



STUDIES ON OLIGOMERIC POLYMERS OF PHENOL-FORMALDEHYDE

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ABSTRACT

Acid catalyzed phenol-formaldehyde resin (PF) was prepared by well-known method. It was treated with 2-chloro ethanol. The resultant ethanolyloxy phenol-formaldehyde resin (EPF) was then treated with 5-chloromethyl-8-hydroxyquinoline hydrochloride (CMQ). The so called obtained oligomeric ligand HQ-EPF was characterized by elemental and spectral analysis. The oligomeric metal chlaties of HQ-EPF with Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} metal ions were prepared and studied for their metal:ligand (M/L), stoichiometry, magnetic moment, spectral features and by thermogravimetry.

Keywords: Phenol-formaldehyde (PF), 5-chloromethyl-8-hydroxyquinoline hydrochloride (CMQ), Spectral studies, Thermogravimetric analysis (TGA),Magnetic moment, Antibacterial and Antifungal activities.

INTRODUCTION

Polymeric ligands derived from 8-hydroxylquinoline (HQ) are reported in literature and its derivatives are good metal precipitant and ion-exchangers¹⁻⁹. The phenol-formaldehyde resins are important material in industries¹⁰⁻¹¹, but its clubbing with 8-hydroxylquinoline (HQ) has not been developed so far. This may afford good ion-exchanger material. Though the 8-hydroxylquinoline (HQ) derivative say 5-chloromethyl-8-hydroxy quinolinol(CMQ) precursor for the synthesis of many coordination polymers, biological active compounds as well as ion-exchanger¹²⁻¹⁵. Thus the present article expresses the synthesis and characterization of a novel oligomeric ligand having phenolic-8-hydroxylquinoline clubbed system and its metal chelates Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} metal ions. The synthetic route is shown in Scheme 1.

EXPERIMENTAL

All the chemicals used were of AR grade and were obtained from local dealer.

Synthesis of Oligomeric Ligand HQ-EPF

The 5-chloromethyl-8-hydroxyquinoline hydrochloride (m.p. 280°C) was prepared by method reported in literature¹⁶. The ethanolyloxy phenol-formaldehyde resin (EPF) prepared by simple reaction of sodium salt of Phenol-formaldehyde resin (PF) resin with 2-chloroethanol¹⁷.

HQ-EPF was prepared by following a method reported for 5-alkoxymethyl-8-quinoline¹⁶. According to this method, Sodium Bicarbonate (0.1mole) was added to a suspension of 5-chloromethyl-8-hydroxyquinoline hydrochloride (0.1 mole) and ethyloxy phenol-formaldehyde resin (EPF)(0.1mole) in THF. The reaction mixture was refluxed for 2.5hrs with frequently stirring. The resulting solution was then made alkaline with dilute ammonia to precipitate out HQ-EPF ligand, which was then filtered and air dried. The yield of was 78% and its melting point was 218-221°C (uncorrected). The predicted structure and formation of polymeric ligand is shown in Scheme-1.

Preparation of Polymeric Chelates

All Polymeric Chelates were synthesized by using metal acetates in a general method described as follows:

A warm clear solution of HQ-EPF in 20% aq.formic acid (200ml) was added to a solution of copper acetate (1.99gm, 0.01mole) in 50% aq.formic acid (50ml) with constant stirring. After complete addition

of metal salt solution, the pH of reaction mixture was adjusted to about 5 with dilute ammonia solution. The polymer chelate is separated out in the form of suspension was digested on a water bath for one hour and eventually filtered, washed with hot water followed by acetone and dimethyl formamide (DMF) and then dried in air at room temp. The yields of all co-ordination polymers were almost quantitative.

Measurements

Elemental analysis of HQ-EPF and its polymeric chelates were carried out on a C,H,N elemental analyzer (Italy). IR spectra of H₂L and the polymeric chelates were scanned on a Nicolet-760D FTIR spectrophotometer in KBr. The metal content analyses of the polymeric chelates were performed by decomposing a weighed amount of each polymeric chelates followed by EDTA (disodium ethylene diamine tetra acetate) titration as reported in the literature¹⁸. Magnetic susceptibility measurements of all the polymeric chelates were carried out at room temperature by the Gouy method. Mercury tetrathiocyanatocobaltate (II), Hg[Co(NCS)], was used as a calibrant. Molar Susceptibilities were corrected for diamagnetism of component atoms using Pascal's constant. The diffuse reflectance spectra of the solid polymeric chelates were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

Thermogravimetric analysis of co-ordination polymers were carried on DuPont 950 TGA analyzer in air at a heating rate of 20C/min.

Antibacterial activities

Antibacterial activity of HQ-EPF ligand and its co-ordination polymers were studied against gram-positive bacteria (*Bacillus subtilis* and *staphylococcus aureus*) and gram-negative bacteria (*E.coli* and *salmonella typhi*) at a concentration of 50µg/ml by agar cup plate method. Methanol system was used as control in this method. The area of inhibition of zone measured in mm.

Antifungal activities

The fungicidal activity of all the compounds was studied at 1000 ppm concentration in vitro. Plant pathogenic organisms used were *penicillium expansum*, *Nigrospora Sp.*, *Trichothesium Sp.*, and *Rhizopus nigricum*. The antifungal activity of ligand and its co-ordination polymers was measured on each of these plant pathogenic strains on a potato dextrose agar (PDA) medium. Such a PDA medium contained potato 200gm, dextrose 20gm, agar 20gm and water one liter. Five days old cultures were employed. The compounds to be tested were suspended (1000ppm) in a PDA medium and autoclaved at 120° C for 15 min. at 15atm. pressure. These medium were poured into sterile Petri plates and the organisms were inoculated after cooling the petri plates. The percentage inhibition for fungi was calculated after five days using the formula given below:

$$\text{Percentage of inhibition} = 100(X-Y) / X$$

Where, X = Area of colony in control plate
Y = Area of colony in test plate

RESULTS AND DISCUSSION

The synthesis of the oligomeric ligand HQ-EPF has not been reported in the literature. The ligand HQ-EPF was isolated in the form of a reddish powder. It was soluble organic solvents such as in DMSO (dimethyl sulfoxide), DMF. The results of elemental analyses of the HQ-EPF ligand (Table-1) are agreed with those predicted on the basis of formula.

The IR spectrum of HQ-EPF features are a broad band extending from 3450-3160cm⁻¹ with maximum at 3320 cm⁻¹, attributed to the OH group. The weak bands around 2893 and 2950 cm⁻¹ may be due to asymmetric and symmetric stretching vibrations of methylene groups(-CH₂-). The bands around 1634, 1575, 1500 and 1440 cm⁻¹ are attributed to the 8-hydroxyquinoline nucleus¹⁹. The others bands are at their respective positions.

The ¹H NMR(δ ppm) spectrum of HQ-EPF also show the signals 2.78(2H,s,CH₂); 3.84-4.45 (4H,t,CH₂); 5.04 (2H,s, CH₂); 4.22 (1H,s,OH); 7.30-6.76(3H,m,Ar-H,); 6.54-8.11 (5H,m,Quinoline). These features

confirm the proposed structure of ligand HQ-EPF. The NMR Data of HQ-EPF shown in experimental part are also confirming the structure of HQ-EPF.

The polymeric chelates derived from HQ-EPF are insoluble in common organic solvents. Hence it is not possible to characterize the co-ordination polymers by molecular mass using conventional methods like osmometry, viscometry etc. These co-ordination polymers do not melt up to 360°C.

On the basis of the proposed structure shown in Scheme-1, the molecular formula of the HQ-EPF ligand is C₁₉H₁₇NO₃, which, upon chelation coordinates with two central metal atom at four co-ordination sites and two water molecules. Therefore, the general molecular formula of the resulting co-ordination polymer is given by [M(HQ-EPF)₂.2H₂O] as shown in scheme-1. This has been confirmed by the results of elemental analyses of all of the five co-ordination polymers and their

parent ligand. The data of elemental analyses reported in Table I are in agreement with the calculated values of C,H and N based on the above-mentioned molecular formula of the parent ligand as well as co-ordination polymers. Examination of data of the metal content in each polymer (Table-1) revealed a 1:1 metal:ligand(M/L) stoichiometry in all of the co-ordination polymers. Comparison of the IR spectrum of the ligand HQ-EPF and those of the co-ordination polymers reveals certain characteristic differences. The broad band at 3400-3100 cm⁻¹ for HQ-EPF has almost disappeared for the spectra of polymers. However, the weak bands around 3200 cm⁻¹ in the spectra of HQ-EPF -Co²⁺, HQ-EPF -Ni²⁺, HQ-EPF -Mn²⁺ indicate the presence of water molecules which may have been strongly absorbed by the polymer sample. The weak band around 1115cm⁻¹ is attributed to the C-O-M stretching frequency¹⁹. The band at 1435 cm⁻¹ in the IR spectrum of HQ-EPF is attributed to the in-plane OH deformation¹⁹. The band is shifted towards higher frequency in the spectra of the polymers indicating formation of metal-oxygen bond. These features suggest that the structure of the co-ordination polymer.

The value of the degree of polymerization of all the co-ordination polymers listed in Table-1 suggest that the average Dp for all the polymers in a range of 5 to 6. Magnetic moments (μ_{eff}) of polymeric chelate are given in Table-1.

The diffusion electronic spectrum of HQ-EPF -Cu²⁺ co-ordination polymers shows two broad bands around 15,385 cm⁻¹ and 22,732 cm⁻¹. The first bands may be due to ²T_{2g} → ²E_g transition. While the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the HQ-EPF -Co²⁺ polymers. The higher value of μ_{eff} of the HQ-EPF -Cu²⁺ polymer support this view^{20,21}. The HQ-EPF -Ni²⁺ and HQ-EPF-Co²⁺ polymers give two absorption bands respectively at 17,257 and 24,014 cm⁻¹ and at 17,248 and 23736 cm⁻¹ which can be assigned respectively to ⁴T_{1g} → ²T_{2g}, ⁴T_{1g} → ⁴T_{1g(P)} transitions. These absorption bands and the values of μ_{eff} indicate an octahedral configuration for the HQ-EPF -Ni²⁺ and HQ-EPF -Co²⁺ polymers^{22,23}. The spectrum of [Mn(HQ-EPF)₂(H₂O)₂] show weak bands at 16,470, 17,689 and 23,166 cm⁻¹ assigned to the transitions ⁶A_{1g} → ⁴T_{1g}(4G), ⁶A_{1g} → ⁴T_{2g}(4G) and ⁶A_{1g} → ⁴A_{1g}, ⁴E_g respectively, suggesting an octahedral structure for the [Mn(HQ-EPF)₂(H₂O)₂] polymer²³. As the spectrum of the [Zn (HQ-EPF)₂(H₂O)₂] polymer is not well resolved, it is not interpreted, but its μ_{eff} value shows that it is diamagnetic as expected.

The TGA data for the polymers are presented in Table-2. The weight loss of the polymer samples at different temperatures indicates that the degradation of the polymers is noticeable beyond 300°C. The rate of degradation becomes a maximum at a temperature lying between 400 °C and 500 °C depending upon the nature of the polymers. Each polymer lost about 55% of its weight when heated up to 700 °C. Inspection of the thermograms of HQ-EPF -Co²⁺, HQ-EPF -Mn²⁺ and HQ-EPF -Ni²⁺ samples revealed that these samples suffered appreciable weight loss in the range 150 to 280°C. This may be due to the presence of water strongly absorbed by the polymers. It has also been indicated earlier that the IR spectra of these three polymer samples have OH bands at around 3200 cm⁻¹ due to associated water.

On the basis of the relative decomposition (% wt. loss) and the nature of thermograms, the co-ordination polymers may be arranged in order in increasing stability as:



This trend also coincides with the stability order already reported for the metal oxinates¹⁹ and for co-ordination polymers of HQ-EPF³.

The antimicrobial activity of HQ-EPF and its co-ordination polymers are presented in Table-3 and 4. The data suggest that all the samples are toxic to bacteria or fungus. The data also suggest that the % age of bacteria or fungus is inhibited in the range of 58 to 80% depending upon the biospecies and co-ordination polymers.

CONCLUSION

The investigation described in the present article reveals the following conclusion:

Polycondensation of 5-chloromethyl-8-hydroxyquinoline hydrochloride and ethyloxy phenol-formaldehyde resin (EPF) yielded a novel oligomeric ligand HQ-EPF. The applicability of the polymeric ligand was explored by preparing polymeric chelates using different divalent metal ion indicating that the HQ-EPF polymeric ligand has good chelating property and high thermal stability.

Table-1: Analytical and Spectral data of the co-ordination polymers of HQ-EPF (H₂L)

Ligand/ Co- ordination polymers	Empirical Formula	Formula Weight	Analyses				$\mu_{\text{eff.}}$ (B.M.)	$\overline{(\text{Mn})}$ ± 60	$\overline{\text{Dp}}$
			%Found(Calculated)						
			%M	%C	%H	%N			
HQ-EPF	(C ₁₉ H ₁₇ NO ₃) _n	307	-	74.2 (74.26)	5.5 (5.53)	4.5 (4.56)	-	-	-
[Cu(HQ-EPF)(H ₂ O) ₂] _n	(Cu.C ₁₉ H ₂₀ NO ₅ .2H ₂ O) _n	405.54	15.6 (15.66)	56.2 (56.22)	4.9 (4.93)	3.4 (3.45)	2.00	2510	6
[Co(HQ-EPF)(H ₂ O) ₂] _n	(Co.C ₁₉ H ₂₀ NO ₅ .2H ₂ O) _n	364.94	16.1 (16.15)	62.4 (62.47)	5.4 (5.48)	3.8 (3.83)	2.88	1896	5
[Ni(HQ-EPF)(H ₂ O) ₂] _n	(Ni.C ₁₉ H ₂₀ NO ₅ .2H ₂ O) _n	364.71	16.0 (16.09)	62.5 (62.51)	5.4 (5.48)	3.8 (3.83)	4.00	2252	6
[Mn(HQ-EPF)(H ₂ O) ₂] _n	(Mn.C ₁₉ H ₂₀ NO ₅ .2H ₂ O) _n	360.94	15.2 (15.22)	6.1 (63.16)	5.5 (5.54)	3.8 (3.87)	4.83	1868	5
[Zn(HQ-EPF)(H ₂ O) ₂] _n	(Zn.C ₁₉ H ₂₀ NO ₅ .2H ₂ O) _n	371.38	17.6 (17.60)	61.3 (61.39)	5.3 (5.38)	3.7 (3.76)	Diamagnetic	1924	5

Table-2: Thermo gravimetric analysis co-ordination polymers of HQ-EPF

Ligand/ Co-ordination polymers	% weight loss at temperature T(°C)					
	100	200	400	500	600	700
H ₂ L	-	5.7	10.5	40.6	45.7	48.6
[CuL(H ₂ O) ₂] _n	2.7	5.4	13.4	42.8	48.2	53.8
[CoL(H ₂ O) ₂] _n	4.8	8.9	16.9	22.5	43.7	59.6
[NiL(H ₂ O) ₂] _n	5.1	8.7	15.2	26.8	45.5	59.8
[MnL(H ₂ O) ₂] _n	5.2	7.1	9.8	15.6	25.4	36.5
[ZnL(H ₂ O) ₂] _n	2.5	3.7	5.3	15.5	23.9	35.8

Table-3: antibacterial activity of co-ordination polymers

Compounds	Zone of Inhibition			
	Gram +Ve		Gram -Ve	
	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Salmonella typhi</i>	<i>E.coli</i>
[CuL(H ₂ O) ₂] _n	57	65	63	64
[CoL(H ₂ O) ₂] _n	63	66	57	62
[NiL(H ₂ O) ₂] _n	64	63	60	58
[MnL(H ₂ O) ₂] _n	61	61	61	64
[ZnL(H ₂ O) ₂] _n	63	60	64	62

Table-4: Antifungal activity of co-ordination polymers

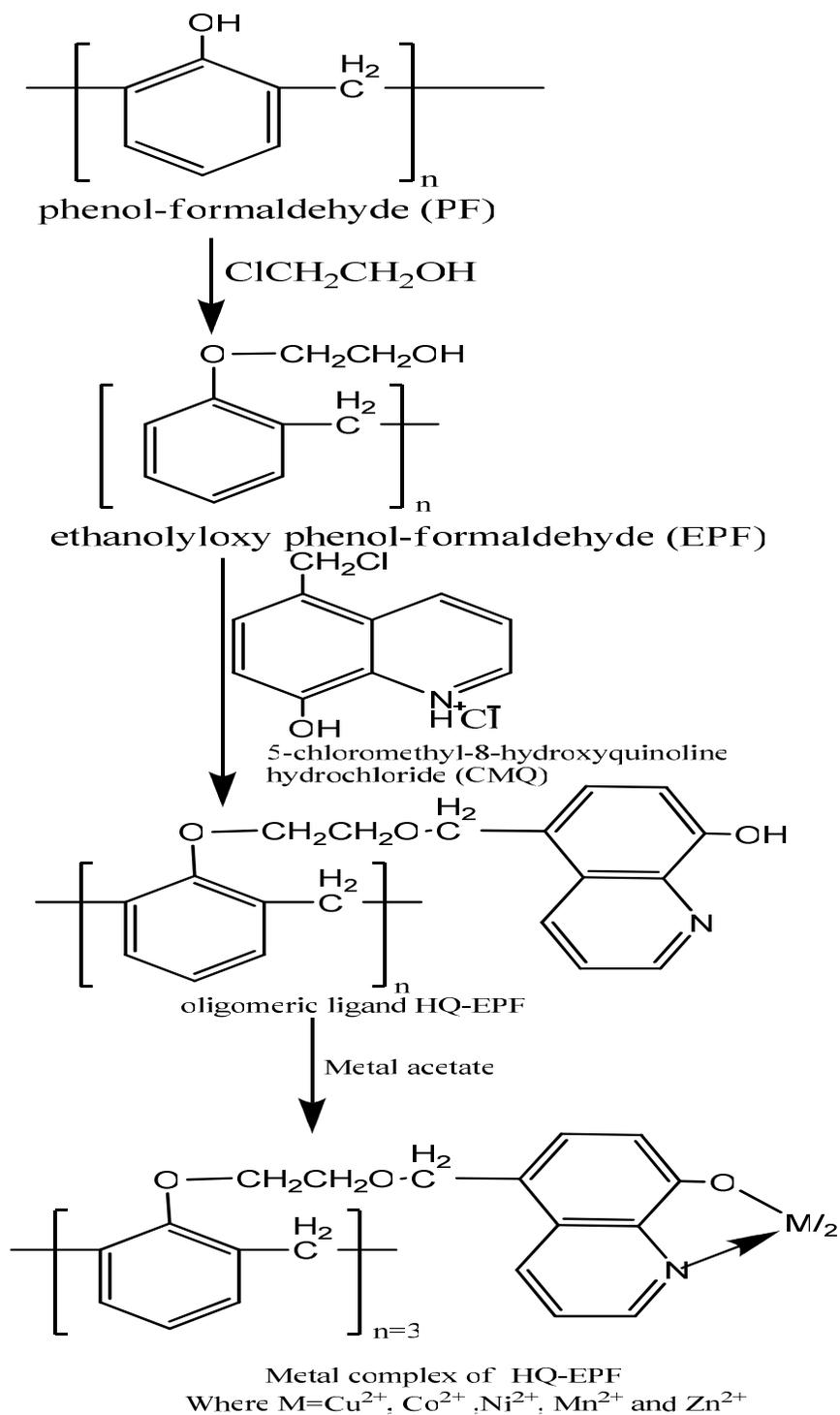
Compounds	Zone of Inhibition at 1000 ppm (%)			
	<i>Penicillium Expansum</i>	<i>Nigrospora Sp.</i>	<i>Trichothesium Sp.</i>	<i>Rhizopus Nigricum</i>
[CuL(H ₂ O) ₂] _n	63	64	62	59
[CoL(H ₂ O) ₂] _n	61	66	63	64
[NiL(H ₂ O) ₂] _n	65	67	67	61
[MnL(H ₂ O) ₂] _n	64	63	64	66
[ZnL(H ₂ O) ₂] _n	61	61	65	63

Further, the polymeric ligand is thermally more stable than its polymeric chelates. Among the five polymeric chelates, M-HQ-EPF chelate is least stable, whereas M-HQ-EPF polymeric chelates is the most stable having a thermal stability comparable to that of chelates may be used as heat resistant material up to 350°C. The polymeric ligand follows a two steps thermal degradation whereas polymeric chelates follow a single step thermal degradation.

A evaluation of the thermal stability of the present polymeric chelates with those of 5-chloromethyl-8-hydroxyquinoline hydrochloride and ethyloxy phenol-formaldehyde (EPF) as a parent groups of polymeric chelates reveals that the HQ-EPF polymeric chelates are thermally more stable. Finally, the magnetic susceptibility results indicate that polymeric chelates of Cu⁺², Ni⁺² and Co⁺² are paramagnetic, whereas that of Zn⁺² is diamagnetic in nature. All the polymers have good microbicidal activity.

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Scheme-1

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