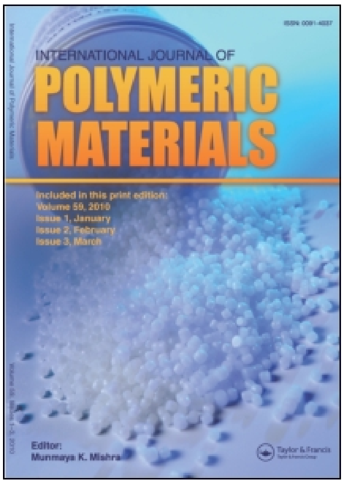

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# Co-ordination Polymers of 5,5′-[1,4-*N*,*N*′-Dimethylene Piperazinylene]-8-Quinolinol (DMPQ)

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Attempts were made to synthesize co-ordination polymers of a new bis oxine bidentate ligand namely 5,5′-[1,4-*N*,*N*′-dimethylene piperazinylene]-8-quinolinol (DMPQ) with different metal ions. The bis bidentate ligand DMPQ polymer was synthesized by 5-chloromethyl-8-quinolinol hydrochloride and piperazine in presence of sodium hydrogen carbonate. The co-ordination polymers of DMPQ with different metal ions like $Cu^{+2}$, $Zn^{+2}$, $Co^{+2}$, $Mg^{+2}$, $Mn^{+2}$ and $Cd^{+2}$ were prepared and characterized by their elemental analysis, IR spectral and magnetic moment studies. The metal content in all the polymers was found to be consistent with (1:1) metal : ligand stoichiometry. The thermal behaviour of each of these co-ordination polymers was examined by TGA in air upto 600°C temperature.

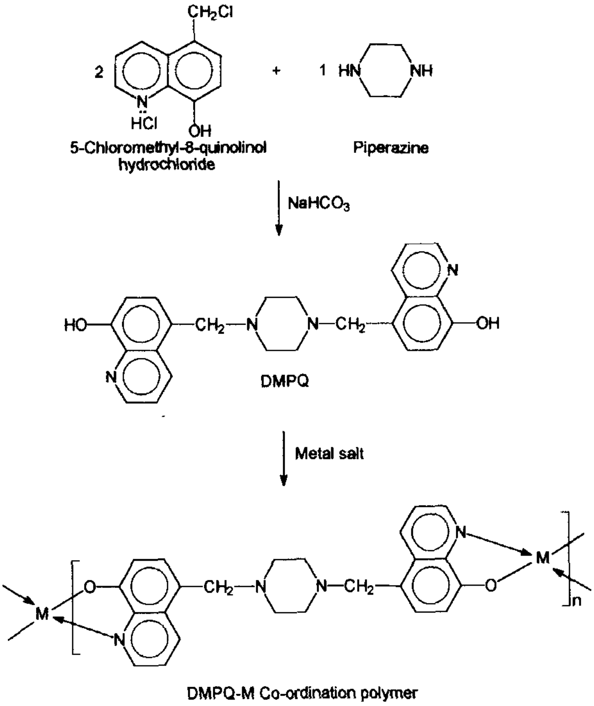
*Keywords:* 5,5′-[1,4-*N*,*N*-dimethylene piperazinylene]-8-quinolinol; metal ions; co-ordination polymers

## INTRODUCTION

Oxine (*i.e.*, 8-quinolinol, 8-HQ) is considered as a good metal precipitant and analytical reagent. Oxine based polymers containing methylene bridge are also well known for their excellent chelating and ion exchange properties due to strong tendency of oxine to form chelates [1-5]. Further several attempts have been made to enhance the chelation property of oxine through formation of co-ordination polymers using bis oxine bidentate ligands [6-8] by simple polymerization reaction or by condensation reaction. The way in which the formation of bis oxine bidentate ligand such as 5,5′-[1,4-*N*,*N*′-dimethylene piperazinylene]-8-quinolinol (DMPQ) is not investigated so far. Hence it was considered interesting to synthesize a novel bis oxine ligand, DMPQ and to study its coordination with various divalent metal ions. Thus, the present paper comprises the synthesis and study of bis oxine bidentate ligand DMPQ and its co-ordination polymers. The whole research work is scanned in Scheme I.

## EXPERIMENTAL

Piperazine, oxine (*i.e.*, 8-quinolinol), ethanol were of LR grade and used without purification. 5-Chloromethyl-8-quinolinol hydrochloride was prepared by method reported in literature [9].



SCHEME I

## Synthesis of 5,5′-[1,4-*N*,*N*′-dimethylene piperazinylene]-8-quinolinol (DMPQ)

To a mixture of piperazine (0.15 mole) and $NaHCO_3$ (0.2 mole), solid 5-chloromethyl-8-quinolinol hydrochloride (0.2 mole) was added gradually with constant stirring. The mixture was kept for 3 hr at room temperature with constant stirring. It was then heated on water bath at 95°C for 4 hr. The resulting mass was filtered, washed with water and then with rectified spirit. The air dried sample did not melt upto 300°C. Yield was about 90%.

## Preparation of Co-ordination Polymers

### *Co-ordination Polymer of DMPQ with $Cu^{2+}$*

To a warm and clear solution of DMPQ (2.55 gm, 0.01 mole) in 20% aqueous formic acid was added with constant stirring. The resulting solution was adjusted to pH 5 with liquor ammonia and digested on a water bath for 1 hr. at 60–70°C. The separated solid was filtered, washed with water and alcohol. It was dried at 100°C for 24 hrs.

A similar procedure was followed to prepare other co-ordination polymers such as DMPQ-$Zn^{2+}$, DMPQ-$Cd^{2+}$, DMPQ-$Co^{2+}$, DMPQ-$Mg^{2+}$, DMPQ-$Mn^{2+}$.

## Apparatus and Methods of Characterization: Elemental Analysis

The carbon, hydrogen and nitrogen contents of DMPQ and its co-ordination polymers were carried out on C, H and N elemental analyzer.

The metal content of co-ordination polymer was found out by decomposition of weighed amount the polymer followed by EDTA titration following standard procedures [10].

IR spectra of parent DMPQ and each of the co-ordination polymers were scanned in KBr on Perkin-Elmer spectrophotometer.

Measurements of magnetic susceptibility and electrical conductivity of all the co-ordination polymers were carried out by Gouy method and Millan megohmmeter respectively. Mercury tetrathiocyanato cobaltate(II) $Hg[Co(CNS)_4]$ was used for calibration for the measurement of magnetic susceptibility.

Thermal behaviour of DMPQ and its co-ordination polymers was investigated by conducting thermogravimetric analysis (TGA). TGA was carried out in a slow stream of air at 10°C/min. heating rate. Du pont thermogravimetric analyzer (TC-10ATA-3000) was used for TGA.

## RESULTS AND DISCUSSION

Synthesis of DMPQ has not been reported earlier. However perusal of literature revealed that derivatives from 5-chloromethyl-8-quinolinol and amines are reported [11, 12]. On the basis of these reports the synthesis of ligand DMPQ was carried out with slight modification of reaction conditions. The bidentate DMPQ thus obtained is in the form of amorphous buff coloured powder. It is insoluble in common organic solvents except formic acid. It does not melt upto 300°C temperature.

Results of C, H and N analysis of DMPQ are consistent with the predicted structure shown in Scheme I. The IR spectrum of DMPQ is shown in Figure 1 (Curve 1). It shows characteristic vibrational frequencies due to 8-hydroxy quinoline moiety, methylene bridge and absence of N —H stretching frequency for the secondary amino group of piperazine. The important IR spectral features are a broad band in the region of $3300-3420\,cm^{-1}$ corresponds to O —H stretching vibration of 8-hydroxy quinoline of ligand DMPQ [6]. The weak band at $2960\,cm^{-1}$ may be due to aliphatic stretching vibrations of bridge methylene group (— $CH_2$ —) of 8-hydroxy quinoline and piperazine moieties. The bands around 1600, 1540, 1520 and $1460\,cm^{-1}$ are attributed to the 8-hydroxy quinoline nucleus [13]. Lastly the absence of N —H stretching frequency for secondary amine, piperazine in the region of $3200-3600\,cm^{-1}$ indicates the bond formation between N —H of piperazine and (— $CH_2$ —) methylene bridge group yielding bis ligand. All the above mentioned features of IR spectrum of DMPQ are consistent with the proposed structure of DMPQ.

The ability of bidentate DMPQ ligand to form co-ordination polymers was examined by preparing its co-ordination polymers with

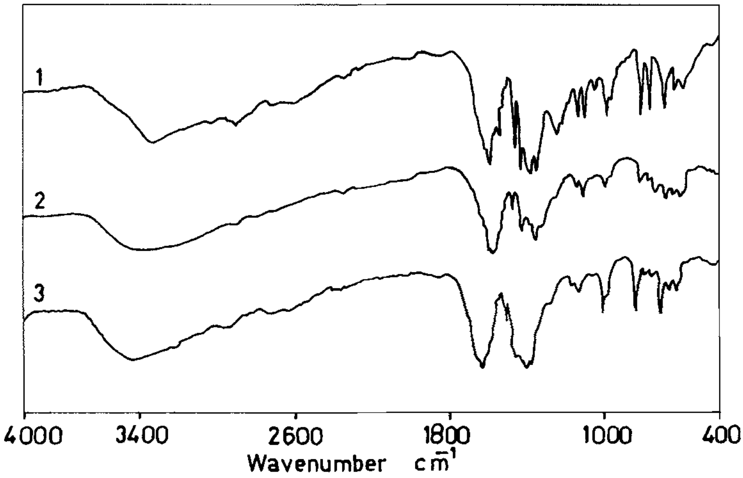


FIGURE 1 IR spectra of selected co-ordination polymers (Curves 2 and 3) and of parent DMPQ (Curve 1).

different divalent metal ions such as $Cu^{+2}$, $Zn^{+2}$, $Cd^{+2}$, $Mn^{+2}$, $Mg^{+2}$ and $Co^{+2}$. These co-ordination polymers are varying in colour from off white to dark brown as shown in Table I and not softened upto 300°C temperature upon heating. They are insoluble in common organic solvents and therefore it is not possible to characterize them by molecular mass using conventional methods like viscometry, osmometry *etc.*. The metal content estimation of each of co-ordination polymer revealed 1:1 metal:ligand (M/L) stoichiometry. This is further supported by C, H, N contents in the polymers.

The IR spectra of selected co-ordination polymers are shown in Figure 1 (Curves 2 and 3). It is observed that they resemble each other in general shape while the comparison of IR spectra of parent DMPQ (Curve 1) with its co-ordination polymers indicated certain characteristic differences.

One of the significant differences to be expected between IR spectra of parent polymer and its co-ordination polymers is the absence of broad band in the region of 3300–3420 $cm^{-1}$ due to O —H stretching vibration frequency in case of co-ordination polymers. This is because the oxygen of O —H group of parent polymeric ligand is involved in the co-ordination with metal ion. However in actual practice it has

TABLE I Characterization of DMPQs and their electrical properties and magnetic succeptibility

| *DMPQ and its metal chelates* | *Colour* | *Elemental analysis* %*C* |  | %*H* |  | %*N* |  | *Metal* (%) |  | *B. M* $\mu_{eff}$ | *Electrical conduct. at* |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | *Calc.* | *Found* | *Calc.* | *Found* | *Calc.* | *Found* | *Calc.* | *Found* |  | 35°*C* *ohm*$^{-1}$ *cm*$^{-1}$ |
| DMPQ | Buff | 70.5 | 70.20 | 6.66 | 6.42 | 16.47 | 16.65 | – | – | – | $2.7 \times 10^{-11}$ |
| DMPQ–Cu (II) | Green | 63.0 | 63.20 | 5.60 | 5.20 | 14.70 | 14.80 | 11.11 | 10.9 | 1.78 | $6.0 \times 10^{-11}$ |
| DMPQ–Cd (II) | Brown | 57.83 | 57.60 | 5.46 | 5.30 | 13.49 | 13.28 | 18.06 | 27.92 | Diamagnetic | $2.3 \times 10^{-11}$ |
| DMPQ–Mn (II) | Maganta | 63.72 | 63.58 | 6.01 | 5.90 | 14.86 | 14.68 | 9.72 | 9.50 | 5.27 | $8.1 \times 10^{-11}$ |
| DMPQ–Mg (II) | Off white | 67.37 | 67.25 | 6.36 | 6.20 | 15.72 | 15.50 | 4.55 | 4.40 | Diamagnetic | $6.2 \times 10^{-11}$ |
| DMPQ–Co (II) | Light green | 63.27 | 63.05 | 5.97 | 5.58 | 14.76 | 14.60 | 10.35 | 10.20 | 4.20 | $6.8 \times 10^{-11}$ |
| DMPQ–Zn (II) | Brown | 62.56 | 62.40 | 5.90 | 5.73 | 14.59 | 14.45 | 11.36 | 11.20 | Diamagnetic | $7.2 \times 10^{-11}$ |

broadened more in the IR spectra of co-ordination polymers compared to that in parent polymer DMPQ. This is explicable by the fact that water molecules might have been strongly absorbed or co-ordinated to the polymer sample during the formation of co-ordination polymers. Another noticeable change is that the band in IR spectrum of DMPQ due to C=N stretching at 1600 cm$^{-1}$ can be shifted towards lower frequency. In addition to these the weak band around 1100 cm$^{-1}$ is attributed to the C—O—M stretching frequency [14]. The band at 1430 cm$^{-1}$ in the IR spectra of DMPQ is assigned to the in plane OH deformation [14] and it is shifted towards higher frequency in the spectra of the co-ordination polymers indicating the formation of metal-oxygen bond. On the basis of above mentioned features the structure of co-ordination polymer is shown in scheme.

The thermal behaviour of parent DMPQ polymer and its metal chelates is investigated by performing thermogravimetric analysis (TGA). The TGA data of all the samples are presented in Table II and Figure 2. The weight loss of polymer sample at different temperatures indicated that the degradation of parent ligand is noticeable above 200°C and that of its co-ordination polymers is noticeable above 400°C. The rate of degradation becomes maximum at a temperature lying between 400–500°C and 500–600°C respectively for the parent ligand and its chelates. Each of the polymer samples lost about 85% weight when heated upto 600°C. In addition to this the data of weight loss at different temperatures of all metal chelates of DMPQ revealed that all have similar mode of decomposition indicating the thermal degradation of metal chelate is independent of nature of metal ion present in polymeric ligand. Inspection of the thermograms of co-ordination polymer revealed that each of these samples decomposes very slowly initially upto 350°C compared to parent ligand DMPQ indicating that co-ordination polymers of DMPQ are more stable than parent the polymeric ligand. The thermograms of co-ordination polymers and the parent DMPQ are shown in Figure 2.

The co-ordination polymers of DMPQ are further characterized by their electrical and magnetic properties. The examination of data furnished in Table I reveals that the electrical conductivity of co-ordination polymer into range of $1.35 \times 10^{-9}$ to $5.90 \times 10^{-11}$. The data of magnetic moment show that the coordination polymers of

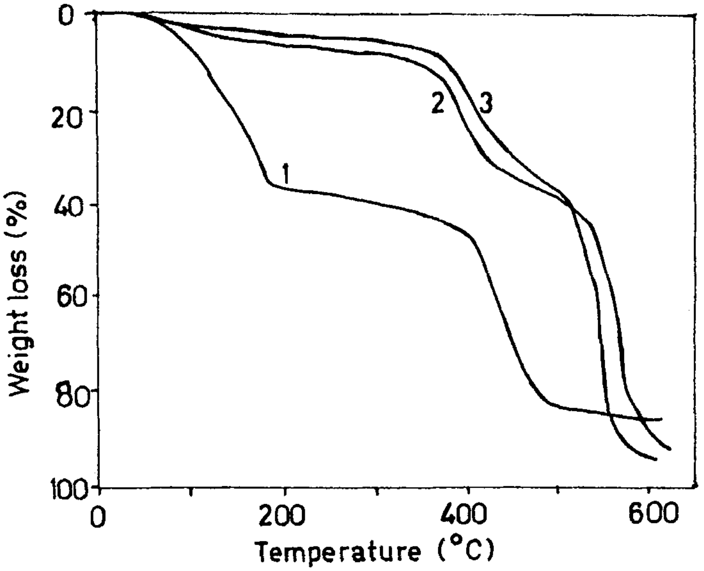


FIGURE 2 Thermograms of co-ordination polymers (Curves 2 and 3) and of parent DMPQ (Curves 1).

TABLE II Thermogravimetric analysis of DMPQ and its metal chelates

| *DMPQ and its metal chelates* | *Weight loss (%) at various temperatures (°C)* | | | | | | |
|---|---|---|---|---|---|---|---|
| | 200 | 300 | 350 | 400 | 450 | 500 | 600 |
| DMPQ | 04 | 41 | 46 | 50 | 70 | 84 | 94 |
| DMPQ-Mn(II) | 04 | 10 | 22 | 35 | 40 | 49 | 86 |
| DMPQ-Mg(II) | 15 | 18 | 19 | 20 | 46 | 50 | 86 |
| DMPQ-Cd(II) | 09 | 12 | 16 | 32 | 45 | 60 | 85 |
| DMPQ-Cu(II) | 10 | 16 | 20 | 34 | 47 | 50 | 84 |
| DMPQ-Zn(II) | 08 | 12 | 20 | 38 | 52 | 56 | 81 |
| DMPQ-Co(II) | 07 | 10 | 20 | 40 | 50 | 60 | 80 |

Cu (II), Mn (II) and Co (II) are paramagnetic while those of Zn (II), Cd (II) and Mg (II) are diamagnetic.

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