Research Article


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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-N MR, 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 est... 

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-aminoo quinoline is shown. The 8-amino quinoline is shown as an optical moiety due to the fact that quinolylazo group shows a high selectivity towards Co²⁺.

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 (−N=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 physicochemical 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 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 HNO₃. ¹HNMR spectra of the ligand were recorded on Bruker ARX 500 MHz operating for proton in DMSO-d₆ 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 10⁰/min. For TG, the instrument was calibrated using calcium oxide 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 – aluminia (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 10⁻³ 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 (I) were synthesized by the acid catalyzed condensation reaction of 2-substituted resorcinol and aromatic aldehydes. 20 mL aqeous 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’ C; λmax 281 nm in DMSO; IR (KBr) 3371.78 (Ar-OH), 2958 (-CH₂) cm⁻¹; ¹H NMR (DMSO-d₆) δ 1.95 ppm (S,6H,CH₂), δ 1.774 ppm (S, 6H CH₃), 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,(M²⁺)936, (M³⁺)951, Anal. calcd. for C₃₅H₄O₆: C, 73.67; H, 5.30; O,21.03 Found: C, 71.35; H, 5.01; O, 10.89.

Synthesis of Compound 2 [Diazotization and Coupling]

A mixture of 8-aminoo quinoline (1.19 gm, 4.5mmol), water (20cm³), and concentrated hydrochloric acid (2.5cm³), 30nmol 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 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 Kieselgel 60 HF254 TLC plates as stationary phase. The crude material was made soluble in hot solution of sodium bi carbonate and than reprecipitated by addition of concentrated hydrochloric acid dropwise. The mixture was stirred for atleast 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; λmax 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,4OH ArH). Anal. calcd. for C₉H₆O₃N₁₂: 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 [8AQC R] Fig.1 were synthesized by azo-coupling reactions of diazonium salt of 8-Amino Quinoline with 5,11,17,23 tetramethyl calix[4]resorcin arene. 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 -ArCH. 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. 8AQC R 5 x 10⁻³M was taken in DMSO. λ max was obtained at 394nm. On titration with various concentrations of Cu²⁺ ions, we found a peak at 803 cm⁻¹. The band at 3450-3400 cm⁻¹ for the complex. Some peaks were seen in region of 1200 cm⁻¹ for the complex. Some
new bands are seen in this region for the azo metal chelates, 755 cm⁻¹ assigned for ring ν and M-OH₂ – a water molecule coordinated in the complex molecule, 497 cm⁻¹ assigned for M-N and 455 cm⁻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 Azoclix[4]resorcinarene metal complex**

The microbiological study of Calix[4]resorcinarene (1), Azo calix[4]resorcinarene dye and Azoclix[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 10 ml of autoclaved Muller Hinton agar into sterilized Petri dishes. 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-SAPCRD 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-SAPCRD rather it has been enhanced marginally. Although the antimicrobial activity of M-SAPCRD is slightly less than that of standard chloramphenicol therefore it is reasonable to propose that M-SAPCRD 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**

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Ligand/Complex</th>
<th>F.W. (g/mol)</th>
<th>Colour</th>
<th>Yield</th>
<th>Dec. Point (°C)</th>
<th>[M⁺⁺] Cal</th>
<th>(Found) %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>HL</td>
<td>1653</td>
<td>Dark Red</td>
<td>71</td>
<td>&gt;300</td>
<td>15.12(16.35)</td>
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<td>2</td>
<td><a href="CuCl%E2%82%82">L</a>₃H₂O</td>
<td>2042</td>
<td>Brown</td>
<td>65</td>
<td>&gt;352</td>
<td>16.21(17.43)</td>
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</tr>
<tr>
<td>3</td>
<td><a href="CuNO%E2%82%83">L</a>₃H₂O</td>
<td>2006</td>
<td>Brown</td>
<td>62</td>
<td>&gt;354</td>
<td>15.85(15.81)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td><a href="CuAc%E2%82%82">L</a>₃H₂O</td>
<td>2230</td>
<td>Black</td>
<td>68</td>
<td>&lt;350</td>
<td>16.7(16.65)</td>
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<td>5</td>
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<td>2142</td>
<td>Dark Brown</td>
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<td>&gt;355</td>
<td>17.19(17.12)</td>
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</tr>
<tr>
<td>6</td>
<td><a href="ZnSO%E2%82%84">L</a>₃H₂O</td>
<td>2149</td>
<td>Black</td>
<td>59</td>
<td>&lt;361</td>
<td>16.25(16.21)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td><a href="ZnAc%E2%82%82">L</a>₃H₂O</td>
<td>2237</td>
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<td>56</td>
<td>&gt;363</td>
<td>17.96(17.75)</td>
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<td>8</td>
<td><a href="NiCl%E2%82%82">L</a>₃H₂O</td>
<td>2283</td>
<td>Dark Red</td>
<td>62</td>
<td>&lt;358</td>
<td>18.41(18.23)</td>
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<td>9</td>
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<td>2388</td>
<td>Dark Red</td>
<td>59</td>
<td>&lt;360</td>
<td>17.97(18.83)</td>
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<td>10</td>
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<td>2211</td>
<td>Dark Red</td>
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<td>&gt;368</td>
<td>18.85(18.62)</td>
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<tr>
<td>11</td>
<td><a href="CoNO%E2%82%83">L</a>₃H₂O</td>
<td>2235</td>
<td>Dark Red</td>
<td>69</td>
<td>&gt;365</td>
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**Table 2. Characteristic IR bands of the azo ligand and their metal chelates as KBr pellets (cm⁻¹)**

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<tr>
<th>Ligand/Complex</th>
<th>(-C=O)</th>
<th>- OH₂</th>
<th>(-N=N=O)</th>
<th>C-H</th>
<th>M-O</th>
<th>M-N</th>
<th>M-OH₂</th>
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<td>HL</td>
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<td>3374</td>
<td>1594</td>
<td>3304</td>
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<td><a href="CuCl%E2%82%82">L</a>₃H₂O</td>
<td>1378</td>
<td>3316</td>
<td>1520</td>
<td>3170</td>
<td>465</td>
<td>549</td>
<td>745</td>
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<tr>
<td><a href="CuNO%E2%82%83">L</a>₃H₂O</td>
<td>1389</td>
<td>3299</td>
<td>1549</td>
<td>3108</td>
<td>471</td>
<td>523</td>
<td>762</td>
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<td>3278</td>
<td>1503</td>
<td>3179</td>
<td>480</td>
<td>534</td>
<td>756</td>
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<td><a href="CuSO%E2%82%84">L</a>₃H₂O</td>
<td>1399</td>
<td>3295</td>
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<td>3149</td>
<td>458</td>
<td>545</td>
<td>766</td>
</tr>
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<td>1365</td>
<td>3297</td>
<td>1532</td>
<td>3129</td>
<td>452</td>
<td>547</td>
<td>754</td>
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<td>1523</td>
<td>3113</td>
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<td>539</td>
<td>764</td>
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Table 3. Optical responses of azo resorcinarene [B] with different metal ions in DMSO

<table>
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<th>Metal ions</th>
<th>Reagent [B] ((\lambda_{\text{max}}))</th>
<th>Complex ((\lambda_{\text{max}}))</th>
<th>(\Delta \lambda)</th>
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<td>394</td>
<td>513</td>
<td>119</td>
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<td>123</td>
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<tr>
<td>Ni(^{+2})</td>
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<td>523</td>
<td>128</td>
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<tr>
<td>Co(^{+2})</td>
<td>394</td>
<td>527</td>
<td>133</td>
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Table 4. Antimicrobial activity (Zone of inhibition in mm) of Compounds 1-4.

<table>
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<th>Name of compound</th>
<th>Zone of inhibition (mm)</th>
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<tr>
<td></td>
<td>E.coli</td>
<td>B.subtilis</td>
<td>S.aureus</td>
<td>B.megaterium</td>
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<tr>
<td></td>
<td>50 ppm</td>
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<tr>
<td>A*</td>
<td>9</td>
<td>8</td>
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A* = Chloramphinicol (Antibiotic control)


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 (λ = 527nm)

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. 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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