

## **Transition metal complexes of 5-(iso-propoxymethyl-8-quinolinol), synthesis, characterization and comparative antimicrobial screening with PMQ metal complexes**

**Ketan B. Patel<sup>1,2\*</sup>, Raksha B. Patel<sup>1</sup>, Kartik B. Vyas<sup>3</sup> and Kiran S. Nimavat<sup>1</sup>**

<sup>1</sup>*Government Science College, Department of Chemistry, Gandhinagar, Gujarat, India*

<sup>2</sup>*JJT University, Rajasthan*

<sup>3</sup>*Sheth L. H. Science College, Department of Chemistry, Mansa, Gandhinagar, Gujarat, India*

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### **ABSTRACT**

*Mixed ligand complexes of transition metal with 8-quinolinols and 5-Propoxymethyl-8-quinolinol have been prepared. Structural, spectroscopic and thermal properties have been studied on the basis of infrared spectra, Mass spectra, NMR spectra, electronic spectra, and elemental analyses. The ligands, metal complexes, control and standard drug were tested for their antimicrobial activity. The metal complexes exhibit good activity against Bacterial strains two Gram +ve and two Gram -ve and two fungal strains compared with parental compounds and moderate in compared to the standard drugs.*

**Keywords:** Transition metal chelates, Oxine, Spectral studies, Magnetic moment and Antimicrobial activity.

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### **INTRODUCTION**

Some 8-hydroxyquinoline derivative has antibacterial and antifungal activity and it is widely used in creams and ointments for the treatment of skin diseases [1]. Clioquinol is an antifungal drug and antiprotozoal drug. It is neurotoxic in large doses. It is a member of a family of drugs called hydroxyquinolines which inhibit certain enzymes related to DNA replication. The drugs have been found to possess activity against both viral and protozoal infections [2]. 8-Quinolinol (8Q) or its derivatives have been introduced as chelating groups. [3-5]. The chelating properties of the compounds of the 8Q series are related to its biological activity [6]. Clioquinol is an antifungal drug and antiprotozoal drug. It is neurotoxic in large doses. It is a member of a family of drugs called hydroxyquinolines which inhibit certain enzymes related to DNA replication. The drugs have been found to have activity against both viral and protozoal infections [7]. 8-hydroxyquinoline (8Q) and its metalloquinolates have attracted great interest because their high thermal stability and good electroluminescence properties make them important prototypical electron transport and emitting materials for OLED devices [8-10]. 8-Hydroxyquinoline (8-quinolinol, oxine, 8Q) might be thought to function as a phenol, but of the 7 isomeric hydroxyquinolines only oxine exhibits significant antimicrobial activity, and is the only one to have the capacity to chelate metals. If the hydroxyl group is blocked so that the compound is unable to chelate, as in the methyl ether, the antimicrobial activity is destroyed. The relationship between chelation and activity of oxine has been investigated [11-13]. Copper 8-quinolinolate (copper oxinate), the copper compound of 8-hydroxyquinoline, is employed as an industrial preservative for a variety of purposes, including the protection of wood and textiles against fungus-caused rotting, and interior paints for food plants. It has 25 times greater antifungal activity than oxine [14]. Mixed-ligand chelates serve as suitable models for valuable information in the elucidation of enzymatic processes of biological relevance [15].

As part of our ongoing work[16-18] on mixed ligand complexes, in this paper we are reporting the newly synthesized complexes of Cu (II) , Ni (II), Co (III), Mn (II), and Zn(II) ions with 5-( iso-Propoxymethyl-8-Quinolinol) as primary and heterocyclic bases, viz., Quinoline (Q), 8-hydroxyquinoline (8-HQ) as secondary ligand. Their antimicrobial activities tested to perform primary selection of these complexes as the therapeutic agents, as well as comparing its microbial activity with PMQ metal chelates [19].

## MATERIALS AND METHODS

### *Reagent and solvents*

All the chemicals and reagents used for the preparation of ligands and complexes were commercial products (E. Merck Ltd, India) and used without further purification. Clioquinol was purchased from Atul Ltd., Agro Chemical Division, Atul, Valsad (India). Luria broth and agar- agar were purchased from SRL, India. Acetic acid and EDTA were purchased from Sigma Chemical Co., India. The organic solvents were purified by recommended method [20].

### *Physical measurements*

The metal content of the complexes were determined by the EDTA titration technique [21] after treating them with mixture of HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (1:1.5:2.5). Elemental analysis was carried out using Perkin Elmer, USA 2400-II CHN analyzer. The magnetic moments were obtained by the Gouy's method using mercury tetrathiocyanatocobaltate (II) as a calibrant ( $\chi_g=16.44\times10^{-6}$  c.g.s. units at 20 °C). Diamagnetic corrections were made using Pascal's constant [22]. The IR spectra were recorded on a FT-IR Nicolet 400D Spectrophotometer using KBr pellets. NMR spectra were recorded on a model Bruker Avance (400MHz). A simultaneous TG/DTG had been obtained by a model 5000/2960 SDT, TA Instruments, USA at heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere.

### *Preparation of ligands*

#### **Synthesis of 5-(iso-Propoxymethyl-8-Quinolinol) (i-PMQ).**

To a suspension of 2.3gm.(0.01mole) of 5-chloromethyl-8-quinolinol (CMQ), isopropanol (3 times.) and 0.84gm. (0.01mole) of sodium bicarbonate (NaHCO<sub>3</sub>) added. The mixture was warmed on the steam bath with occasional shaking until most of the alcohol had been evaporated. The pale yellow solid was dissolved in water and made basic with 5 % ammonium hydroxide. The white solid was collected on a filter and dried to give 1.95 gm. (80% yield), having m.p-65° C. (Uncorrected).FT-IR (KBr, cm<sup>-1</sup>):  $\nu$ (-OH<sub>s</sub>) 3354,  $\nu$ (-CN) 1218, <sup>1</sup>H NMR (DMSO-d<sub>6</sub> 400 MHz):  $\delta$  4.75 (CH<sub>2</sub>- protons),  $\delta$  1.15 (CH<sub>3</sub>- protons),  $\delta$  7.1 to 7.64 (9H, m, aromatic protons),  $\delta$  8.5 (1H, s, OH- protons), Elemental analysis found (%):C, 71.68; H, 6.70; C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub> (217) requires (%): C, 71.88, H, 6.91.

### *Preparation of Metal Complexes*

#### **(I) Formation of Cu<sup>2+</sup> Complexes**

A water solution of Cu (NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O was added to dimethyl formamide solution of ligand (i-PMQ) followed by addition of 8-HQ in ethanol; the pH was adjusted to 4.5-6.0 with dilute NaOH solution. The resulting solution was refluxed for 7 h and then heated over a steam bath to evaporate up to half of the volume. The reaction mixture was kept overnight at room temperature. A dark green colored crystalline product was obtained. The yield of a purified complex was 58%. The obtained product was washed with ether and dried over vacuum desiccators. The reaction scheme is shown in **Fig: 1** and Analytical and physical data are shown in **Table 1**.

#### **(II) Formation of Ni<sup>2+</sup> Complexes**

Ni<sup>2+</sup> complexes were synthesized by same method used for Cu<sup>2+</sup> complexes. A light blue colored crystalline product was obtained. The yield of a purified complex was 67%.

#### **(III) Formation of Co<sup>2+</sup> Complexes**

Co<sup>2+</sup> complexes were synthesized by same method used for Cu<sup>2+</sup> complexes. A light brown colored crystalline product was obtained. The yield of a purified complex was 65%.

#### **(IV) Formation of Mn<sup>2+</sup> Complexes**

Mn<sup>2+</sup> complexes were synthesized by same method used for Cu<sup>2+</sup> complexes. A light pink colored crystalline product was obtained. The yield of complex was 66%.

#### **(V) Formation of Zn<sup>2+</sup> Complexes**

Zn<sup>2+</sup> complexes were synthesized by same method used for Cu<sup>2+</sup> complexes. A pale yellow colored powder product was obtained. The obtained product was washed with ether and dried over vacuum desiccators. The yield was 62%.

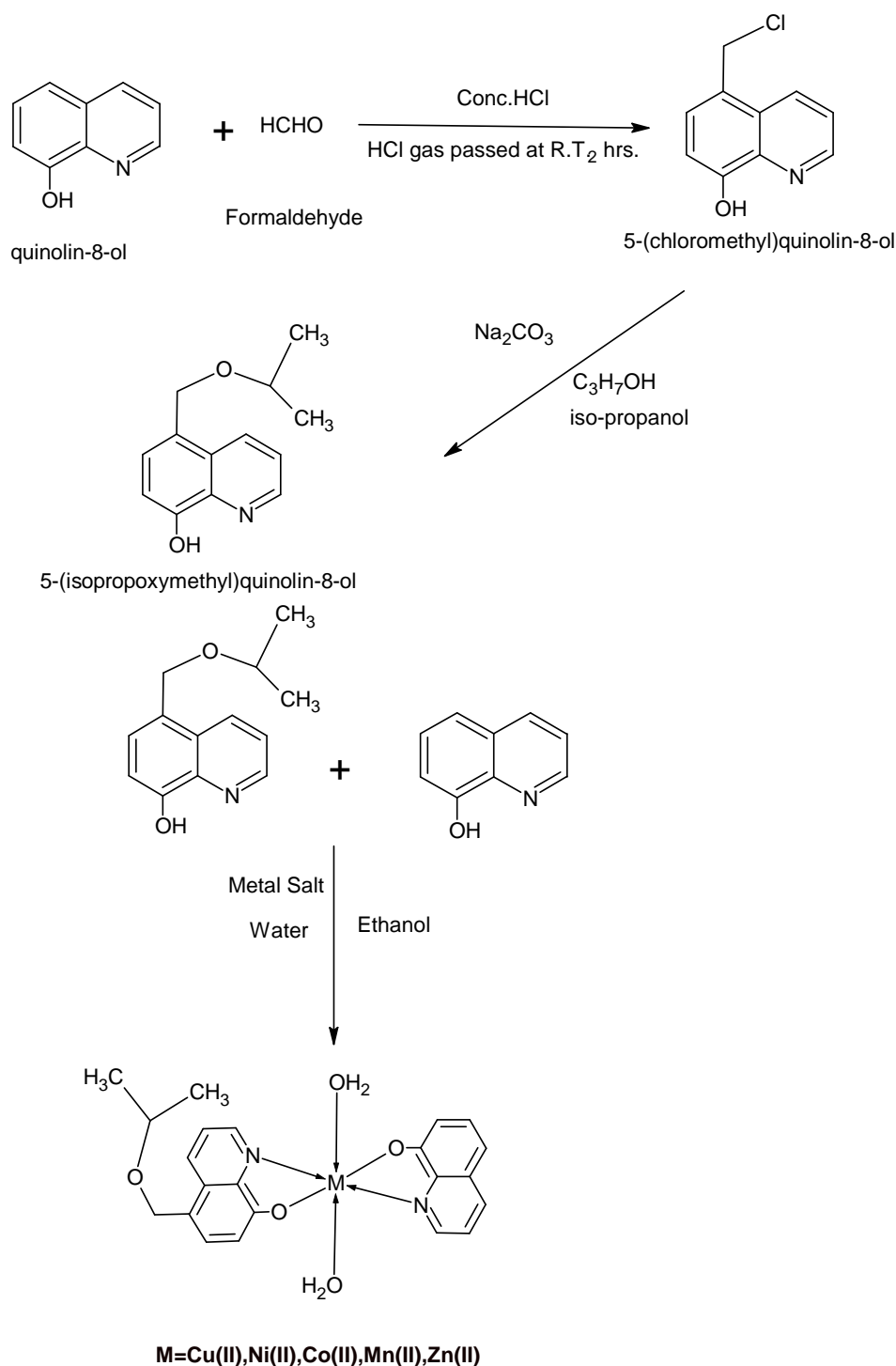


Fig.1 General synthesis of complexes.

*Antimicrobial studies***Antifungal activity**

The antifungal activity of the standard fungicide (Clioquinol), ligand and complexes were tested for their effect on the growth of microbial cultures and studied for their interaction with *Aspergillus Niger* and *Trichothesium Sp.* using Czapek's agar medium having the composition, glucose 20gm., starch 20gm., agar-agar 20gm. and distilled water 1000 ml. To this medium was added requisite amount of the compounds after being dissolved in methanol so as to get the certain concentrations (50, 100 and 200 ppm). The medium then was poured into petri plates and the spores of fungi were placed on the medium with the help of inoculum's needle. These petri plates were wrapped in polythene bags containing a few drops of alcohol and were placed in an incubator at 30 °C. The controls were also run and three replicates were used in each case. The linear growth of the fungus was recorded by measuring the

diameter of the fungal colony after 96 h and the percentage inhibition was calculated by the equation: % Inhibition  $D(C - T/C) 100$ .

Where C and T are the diameters of the fungal colony in the control and the test plates, respectively [23].

#### Antibacterial activity

Antibacterial activity was tested against Gram -ve (*Escherichia coli* and *Ps. Aeruginosa*, *Bacillus subtilis*) and Gram +ve (*Becillus megaterium* and *Staphylococcus aureus*) using the paper disc plate method [24, 25]. Each of the compounds was dissolved in methanol and solutions of the concentrations (500 and 1000 ppm) were prepared separately. Paper discs of Whatman filter paper (No. 42) of uniform diameter (2 cm) were cut and sterilized in an autoclave. The paper discs soaked in the desired concentration of the complex solutions were placed aseptically in the Petri dishes containing nutrient agar media (agar 20gm, C beef extract 3 gm, C peptone 5gm.) seeded with *E. coli* and *B. subtilis* bacteria separately. The Petri dishes were incubated at 37°C and the inhibition zones were recorded after 24 h of incubation. The antibacterial activity of common standard antibiotic Streptomycin was also recorded using the same procedure as above at the same concentrations and solvent. The %Activity Index for the complex was calculated by the formula as under:

$$\% \text{ Activity Index} = D \text{ Zone of inhibition by test compound} \times 100 / \text{Zone of inhibition by standard}$$

### RESULTS AND DISCUSSION

The toxic effect of all the complexes on fungi is shown in **Table 3**. The results give the following conclusions. All the complexes are toxic more or less to fungi. The substitution of phenyl rings does not have more effect on the fungicidal activity of complexes. In each series the Cu-complexes have much toxicity. This is expected because the copper salts are mostly used as fungicides. Most of the complexes inhibit the growth of the above organisms which cause deace in many plants.  $\text{Cu}^{+2}$  metal complexes are more toxic than others. For comparative analysis of microbial activity of i-PMQ metal chelates and PMQ metal chelates, results of PMQ metal chelates are also tabulated in **Table 3**, while comparing results it was found that most of the metal chelates of i-PMQ shows little higher toxic than the PMQ metal chelates with few exception.

#### IR spectra

The important infrared spectral bands and their assignments for the synthesized ligands and complexes were recorded as KBr discs and are presented in **Table 2**. The IR data of the free ligands and its metal complexes were carried out within the IR range 4000–400  $\text{cm}^{-1}$ .

In the 8-hydroxyquinoline complexes of divalent metals, the  $\nu(\text{C-O})$ , appeared at 1120  $\text{cm}^{-1}$  region and the position of the band slightly varies with the metal. The  $\nu(\text{C-O})$ , observed in the free oxine molecule at 1090  $\text{cm}^{-1}$ , shifted to higher frequencies in all the mixed ligand complexes giving a strong absorption band at 1110  $\text{cm}^{-1}$ . This clearly indicates the coordination of 8-hydroxyquinoline in these complexes. In the investigated heterochelates, the band observed in the region 3400-3500, 1295-1300, 860-870 and 715-717  $\text{cm}^{-1}$  are attributed to -OH stretching, bending, rocking and wagging vibrations, respectively due to the presence of water molecules.[26] The evidence of complexes formation clear by appearance of new bands at 418–432 and 507–516  $\text{cm}^{-1}$ , which are assigned to  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$ , respectively [27,28].

#### Reflectance spectra and magnetic measurements

In order to shed some light on the geometrical structure of the complexes, the reflectance spectra of the complexes were recorded in the solid phase at room temperature. The reflectance spectra of the Mn(II) complex shows absorption bands at ~16121, ~18595 and ~23410  $\text{cm}^{-1}$  assignable to  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$ ,  ${}^4\text{E}_g$  transitions, respectively, in an octahedral environment around the Mn(II) ion. The magnetic moment value of the Mn (II) complex is 5.91 B.M. due to a high-spin  $d^5$ -system with an octahedral geometry [29]. For the Co (II) complex, the reflectance spectra exhibits the bands of medium intensity at ~8540, ~19040 and ~22980  $\text{cm}^{-1}$ , which may reasonably be assigned to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transitions, respectively, of an octahedral geometry around the metal ion [30] and the magnetic moment value is observed to be of 3.87 B.M. The electronic spectra of the Ni(II) complex exhibits absorption bands at ~13121 and ~22498  $\text{cm}^{-1}$  assignable to,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  transitions respectively, in an octahedral geometry. The value of the magnetic moment (2.82 B.M.) may be taken as additional evidence for their octahedral structure [31–34]. The Cu(II) complex display a broad band at ~15763  $\text{cm}^{-1}$  due to the  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition and the magnetic moment value is 1.73 B.M., which is equal to spin-only value (1.73 B.M.) expected for an unpaired electron, which offers the possibility of an octahedral geometry [35].

Table 1 Analytical and physical parameters of ligand and complexes.

| Compounds                   | Molecular formula  | M. wt gm/mole | Yield % | % Metal analysis |       | Elemental analysis |       |      |       |      |       |
|-----------------------------|--|---------------|---------|------------------|-------|--------------------|-------|------|-------|------|-------|
|                             |  |               |         | Cal.             | Found | % C                |       | % H  |       | % N  |       |
|                             |  |               |         |                  |       | Cal.               | Found | Cal. | Found | Cal. | Found |
| HL-4 or (i-PMQ)             | C <sub>13</sub> H <sub>15</sub> NO <sub>2</sub>                                | 217           | 80      | ---              | ---   | 71.88              | 71.68 | 6.91 | 6.70  | 6.45 | 6.32  |
| (i-PMQ)8HQ Cu <sup>+2</sup> | C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> Cu <sup>+2</sup> | 459.98        | 58      | 13.81            | 13.80 | 57.44              | 57.42 | 5.26 | 5.21  | 6.09 | 6.05  |
| (i-PMQ)8HQ Mn <sup>+2</sup> | C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> Mn <sup>+2</sup> | 455.13        | 67      | 12.90            | 12.86 | 58.06              | 58.02 | 5.32 | 5.29  | 6.16 | 6.12  |
| (i-PMQ)8HQ Co <sup>+2</sup> | C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> Co <sup>+2</sup> | 451.37        | 66      | 12.17            | 12.07 | 58.54              | 58.51 | 5.36 | 5.31  | 6.21 | 6.18  |
| (i-PMQ)8HQ Zn <sup>+2</sup> | C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> Zn <sup>+2</sup> | 455.37        | 65      | 12.94            | 12.95 | 58.03              | 58.01 | 5.31 | 5.19  | 6.15 | 6.10  |
| (i-PMQ)8HQ Ni <sup>+2</sup> | C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> Ni <sup>+2</sup> | 461.85        | 62      | 14.16            | 14.08 | 57.21              | 57.15 | 5.24 | 5.19  | 6.07 | 6.05  |

Table 2 FT-IR data of synthesized ligand &amp; its Cu (II) complex.

| Compounds    | Frequencies Cm <sup>-1</sup> |                      |                              |           |                      |
|--------------|------------------------------|----------------------|------------------------------|-----------|----------------------|
|              | -OH                          | Aromatic             | 8-HQ Moiety                  | C-N       | -CH <sub>2</sub>     |
| (i-PMQ)      | 3800-2600                    | 1599<br>1507<br>3028 | 1638<br>1575<br>1698 1470    | 1275-1298 | 2850<br>2920<br>1450 |
| (i-PMQ)8HQCu | 3500-2600                    | 1578<br>1478<br>3062 | 1610<br>1578<br>1509<br>1478 | 1299      | 2888<br>2969<br>1409 |

Table 3 Antimicrobial activity of synthesized compounds.

| Sample                       | Zone of inhibition (in mm) |                 |                            |                               |                       |                |
|------------------------------|----------------------------|-----------------|----------------------------|-------------------------------|-----------------------|----------------|
|                              | Antifungal activity        |                 | Gram + Ve                  |                               | Gram -Ve              |                |
|                              | <i>Trichothesium Sp.</i>   | <i>A. niger</i> | <i>Becillus megaterium</i> | <i>S.taphylococcus aureus</i> | <i>Ps. aeruginosa</i> | <i>E.-coli</i> |
| HL-3(PMQ)                    | 55                         | 53              | 11                         | 10                            | 09                    | 10             |
| HL-4(i-PMQ)                  | 62                         | 59              | 21                         | 17                            | 18                    | 21             |
| (PMQ) 8HQ Cu <sup>+2</sup>   | 78                         | 81              | 13                         | 18                            | 18                    | 19             |
| (i-PMQ) 8HQ Cu <sup>+2</sup> | 83                         | 91              | 22                         | 21                            | 20                    | 17             |
| (PMQ) 8HQ Mn <sup>+2</sup>   | 53                         | 57              | 19                         | 23                            | 22                    | 21             |
| (i-PMQ) 8HQ Mn <sup>+2</sup> | 59                         | 57              | 12                         | 09                            | 05                    | 09             |
| (PMQ) 8HQ Co <sup>+2</sup>   | 63                         | 70              | 08                         | 08                            | 12                    | 12             |
| (i-PMQ) 8HQ Co <sup>+2</sup> | 69                         | 66              | 16                         | 12                            | 09                    | 12             |
| (PMQ) 8HQ Zn <sup>+2</sup>   | 67                         | 71              | 17                         | 14                            | 18                    | 13             |
| (i-PMQ) 8HQ Zn <sup>+2</sup> | 70                         | 81              | 17                         | 20                            | 19                    | 14             |
| (PMQ) 8HQ Ni <sup>+2</sup>   | 63                         | 67              | 23                         | 11                            | 20                    | 17             |
| (i-PMQ) 8HQ Ni <sup>+2</sup> | 60                         | 60              | 14                         | 11                            | 06                    | 11             |

## CONCLUSION

The complexes were obtained as colored powdered materials and were characterized using IR spectra, electronic spectra, and magnetic measurements. The compounds were insoluble in ethanol, methanol, DMF, acetone, ether, hexane, chloroform, THF, and dichloromethane, and soluble in DMSO. The elemental analyses were in good agreement with the complexes. From the antimicrobial activity data, it is observed that the complexes exhibit higher activity than the free ligands, and the control (DMSO). The increase in antimicrobial activity of the complexes may be due to the metal chelation. From comparative analysis as shown in **Table 3**, it is observed that all the metal complexes are more potent biocidal than the ligand and most of the i-PMQ metal chelates are more active than PMQ metal chelates. The zone of inhibition was measured (in mm) around the disc and the results are represented in **Table 3**.

## Acknowledgements

The authors are grateful to Dr. P.A. Vadher, Principal, Govt. Science College, Gandhinagar, Gujarat, India, for providing the necessary laboratory facilities. Also thankful to Department of microbiology, Government Science College, Gandhinagar, Gujarat, India, for helping in microbial studies.

## ABBREVIATION

8HQ = 8- Hydroxy Quinoline

HL<sub>3</sub> = 5-(Propoxymethyl-8-Quinolinol) (PMQ).

HL<sub>4</sub>= 5-(iso-Propoxymethyl-8-Quinolinol) (i-PMQ).

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