S. P. Patel et al, Materials Sci. Res. India 02(1) 23-28 (2004)

# COORDINATION POLYMERS OF N,N' DI-(8 HYDROXYQUINOLINOLYL-5) METHYL) N,N' DIETHYL-1, 2-ETHANE DIAMINE (QEED)

S. P. PATEL, C. P. BHASIN[1], A. D. PATEL[1] and D. S. RAJ[2]

[1]Department of Chemistry, Hemchandracharya North Gujarat University, Patan-384265 (India)
[2]Principle, J and J Science College, Nadiad-387001 (India)

(Received, February 26, 2004)

**ABSTRACT**

Coordination polymers containing a novel bis (oxine) bidentate ligand, namely N,N' -di(8-hydroxyquinolinoly 1-5 methyl) -N,N' -diethyl-1,2-ethanediamine (QEED) have been prepared with the metal ions Zn(ll), Cu(ll), Ni (II), Co (II), and Mn(il). The novel bis-(bidenate) ligand was synthesized by condensation of 5-chloromethyl-8-hydroxyquinoline hydrochloride with N,N' -diethyl-1,2 ethanediamine in the presence of a base catalyses. All of these coordination polymers and the parent ligand were characterized by elemental analyses and IR spectral and diffuse reflectance spectral studies. The thermal stability and number-average molecular weights (Mn) of all of the coordination polymers were determined by Thermogravimetric analyses and non-aqueous conductometric titrations, respectively. In addition, all of the coordination polymers have been characterized by their magnetic suspectibilities.

**Keywords:** Coordination polymers, bis (oxine) bidenate ligand, N,N' -di(8-hydroxyquinolinolyl-5-methyl)-N,N' diethyl 1, 2-ethanediamine (QEED), infrared spectra, diffuse reflectance spectra, thermogravimetry, magnetic susceptibility, conductometric titration.

## INTRODUCTION

## MATERIALS

## EXPERIMENTAL

The coordination chemistry of bis (oxine), bidenate ligand, has been extensively investigated for their metal gripping properties13. In this context bis(oxine) legends with two oxine units joined by a bridge of 5,5' methylene (-CH,-), 5,5' - Sulfonyl (SO.,-), 5,5' - dimethylene sulfide (-CH2-S-CH2-) All chemicals were of analytical grade. The synthesis of N,N' -di(8-hydroxyquinolinoly-5-methyl)-N,N'-diethyl-1,2 -ethanediamine **(QEED)** was carried out in two steps. The preparation of 5-chloromethy-8-hyroxyquinoline hydrochloride 12 and -CH-0-CH2- are reported in literature410.

Recently we have reported the synthesis and characterization of coordination polymers based on the bis-oxine ligand joined with a bridge, -H2C-0-Ph-0-CH2 (Ph=1, 3 phenylene has been replaced11. This work has been further thought with the view of investigation the chelating ability of a bis-8-quinolinol bis (bidenate) legend by introducing the bridge of ethane diamine between two 8-hydroxyquinoline moieties. Accordingly, the present work deals with the synthesis and characterization of a bis (oxine) legend, namely N,N' -di (8-hydroxyquinolyl-5 methy)-N,N' -diethyl-1,2-ethanediamine (QEED) and its coordination polymers with Zn (II), Cu(ll) Ni(ll), Co(ll) and Mn(ll) metal ions.

**according to a literature method**

Preparation of Polymers of N,N'-di(8-hydroxyquinoloyl-5-methyl) N,N'-diethyl-1,2-ethanediamine (QEED) QEED was prepared as follows- For, example to a suspension of 5-chloromethyl-8-hydroxyquinoline hydrochloride (23g, 0.02 mol), N,N'-diethyl-1,2-ethane diamine

(17.5g, t).1 mol) in an acetone-water mixture was added. K2C03 (5.3gm, 0.03 mole) was added as an acid acceptor. The resulting mixture was refluxed for 3 h with occasional shaking the resulting suspension, which contained for a green precipitate, was poured into ice cold (500ml) water and then filtered. The solid product was collected and dried to give **QEED** (80% yield). Analysis for C26H30N4O2; Calculated (%):

C72.55; H.6.97; N, 13.02.

**Preparation of coordination polymers**

For example, Cu(ll); a solution of copper acetate (1.9g, 0.001) in aqueous formic acid (50 ml, 50%) was added drop wise to a solution of QEED (3.30G, 0.01 mol) in aqueous formic acid (240 ml, 20%) with stirring. The reaction mixture was heated on a water bath for 0.5h. The reaction mixture was made alkaline by the addition of diltute aqueous ammonia until the precipitation was completed. The polymer separated of in the form of a suspension and was digested on boiling water bath. Finally, the resultant solid brownish yellow precipitates was collected by filtration and washed with hot water, dimethylformamide (DMF) and then acetone. The polymer (QEED-Cu[ll], was air dried. A similar procedure was used to prepare the QEED-Co(ll), QEED-Ni(ll), QEED-Mn(ll) and QEED-Zn(ll).The yields of all coordination polymers were almost quantitative.

**Measurements**

The metal analysis of co-ordination polymers comprised decomposition of a weighed amount of the polymer followed by EDTA titration using a standard procedure [13]. The percentage composition. (C, H and N) for the coordination polymers was determined by a C, H, N Elemental analyzer (Table 1).The IR spectra of the bis-ligand QEED and of each of the coordination polymers samples were scanned as KBr pellets using a FTIR spectrophotometer. The solid diffusion, reflectance spectra of all the coordination polymers were recorded on Shimadzu spectrophotometer with a solid reflectance attachment MgO was employed as the reference compound.

The number average molecular weights (Mn) of all the coordination polymers were estimated by end-group analysis. End-Group analysis of the hydroxyl group was carried out by non-aqueous conductometric titration using pyridine as solvent and sodium methoxide as titrant base1415.

Magnetic susceptibility measurements of al the coordination polymers were carried out at room temperature by the Gouy method. Mercury [tetrathiocynatocobalt] Hg [Co(NCS)„] was used for the instrument calibration8. Molar susceptibilities were corrected for diamagnetism of the component almost using Pascal's constant18.

Thermogavimetry of all these coordination polymers was carried out using a Dupont thermogravimetric analyzer (TGA). The data are reported in Table III.

## RESULT AND DISCUSSION

The synthesis of the bis (bidentate) legend N,N' -di(8-hydroxyquinolinolyl-5-methyl)-N, N'-diethyl-1, 2-ethanediamine (QEED), has not been previously reported. The synthesis QEED was performed by chloromethylation of the oxine followed

Table-1: Analytical data for the coordination polymers of QEED.

| Co-ordination polymers | Colour | N% Elemental | | M% Mn | | |
|---|---|---|---|---|---|---|
| | | Cal | Found | Cal | Found | |
| QEED-Cu (II) | Green | 10.61 | 10.5 | 12.04 | 11.9 | 5255 |
| QEED-Ni (II) | Green | 10.71 | 10.6 | 11.23 | 11.1 | 5227 |
| QEED-Co (II) | Yellow brown | 10.7 | 10.6 | 11.22 | 11.15 | 5227 |
| QEED-Mn (II)' | Light green | 10.79 | 10.6 | 10.58 | 10.45 | 5189 |
| QEED-Zn (II) | Yellow green | 10.63 | 10.5 | 12.41 | 12.3 | 5263 |

by condensation with N, N'-diethyl-1,2-ethane diamine. (Scheme 1).

The IR spectrum of H2L is shown fig. 1. The important IR spectral features (not shown in figure) are (i) a broad band from 3550 cnr1 to 3200 cm1 that is attributed to the hydrogen-bonded OH group17, (ii) The weak bands near 2950 cnr1 and 2800 cm-1 that are due to asymmetric and symmetric stretching vibrations of methylene groups (CH2) of the -CH2-0-CH3-bridge. (Ill) The weak band at 1110m-1 that confirm the presence of a dialkyl ether function. And (iv) the bands near 1610, 1508, 1470 and 1420 cm1 that are the characteristic frequencies of the

hydroxyquinoline nucleus12. The weak band around 1085 and 1118cm 1 may also be attributed to the ether group bridge. It was also observed that HjL has numerous IR spectral features in common with those of 5,5-methylene bis (8-hydroxyquinoline)1. These features support the proposed structure of H2L. The coordination polymers derived from H2L are insoluble in common organic solvents. All these coordination polymers decomposed at approximately 250°C. The molecular mass was estimated by evaluating the number of terminal OH groups using non- aqueous conductometric titration. Perusal of the literature revealed that there are few reports regarding the determination of the number average molecular weight (Mn) of coordination polymers [18-21]. However, efforts are made by the present authors to estimate Mn of the H2L coordination polymers by utilizing the non-aqueous conductometric titration method under controlled experimental conditions22. For the sake of convenience the required amount of coordination polymer was suspended in pyridine for 24h. It was observed that the properties of polymers did not change in the presence of pyridine.

Assuming that the only end-groups in the polymers are OH, the titration was carried out by addition of controlled volume of NaOMe, since more volume of NaOMe may cause de-coordination of polymers. A discernible break was observed in the titration curve and the molecular weights were calculated as shown in Table 1. Examination of the

Table-2: Infrared frequencies (cm1) of QEED coordination polymers

| Coordination | (OH) | C=N) | (C-N-C) | (C-0) | (M-N) | (M-O) |
|---|---|---|---|---|---|---|
| QEED-Cu(ll) | 3540 | 1602 | 1105 | 1353 | 776 | 500 |
| QEED-Ni (II) | 3600 | 1602 | 1100 | 1367 | 769 | 500 |
| QEED-Co (II) | 3520 | 1595 | 1105 | 1353 | 776 | 580 |
| QEED-Mn(ll) | 3500 | 1602 | 1105 | 1353 | 762 | 500 |
| QEED-Zn(ll) | 3510 | 1595 | 1100 | 1353 | 762 | 500 |

g Transition

Table-3; Reflectance spectral and magnetic moment data of the QEED coordination

| Co-ordination polymers | Colour | N% | | M% | |
|---|---|---|---|---|---|
| | | Cal | Found | Cal | Found |
| QEED-Cu (II) | Green | 10.61 | 10.5 | 12.04 | 11.9 |
| QEED-Ni (II) | Green | 10.71 | 10.6 | 11.23 | 11.1 |
| QEED-Co (II) | Yellow brown | 10.7 | 10.6 | 11.22 | 11.15 |
| QEED-Mn (II)' | Light green | 10.79 | 10.6 | 10.58 | 10.45 |
| QEED-Zn (II) | Yellow green | 10.63 | 10.5 | 12.41 | 12.3 |

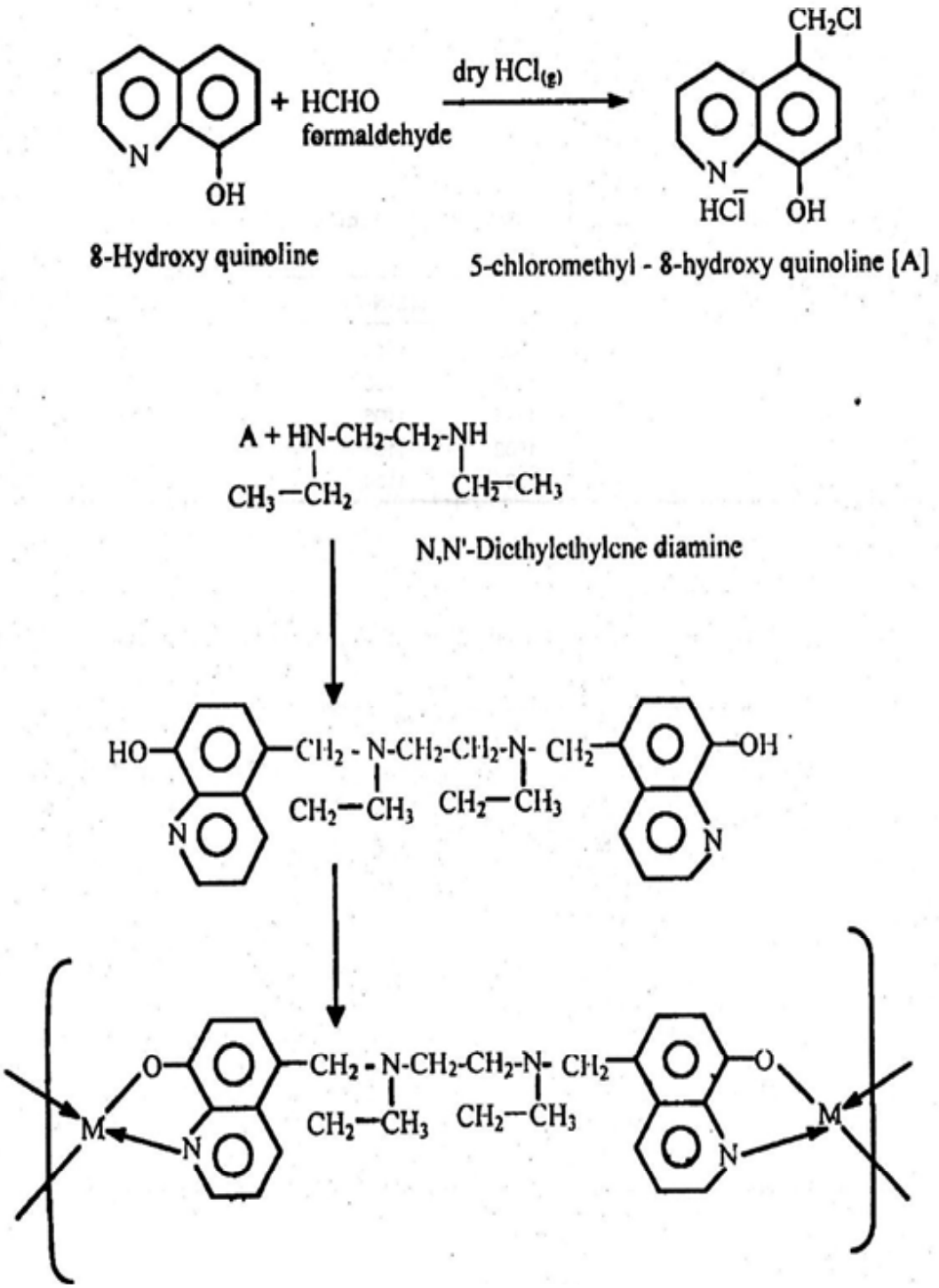
+ HCHO
formaldehyde
dry HCl(g)
CH2Cl
OH
HCl
8-Hydroxy quinoline
5-chloromethyl - 8-hydroxy quinoline [A]
A + HN-CH2-CH2-NH
CH3—CH2
CH2—CH3
N,N'-Diethylethylene diamine
HO
OH
CH2 - N-CH2-CH2-N- CH2
M

**Fig.1**

Table-4: Thermogravimetric analysis (TGA) of the co-ordination polymer of QEED.

| Co-ordination polymers | % Weight loss at temperature T (°C) | | | | | |
|---|---|---|---|---|---|---|
| | 100 | 200 | 250 | 300 | 400 | 500 |
| QEED-Cu(ll) | | | | | | |
| QEED-Ni(ll) | 8.55 | 14.01 | 55.5 | 82.0 | - | - |
| | 10.0 | 14.01 | 24.7 | 36.01 | 65.1 | - |
| QEED-Co(ll) | 8.0 | 13.2 | 45.0 | 56.01 | 88.1 | - |
| QEED-Mn(ll) | 8.0 | 12.1 | 23.0 | 35.0 | 67.0 | 81.0 |
| QEED-Zn(ll) | 8.0 | 12.0 | 21.0 | 32.0 | 66.1 | 82.0 |

metal content in the polymers (table 2) reveals a 1:1 metal: legend (M/L) stoichiometry for all the polymers.

The IR spectra of all the coordination polymers of H2L are not shown. Comparison of the IR spectrum of the legend H2L (see above) and those of the coordination polymers reveal certain characteristic difference. Thus, the broad band in the region from 3550 to 3200 cm-1 for H2L is absent in the spectra of the polymers. This is consistent with the involvement of OH groups in a coordinate interacting with the polymers.

However, the weak band near 3400 cm-1 for H2L-Mn11 indicates that water molecules might be strongly absorbed by the polymer sample. This point will be discussed later. The band in H2L due to C=N stretching at 1600 cm-1 is shifted towards lower frequency (ca 1558 cm-1) in the coordination polymers. The red shift suggests coordination of metal ion through the nitrogen of 8-hydroxyquinoline. In addition, a weak band at 1100cm-1 is attributed to the C-O-M stretching frequency16. The band at 1430cm-1 in QEED is assigned to the in-plane OH deformation [16]. This band is shifted toward higher frequency (1468 cm-1) in the spectra of the polymers and supports the formation of a metal-oxygen bond.

The magnetic moments (ìeft) of the polymeric chelated are given in Table3. The diffuse electron spectrum of QEED-Cu11 coordination polymer shows two broad bands near 15.625 cm-1 and 22.222 cm-1. The first band may be due to 2Tg ! 2E transition while the second may be due to charge transfer. The first band shows some structural characteristics that suggest a distort octahedral geometry. The higher theoretical value of neff of the QEED-Cu[ll] polymer supports this view. The QEED-Ni[U] and QEED-Co[fl] polymers exhibit two absorption bands at 16,000 and 23,809cm-1, respectively. These bands are assigned to the ITIg !2T2g. 1T1g !2T2g (P) transitions, respectively 22 both the absorption bands and the values of ãeff lower then required
for a spin value only state.

The TGA data of all the co ordination polymers are summarized in Table 4. The coordination polymers are as thermally stable as bis (8-hydrox-5-quinolymethylene) sulfide (BHQS) and 5,t'-methylene bis(oxine) (MBQ)1,3.

All the polymers decompose in single step. They start their degradation at around 100°C. The rapid degradation after this temperature may be due to catalytic oxidation by metal oxide which form in situ during decomposition if the polymer. These relative order of thermal stability of the coordination polymers is Cu<Co<Ni<Mn.

**ACKNOWLEDGEMENT**

The author are thankful to Ami Chemicals and Dr. Ymp Research Centre. Nadiad, for assistance in research as well as to carry out analysis abroad. The authors also grateful to Head, Department at Chemistry. Hemchandracharya North Gujrat University, Patan, for encouragement and assitance in research.

**REFERENCES**


1. Horowitz E and Pessor T P, *J Inorg Nucl Chem,* 26, 139 (1964)
2. Bailer J C, Judd M L Jr and Mclean M J, WADC, *Technical Reports,* 58-61. Part-ll, 116 (1969)
3. Patel R D, Patel H S and Patel S R, *Eur Polym J Chem,* 23, 229 (1987)
4. Shah T B, Patel H S, and Dixit R B, *OriontJ Chem,* 15,107 (1999)
6. Manolava N, Lgnatova M, Rashkov I, *Eur Polym J,* 34, 1133(1938)
7. Raj L M, Raj M M, Patel H S and Shah T B, *Eur Polym J,* 5, 35, 1537 (1999)
8. Shah T B, Patel, Dixit R B and Dixit B C, Inter, *J Poly Analysis and Characterization* (In press) (2002)
9. Shah T B, Patel H S, Dixit R B and Dixit B C, *IndJ Inorg Chem* (In press) (2001)
10. S. P. Patel *et al, Materials Sci Res . India 02(1) 23-28 (2004)*
11. Pandya J M and Patel D C, *Bull Chem Sci* Vol. 1, 29-33 (2002)
12. Shah T B, Patel H S, Dixit R B, *Synth React Inor Mat Org Chem,* 31, 649-660 (2001)
13. Patel K D, Pachani S C, *Ultra Scientist of Physical Sciences,* 15(2), 195 (2003)
14. Burkhalter J H and Laib R I, *J Org Chem,* 26, 4078 (1961)
15. Vogel A I, *"Inorganic Quantitative Analysis"* ELBS, London (1978)
16. Chatterjee S K and Gupta N D, *J Poly Sci* Part A-1, 11, 1261 (1973)
17. Mitra R P and Chatterjee S K, *Indian J Chem* 1.62 (1963)
18. Figgis B N and Lewis J, *"Modern Coordination Chemistry,"* Wiley Interscience, N J (1964)
19. Figgis R G, Freiser H F, Priedel R, Hilliand L E and Johnston R D, *Spectrochem Acta,* 8, 1 (1958)
20. Patilusse *et al,* Abstracts of papers, *22&h ACS National Meeting New York, USA,* Sept. 7-11, (2003)
21. Nierengarten *et al, Euro J Inorg Chem,* 573-579 (2003)
22. Paulusse *et al, Chem Comm.* 13,1494-1495 (2003)
23. Cho ef *al, Macro Mole Chem Phys,* 203 (17), 2495-2500 (2002)
24. Patel R N and Patel S R, Angew, *Macromol Chem,* 96, 85 (1981)
25. Lever A B P, *Inorg Electronic spectroscopy,* 2nd ed. Elsevier, Amsterdam (1984)