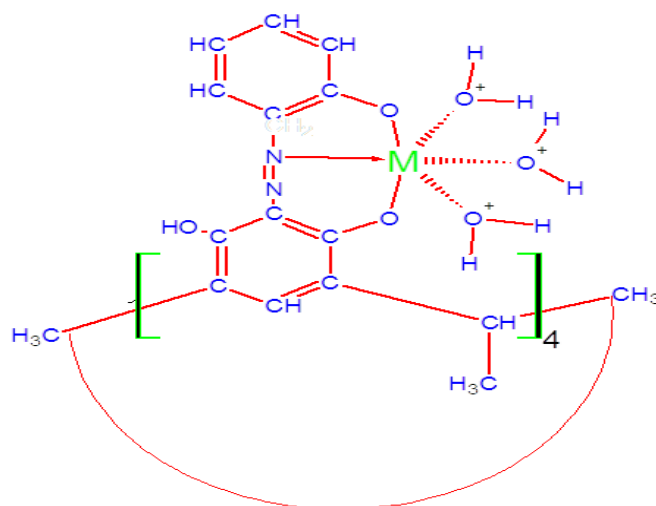
Sr. No	Ligand/Complex	F.W. (g/mol)	Colour	Yield	Dec.Point (°C)	[M ⁺²] Cal (Found)%
1	HL	1025	Dark Red	71	>300	
2	[(L)(CuCl ₂) ₄].3H ₂ O	1414	Brown	65	>370	17.96(17.75)
3	[(L)(CuNO ₃) ₄].3H ₂ O	1378.2	Brown	62	>365	18.41(18.23)
4	[(L)(CuAc ₂) ₄].3H ₂ O	1602	Black	68	>363	15.85(15.81)
5	[(L)(CuSO ₄) ₄].3H ₂ O	1514	Dark Brown	64	>365	16.7(16.65)
6	[(L)(CoAc ₂) ₄].3H ₂ O	1583.6	Dark Red	65	>350	14.87(14.83)
7	[(L)(CoNO ₃) ₄].3H ₂ O	1607.6	Dark Red	69	>354	14.65(14.62)
8	[(L)(ZnSO ₄) ₄].3H ₂ O	1521.6	Black	59	>361	17.19(17.12)
9	[(L)(ZnAc ₂) ₄].3H ₂ O	1609.6	Black	56	>363	16.25(16.21)

Table 2: Characteristic IR bands of the azo ligand and their metal chelates as KBr pellets (cm⁻¹).

Ligand/Complex	(-C-O)	- OH ₂	(-N=N-)	C-H	M-O	M-N	M-OH ₂
HL	1410	3429	1607	3188			
[(L)(CuCl ₂) ₄].3H ₂ O	1378	3316	1520	3170	465	549	755
[(L)(CuNO ₃) ₄].3H ₂ O	1389	3299	1549	3108	471	523	760
[(L)(CuAc ₂) ₄].3H ₂ O	1370	3278	1503	3179	480	534	754
[(L)(CuSO ₄) ₄].3H ₂ O	1399	3295	1526	3149	458	545	761
[(L)(CoAc ₂) ₄].3H ₂ O	1385	3300	1531	3167	454	548	757
[(L)(CoNO ₃) ₄].3H ₂ O	1389	3296	1523	3113	465	539	764
[(L)(ZnSO ₄) ₄].3H ₂ O	1394	3312	1530	3170	438	524	756
[(L)(ZnAc ₂) ₄].3H ₂ O	1399	3298	1512	3167	461	541	758

Table 3: Antibacterial Activity of Azo-metal Chelates.

Sr. No	Ligand/Complex	Diameter of zone of inhibition in mm for E.coli	Diameter of zone of inhibition in mm for S.aureus
1	HL	7	8
2	[(L)(CuCl ₂) ₄].3H ₂ O	9	9
3	[(L)(CuNO ₃) ₄].3H ₂ O	10	10
4	[(L)(CuAc ₂) ₄].3H ₂ O	9	10
5	[(L)(CuSO ₄) ₄].3H ₂ O	8	9
6	[(L)(CoAc ₂) ₄].3H ₂ O	9	8
7	[(L)(CoNO ₃) ₄].3H ₂ O	10	10
8	[(L)(ZnSO ₄) ₄].3H ₂ O	8	7
9	[(L)(ZnAc ₂) ₄].3H ₂ O	9	9



Graphical Abstract

CONCLUSION

We have developed an economical, using less solvent, very efficient microwave assisted method of synthesis of novel azo-calix[4]resorcinarene supramolecular dyes. The reported microwave assisted methods can be viable alternative to the conventional method of synthesis. made to enable it to complex with various metal ions. These complexes were studied by UV, IR, TGA, DTA, and ESR techniques. AAS of metal ions reviewed that 4:1 (M:L) complex is established. The stoichiometry of the azo-metal chelates was also determined by the spectroscopic titration method. The synthesized azo calix[4] resorcinarene dyes have been examined and showed reasonably good antimicrobial activity against selected microbes namely, *E. coli*, *S. aureus* applications of the synthesized azocalix[4] resorcinarene dyes for extraction of various bivalent and trivalent metal ions, screening of biological activity and their use as direct dyes on cotton, silk, wool, acrylic and nylon are under progress.

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