

Research Article

Synthesis, Characterisation, Binding Behaviour and Antimicrobial Activity of Azocalix[4]Resorcinarene dye derived from 8-aminoquinoline

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Abstract: The chemistry of metal complexation containing azo group has been a subject of greater interest in the 21st century. A novel azocalix[4]resorcinarene, 5,11,17,23, tetra methyl calix[4]resorcinarene 1, was prepared by linking 8-aminoquinoline to calix[4]resorcinarene through a diazo-coupling reaction having a conjugated chromophoric azo (-N=N-) group in lower-rim was synthesized by conventional technique. Based on it, a simple, sensitive and selective spectrophotometric method was developed for the determination of Ni²⁺. 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, Nickel] complexes of azo-calix[4]resorcinarene were synthesized in different molar ratio of metal and ligand in DMSO-Water 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, and DTA, 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 *E.coli*, *B.subtilis*, *S.aureus* and *B.megaterium* respectively compared to ligand.

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

INTRODUCTION

The design and synthesis of new chemosensors for metal ions is an important subject in the field of supramolecular chemistry due to their fundamental role in biological, environmental, and chemical processes[1]. 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[2,3].

Calix[4]resorcinarenes structurally similar to calixarenes shows interesting receptor properties, performs as building blocks for large supramolecular assemblies of fascinating architecture[4,5]. 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 [6-8]. Synthesis of Calix[4]resorcinarenes was done by acid catalyzed cyclocondensation of resorcinol with various aliphatic and aromatic aldehydes[9-13]. Calixresorcinarenes

possess properties which continue to draw research interests due to its prospective relevance as macrocyclic receptors[14], as dendrimers in biological systems[15], nano-capsule, nanoparticles[16], optical chemosensors[17], supramolecular tectons[18], host molecules[19], as components in liquid crystals[20], photoresists[21], selective membranes[22], surface reforming agents[23], HPLC stationary phases[24], as ion channel mimics[25], and metal ion extraction agents[26]. 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[27]. Azo dyes consisting at least 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[28].

Resorcinarenes are macrocyclic compounds that are composed of four resorcinol units joined together at the 4 and 6 positions by a methine bridge. Resorcinarenes are cyclic tetramers conveniently synthesized by condensing resorcinol with appropriate aldehydes. They possess a bowl-shaped polyhydroxy aromatic cavity. They are a class of synthetic macrocyclic molecules which have been the subject of

research for many years. Calix[4]resorcinarenes, a structural similar complex of calixarenes, presents interesting receptor properties and can act as building blocks for large supramolecular assemblies of a fascinating architecture[29,30]. Azo compounds are highly coloured that enjoy widespread use as dyes and pigments in a variety of applications that include textile dyeing as well as non-linear and photoelectronics, especially in optical information storage[31]

Although known for a long time for dyeing as well as medicinal properties, the structures and protective properties of natural dyes have been recognized only in the recent past. Many of the synthetic dyes used for dye extraction are classified as medicinal, and some of these have recently been shown to possess remarkable antimicrobial activity[32]

In this paper we would like to present synthesis of new derivative of calix[4]resorcinarene by condensation of 2-methyl resorcinol and *p*-hydroxy benzaldehyde. Further functionalization by azo linkage through amino compound like 8-amino quinoline is shown

The 8-aminoquinoline was chosen as an optical moiety due to the fact that quinolylazo group shows a high selectivity towards Co^{2+} .

Preliminary complexation studies with transition metal ions like Copper, Zinc, Nickel and Cobalt in solid state various transition metal ions is shown and compared. Microbiological studies are also shown. Azo dyes consisting at least one conjugated chromophore azo ($-\text{N}=\text{N}-$) group plays a significant role as organic colorants and are considered most versatile and largest among all classes of dyes. 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, and TG-DTA analysis the biological activities of the synthesized complexes have also been examined against pathogenic bacterial strains namely *E.coli*, *B.subtilis*, *S.aureus* and *B.megaterium* possessed good activity against these bacteria[38].

EXPERIMENTAL

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 pellets 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. 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[39]. 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[40,41].

Synthesis of Ligand (Compound 1)

5,11,17,23 tetramethyl calix[4]resorcin arene was synthesized as described elsewhere. Parent calix[4]resorcinarene skeletons (**1**) were synthesized by the acid catalyzed condensation reaction of 2-substituted resorcinol and aromatic aldehydes. 20 mL aqueous solution of 2-methyl resorcinol (5 g, 0.040 mol) in 5 mL hydrochloric acid was added to 15 mL solution of *p*-hydroxy benzaldehyde (4.88 g, 0.040 mol) in methanol containing 5 mL of hydrochloric acid with constant stirring and then refluxed for 4-5 hours at 75°C . Pink coloured precipitates were obtained which were washed with cold methanol and further recrystallized in DMF-methanol mixture.

Characterization of compound A

Pinkish white powder; mp $> 300^\circ\text{C}$; λ_{max} 281 nm in DMSO; IR (KBr) 3371.78 (Ar-OH), 2958 ($-\text{CH}_3$) cm^{-1} ; ^1H NMR (DMSO-d_6) δ 1.95 ppm (s, 6H, CH_3), δ 1.774 ppm (s, 6H CH_3), δ 6.1-6.5 ppm (d, 16 ArH), δ 8.725 ppm (s, 4H OH) δ 7.48 ppm (s, 4H OH) δ 7.073 ppm (s, 4H OH). MS: 913, (M^{+1}) 914, ($\text{M}^{+\text{Na}}$) 936, ($\text{M}^{+\text{K}}$) 951, Anal. calcd. for $\text{C}_{56}\text{H}_{48}\text{O}_{12}$: C, 73.67; H, 5.30; O, 21.03 Found: C, 71.35; H, 5.01; O, 21.03, 10.89.

Synthesis of Compound 2 [Diazotization and Coupling]

A mixture of 8-amino quinoline (1.19 gm, 4.5 mmol), water (20 cm^3), and concentrated hydrochloric acid (2.5 cm^3 , 30 mmol) was stirred until clear solution was obtained. The resulting clear solution

was cooled to 0-5°C and a solution of sodium nitrite (0.12g, 4.9mmol) in 5ml of water was then added dropwise, maintaining the temperature below 5°C.

Calix[4]resorcinarene (1gm, 1.0mmol) was dissolved in sodium hydroxide(12mmol) 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 8-amino quinoline 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 Kiesegel 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.

Characterization of compound 2

Reddish brown powder; mp > 300°C; λ_{\max} 394 nm in DMSO; IR (KBr) 3429.78 (Ar-OH), 1565.38 (-N=N-) cm^{-1} ; ¹H NMR (DMSO-d₆) δ 1.95 ppm (S,6H,CH₃), δ 1.774ppm (S, 6H CH₃), δ 6.1-6.5 ppm (d,8H ArH), δ 8.725 ppm (s, 4H OH) δ 7.48 ppm (s, 4H OH) δ 7.073 ppm (s, 4H OH) δ 6.3-7.5 ppm (m,40H ArH). Anal. calcd. for C₉₂H₆₈O₁₂N₁₂: C, 72.05; H, 4.47; N, 10.96. Found: C, 69.72; H, 4.11; N, 10.34.formula weight 1533.59

Synthesis of Azo-metal Chelates (4).

Metal Complexes were synthesized by addition of a hot aqueous 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 DMSO 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 6.5 pH for Cobalt Complexes. The complexes precipitated were filtered, washed with ethanol and dried in vacuum desiccators over anhydrous calcium chloride **Fig.2**.

RESULTS AND DISCUSSIONS

(8-Amino Quinoline)- Calix[4]resorcinarene dyes [8AQCRD] **Fig.1** were synthesized by azo-coupling reactions of diazonium salt of 8-Amino Quinoline with 5,11,17,23 tetramethyl calix[4]resorcinarene. In ¹H NMR spectra of Compound (1) displayed a peak at 8.7-7.6 ppm, for phenolic -OH, and one singlet at 5.48 for -Ar₃CH. In addition, compound (1) gave overlapping two doublets around 6.49 and 6.37 ppm for aromatic -CH and The ¹³C NMR (DMSO-d₆) spectrum of ligand displayed singlet at 123-125 and 150,153 ppm

for aromatic carbons. In addition ligand displayed one quartet at 22.0 ppm for methyl group at the bridge and one doublet at 42.1 ppm for bridged methane group.

Metal(II)Chelates [M-8APCRD] 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 **Fig.3**. The physical properties and analysis of metal cations for the dyes and metal chelates have been represented in **Table 1**. 8AQCRD 5 x 10⁻⁵M was taken in DMSO. λ_{\max} was obtained at 394nm. On titration with various concentrations of Cu⁺² ions, we found a different peak in visible region around 513nm. So a noticeable change was obtained around 119 nm. On titration with Zn⁺², we found a peak at 517nm. There was a noticeable change of 123nm. Again on titrating with Ni⁺² a peak at 522nm was found. A shift was obtained of about 128nm. On titration with Co⁺² a peak was obtained at 527nm and maximum shift was seen which is about 133 nm.

IR spectra study

The IR data of azo dyes and their metal chelates have been mentioned in the **Table 2**. Absorption in the region of 4000-2500 cm^{-1} involves the bands of -OH, -NH as well as those of the C-H phenyl and C-H aliphatic and associated water molecules in the compounds. The band at 3450-3400 cm^{-1} in the IR spectra of the ligand can be attributed to the -OH--N intramolecular hydrogen bonding, while there is absence of this band in the spectra of the metal chelates indicating deprotonation of phenolic -OH groups, by this means showing its coordination to the metal ions[42]. The band at 3450-3400 cm^{-1} is assigned to -OH weakly while 3400-3300 cm^{-1} stands for strongly bonded -OH stretching frequency of coordinated water molecules in azo-metal chelates. In the region of 2500-1400 cm^{-1} bands for C-O, -N=N- and -C=C- are present. 1450-1400 cm^{-1} and 1600-1650 cm^{-1} are assigned to phenolic -C-O vibrations and -N=N- vibrations, respectively in the ligand[40]. A bathochromic shift is observed for the above vibrations to 1400-1350 cm^{-1} and 1550-1500 cm^{-1} for respective -C-O and -N=N- vibrations, indicating the bonding of ligand with metal ion through azo nitrogen[43]. 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 1200-1210 cm^{-1} which changed to 1990-1200 cm^{-1} . In the region of 1000-400 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 m-(azo quinoline) 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 **Table 3**. It was found that all of the spectra show a strong absorption maximal in the 560–480 nm ranges with high extinction coefficients. As **Table 3** shows, the absorption maximum of the azo-metal chelates demonstrated a bathochromic shift between ca. 100 nm in comparison with m-(azo quinoline) calix[4]resorcinarene dye.

Antibacterial Study of compound Azocalix[4]resorcinarene metal complex

The microbiological study of Calix[4]resorcinarene (1), Azo calix[4]resorcinarene dye and Azocalix[4]resorcinarene metal complexes were carried out against *Staphylococcus aureus*, *Escherichia coli*, *Bacillus megaterium* and *Bacillus subtilis* using Muller Hinton Agar media (Hi media). Paper disc method was used for carrying out the microbiological activity. Base plates were arranged by transferring 10ml of autoclaved Muller-Hinton agar into sterilized Petri dish and allowed to settle. Molten autoclaved Muller Hinton was kept at $48\text{ }^\circ\text{C}$ and was incubated with culture of the *Staphylococcus aureus*, *Escherichia coli*,

Bacillus megaterium and *Bacillus subtilis* then poured over the base plate. The discs were air dried and placed on the top of agar layer. The solution of all compounds was prepared at two different concentrations. The plates were then incubated for 18 h at room temperature. azo-dye 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* and *S.aureus*.

The antimicrobial effect of Azo complex on bacteria such as *Staphylococcus aureus*, *Escherichia coli*, *Bacillus megaterium* and *Bacillus subtilis* were compared with standard antibiotics such as chloramphenicol as well as the compounds calix[4]resorcinarene (1), and Azo calix[4]resorcinarene(2) and 8 amino quinoline. Zone of inhibition is the only criterion which has been used to compare the antimicrobial activity. On this basis it was observed that the antimicrobial activity of M-8APCRD is generally more than the compound no. (1), (2) and (3) except with *s. aureus*. This observation has lead us to conclude that antimicrobial activity of compound 1,2 and 3 has not been compromised with the formation of M-8APCRD rather it has been enhanced marginally. Although the antimicrobial activity of M-8APCRD is slightly less than that of standard chloramphenicol therefore it is reasonable to propose that M-8APCRD hold the potential of their use as good antibacterial agent **Table 4**.

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 ($^\circ\text{C}$)	$[\text{M}^{+2}]$ Cal	(Found)%
1	HL	1653	Dark Red	71	>300		
2	$[(\text{L})(\text{CuCl}_2)_4].3\text{H}_2\text{O}$	2042	Brown	65	>352	15.12(16.35)	
3	$[(\text{L})(\text{CuNO}_3)_4].3\text{H}_2\text{O}$	2006	Brown	62	>354	16.21(17.43)	
4	$[(\text{L})(\text{CuAc}_2)_4].3\text{H}_2\text{O}$	2230	Black	68	>350	15.85(15.81)	
5	$[(\text{L})(\text{CuSO}_4)_4].3\text{H}_2\text{O}$	2142	Dark Brown	64	>355	16.7(16.65)	
6	$[(\text{L})(\text{ZnSO}_4)_4].3\text{H}_2\text{O}$	2149	Black	59	>361	17.19(17.12)	
7	$[(\text{L})(\text{ZnAc}_2)_4].3\text{H}_2\text{O}$	2237	Black	56	>363	16.25(16.21)	
8	$[(\text{L})(\text{NiCl}_2)_4].3\text{H}_2\text{O}$	2283	Dark Red	62	>358	17.96(17.75)	
9	$[(\text{L})(\text{NiSO}_4)_4].3\text{H}_2\text{O}$	2388	Dark Red	59	>360	18.41(18.23)	
10	$[(\text{L})(\text{CoAc}_2)_4].3\text{H}_2\text{O}$	2211	Dark Red	65	>368	17.97(18.83)	
11	$[(\text{L})(\text{CoNO}_3)_4].3\text{H}_2\text{O}$	2235	Dark Red	69	>365	18.85(18.62)	

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	1467	3374	1594	3304			
$[(\text{L})(\text{CuCl}_2)_4].3\text{H}_2\text{O}$	1378	3316	1520	3170	465	549	745
$[(\text{L})(\text{CuNO}_3)_4].3\text{H}_2\text{O}$	1389	3299	1549	3108	471	523	762
$[(\text{L})(\text{CuAc}_2)_4].3\text{H}_2\text{O}$	1370	3278	1503	3179	480	534	756
$[(\text{L})(\text{CuSO}_4)_4].3\text{H}_2\text{O}$	1399	3295	1526	3149	458	545	766
$[(\text{L})(\text{NiCl}_2)_4].3\text{H}_2\text{O}$	1365	3297	1532	3129	452	547	754
$[(\text{L})(\text{NiSO}_4)_4].3\text{H}_2\text{O}$	1386	3183	1524	3205	421	588	749
$[(\text{L})(\text{ZnSO}_4)_4].3\text{H}_2\text{O}$	1394	3312	1530	3170	438	524	746
$[(\text{L})(\text{ZnAc}_2)_4].3\text{H}_2\text{O}$	1399	3298	1512	3167	461	541	758
$[(\text{L})(\text{CoAc}_2)_4].3\text{H}_2\text{O}$	1385	3300	1531	3167	454	548	757
$[(\text{L})(\text{CoNO}_3)_4].3\text{H}_2\text{O}$	1389	3296	1523	3113	465	539	764

Table 3. Optical responses of azo resorcinarene [B] with different metal ions in DMSO

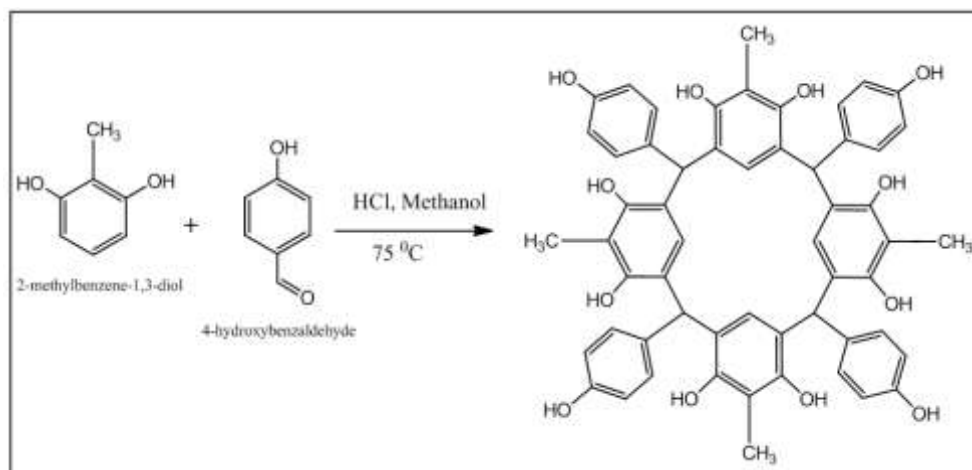
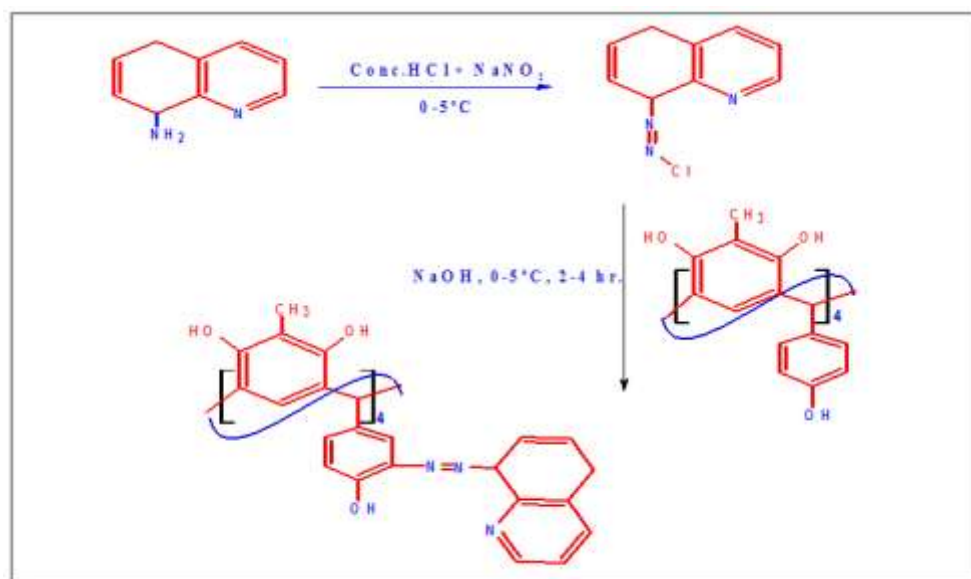
Metal ions	Reagent [B] (λ_{max})	Complex (λ_{max})	$\Delta\lambda$
Cu ⁺²	394	513	119
Zn ⁺²	394	517	123
Ni ⁺²	394	523	128
Co ⁺²	394	527	133

Table 4. Antimicrobial activity (Zone of inhibition in mm) of Compounds 1-4.

Name of compound	Zone of inhibition (mm)							
	<i>E.coli</i>		<i>B.subtilis</i>		<i>S.aureus</i>		<i>B.megaterium</i>	
	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm
A*	9	8	10	10	9	8	9	7
1	6	4	7	4	8	8	6	5
2	6	5	7	7	5	5	6	6
3	7	6	6	6	5	5	6	5
4	9	8	7	8	8	8	9	9

A* = Chloramphenicol (Antibiotic control)

(1) Calix[4]resorcinarene, (2) Azo calix[4]resorcinarene, (3) 8-Amino quinoline, (4) Azo-metal Chelates

**Scheme 1: Synthetic route for azocalix[4]resorcinarene****Scheme 2: Synthesis of 8-Amino Quinoline Calix[4]resorcinarene dye**

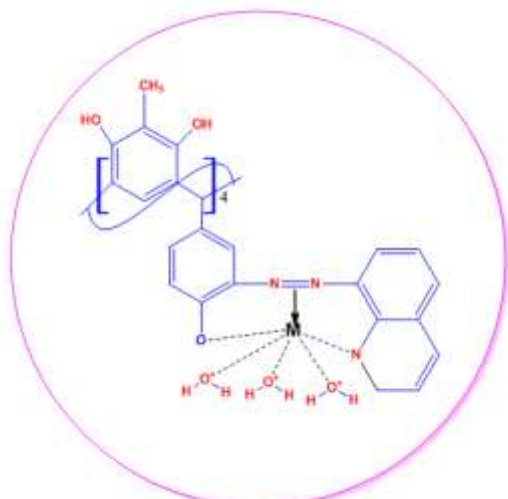


Fig. 1 Chemical Structure of Azo Metal(II) Chelates

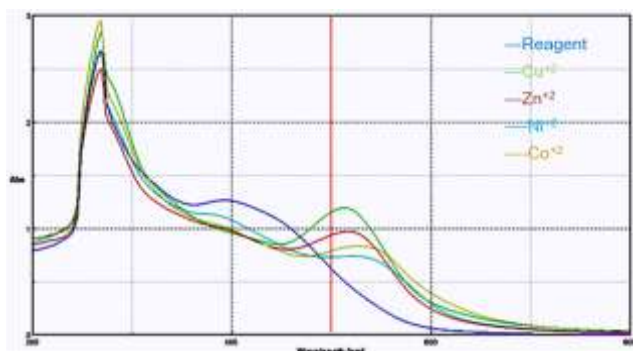


Fig.2 Electronic Spectra of the Azo ligand and its metal chelates.

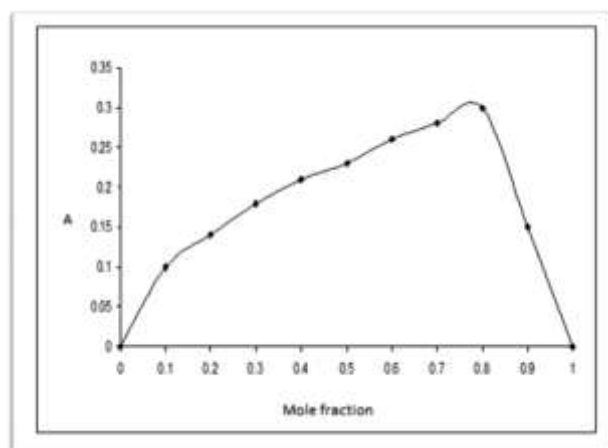


Fig. 3 Job's Diagram for the azo-Cobalt Chelate ($\lambda = 527\text{nm}$)

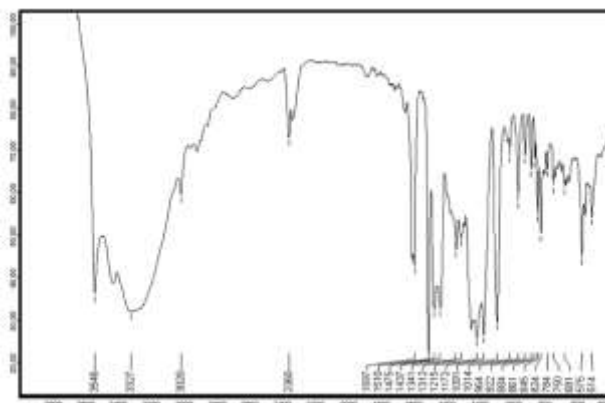


Fig.3 IR Spectra of Calix[4]resorcinarene

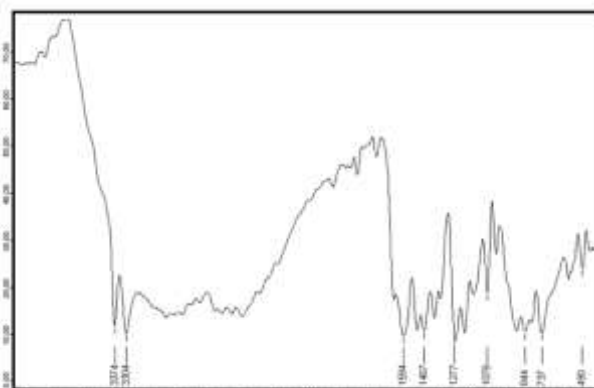


Fig.5 IR Spectra of Azo Calix[4]resorcinarene Dye

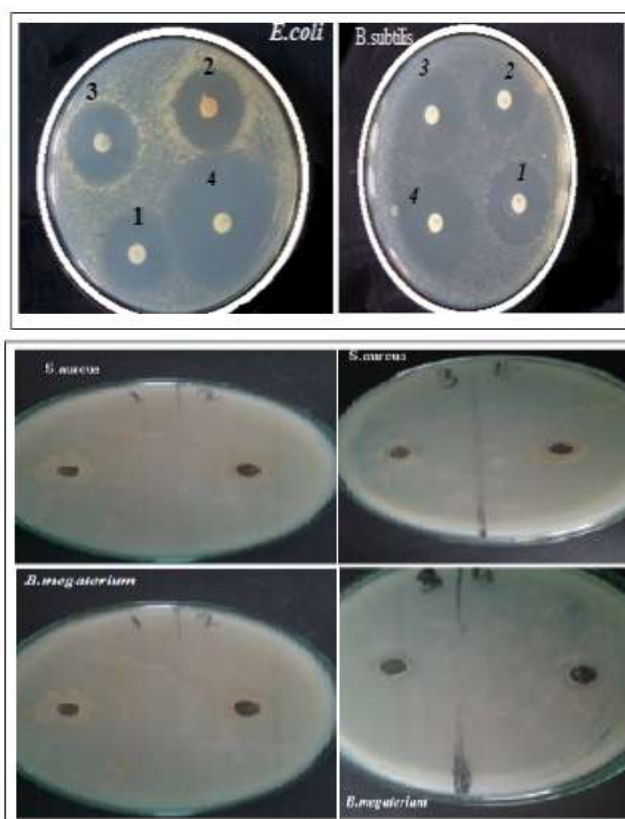


Fig.6 Antimicrobial Activity of Compound 1,2 & their Metal chelates

CONCLUSION

We have developed an economical, using less solvent, very efficient microwave assisted method of synthesis of novel azo-calix[4]resorcinarene supramolecular dyes, made to enable it to complex with various metal ions. These complexes were studied by UV, IR, TGA, and DTA, 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 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. Azo calix[4]resorcinarene dye and its metal complex have potential, exhibited reasonably good antimicrobial activity, when compared with standard *Chloramphenicol*, through the electrostatic attraction between positively charged metal complex and negatively charged cell membrane of microorganisms. This suggests their potential use as antimicrobial agent as well as for selective

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