Pelagia Research Library

Oligomeric Ligand Based on Novolac Resin

Jayendrakumar J. Chauhan, F. B. Bux[1] and Arun Singh*[2]

[1]Department of Chemistry, Govt. Geetanjali Girls P. G. College, Bhopal
[2]Rajya Shiksha Kendra, Bhopal.

_____

ABSTRACT

Acid catalyzed phenol-formaldehyde (PF) i.e. novolac resin was prepared by established method and then it was treated with succinic anhydride. The resultant oligomeric ligand called phthalated novolac designated as SPH-PF and was characterized by elemental and spectral analysis. The oligomeric metal chalets of SPH-PF 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, number-average molecular weight($\overline{Mn}$) and by thermogravimetry.

Keywords: Novolac resin, Number average molecular weight ($\overline{Mn}$), IR, NMR, Reflectance, Thermogravimetric analysis (TGA), Magnetic moment, Antibacterial and Antifungal activities.

_____

INTRODUCTION

Phenolic resins are commodity materials for wide applications [1-3]. They are bifurcated into novolac and resoles. Particularly novolac are acid catalyzed products. Number of modifications of these resins is made for further application [4-8]. One of the area in which the novolac having pendent metal complexing ligand has not been reported. So it was thought interesting to oligomeric ligand based on novolac. Thus the present communication confirms the studies oligomeric ligand having succinic acid as pendent ligand. Hence the present article describes the synthesis and characterization of a novel oligomeric ligand SPH-PF and its coordination polymers with Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} metal ions. The whole research scanned in scheme 1.

MATERIALS AND METHODS

Materials
All the chemicals used were of AR grade and were obtained from local dealer.
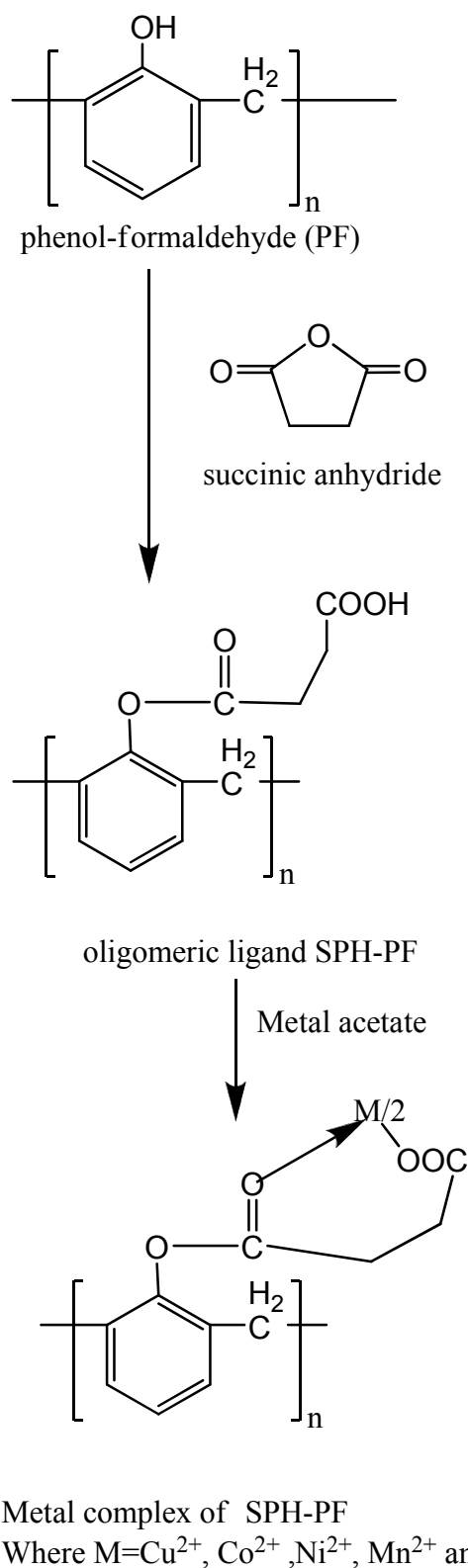
PROCEDURE
Synthesis of Oligomeric Ligand PH-PF
The novolac resin (Phenol-formaldehyde (PF) resin) was prepared by method reported in literature [9].

SPH-PF was prepared by a reported method as follow [10]:

According to this method, novolac resin (0.01mole) was dissolved in 50 ml of tetrahydrofuran solvent; 10-20 g of crushed ice was added. The 1.5 g (1.5ml) of succinic anhydride in 50ml tetrahydrofuran was added to this solution by shaking the mixture vigorously for 30-60 seconds. Then it was refluxed for 3hrs, the precipitates of ester separated. The yield of was 86 % and its melting point was 211-213°C (uncorrected). The predicted structure and formation of polymeric ligand designated as SPH-PF is shown in Scheme-1.

phenol-formaldehyde (PF)

succinic anhydride

oligomeric ligand SPH-PF

Metal acetate

Metal complex of SPH-PF
Where M=Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}

scheme-1

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

To a solution of SPH-PF (20.6 g,0.1 mole) in ethanol-acetone (1:1v/v) mixture (150 ml), 0.1N KOH solution was added dropwise with stirring. The pasty precipitates were obtained at neutral pH. These were dissolved by addition of water up to clear solution. It was diluted to 250 ml. by water and was known as stock solution. 25 ml of the stock solution (which contains 0.01 mole SPH-PF) was added drop wise to the solution of metal salt (0.005 mole for divalent metal ions) in water at room temperature. Sodium acetate or ammonia was added up to complete precipitation. The precipitates were digested on water bath at 80° C for 2h. The digested precipitates of chelates were filtered washed with water and air dried. It was amorphous powder. Yield was almost quantitative. The detail are given in Table-1

Measurements:
Elemental analysis of SPH-PF and its Polymeric chelates were carried out on a C,H,N elemental analyzer (Italy). IR spectra of H_2L 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 literature [11]. Magnetic susceptibility measurements of all the polymeric chelates were carried out at room temperature by the Gouy method. Mercury tetrathiocynatocobaltate (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.

The number average molecular weight $(\overline{Mn})$ of all the Polymeric chelateswere determined by method reported in earlier communications [12].

Table - 1: Analytical And Spectral Data of The Polymeric Chelates Of SPH-PF(H_2L)

Ligand/ Co-ordination polymers	Empirical Formula	Formula Weight	Analyses %Found(Calculated)			$\mu_{eff.}$ (B.M.)	$(\overline{Mn}) \pm 60$	$\overline{Dp}$
			%M	%C	%H			
SPH-PF	$C_{11}H_{10}O_4$	206	-	64.0 (64.07)	4.8 (4.85)	-	-	-
$[Cu(SPH-PF)_2(H_2O)_2]_n$	$Cu.C_{22}H_{22}O_{10}$	489.54	12.9 (12.97)	53.9 (53.92)	4.4 (4.49)	2.03	3002	6
$[Co(SPH-PF)_2(H_2O)_2]_n$	$Co.C_{22}H_{22}O_{10}$	484.94	12.1 (12.15)	54.4 (54.48)	4.5 (4.53)	2.88	2860	6
$[Ni(SPH-PF)_2(H_2O)_2]_n$	$Ni.C_{22}H_{22}O_{10}$	484.71	11.9 (12.11)	54.4 (54.46)	4.5 (4.53)	4.02	2490	5
$[Mn(SPH-PF)_2(H_2O)_2]_n$	$Mn.C_{22}H_{22}O_{10}$	480.94	11.4 (11.42)	54.8 (54.89)	4.5 (4.57)	4.84	2968	6
$[Zn(SPH-PF)_2(H_2O)_2]_n$	$Zn.C_{22}H_{22}O_{10}$	491.38	13.2 (13.30)	53.7 (53.72)	4.4 (4.47)	Diamagnetic	2536	5

Table- 2: Thermo Gravimetric Analysis Polymeric Chelates of PH-PF

Ligand/ Co-ordination polymers	% weight loss at temperature $T(^0C)$					
	100	200	400	500	600	700
H_2L	-	5.1	9.6	39.9	45.1	48.0
$[CuL_2(H_2O)_2]_n$	2.0	4.8	12.8	42.2	47.6	53.2
$[CoL_2(H_2O)_2]_n$	4.2	8.2	16.2	21.9	43.1	59.0
$[NiL_2(H_2O)_2]_n$	4.5	8.1	14.5	26.1	45.0	59.2
$[MnL_2(H_2O)_2]_n$	4.6	6.5	9.2	15.0	24.8	35.9
$[ZnL_2(H_2O)_2]_n$	1.9	3.1	4.6	14.8	23.2	35.0

Thermogravimetric analysis of Polymeric chelateswere carried on DuPont 950 TGA analyzer in air at a heating rate of 20C/min.

Table- 3: Antibacterial Activity of Co-Ordination Polymers

Compounds	Zone of Inhibition			
	Gram +Ve		Gram –Ve	
	Bacillus subtilis	*Staphylococcus aureus*	*Salmonella typhi*	*E.coli*
$[CuL_2(H_2O)_2]_n$	54	61	60	61
$[CoL_2(H_2O)_2]_n$	60	62	54	58
$[NiL_2(H_2O)_2]_n$	59	60	57	55
$[MnL_2(H_2O)_2]_n$	57	57	59	60
$[ZnL_2(H_2O)_2]_n$	58	56	60	58

Antibacterial activities
Antibacterial activity of SPH-PF ligand and its Polymeric chelateswere studied against gram-positive bacteria (*Bacillus subtilis and staphylococcus aureus*) and gram-negative bacteria (*E.coli and salmonella typhi)* at a

1104

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 Polymeric chelateswas measured on each of these plant pathogenic strains on a potato dextrose agar (PDA) medium. Such a PDA medium contained potato 200gm,dextrose 20gm,agar20gm 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:

Percentage of inhibition = 100(X-Y) / X

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

Table- 4: Antifungal Activity of Polymeric Chelates

Compounds	Zone of Inhibition at 1000 ppm (%)			
	Penicillium Expansum	*Nigrospora Sp.*	*Trichothesium Sp.*	*Rhizopus Nigricum*
$[CuL_2(H_2O)_2]_n$	60	60	57	55
$[CoL_2(H_2O)_2]_n$	57	63	59	60
$[NiL_2(H_2O)_2]_n$	62	62	64	58
$[MnL_2(H_2O)_2]_n$	59	60	60	62
$[ZnL_2(H_2O)_2]_n$	56	58	61	57

RESULTS AND DISCUSSION

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

The IR spectrum of SPH-PF features are a broad band extending from 3450-3160cm^{-1} with maximum at 3320 cm^{-1}, attributed to the OH group [13]. The weak bands around 2893 and 2950 cm^{-1} may be due to asymmetric and symmetric stretching vibrations of methylene groups($-CH_2-$). The others bands are at their respective positions.

The ^{1}H NMR(δ ppm) spectrum of SPH-PF also show the signals 3.84-4.45 (6H,s,CH$_2$) ; 4.22 (1H,s,OH); 7.30-6.76(4H,m,Ar-H,).These features confirm the proposed structure of ligand PH-PF. The NMR Data of SPH-PF shown in experimental part are also confirming the structure of PH-PF.

The Polymeric chelatesderived from SPH-PF are insoluble in common organic solvents. Hence it is not possible to characterized the Polymeric chelates by molecular mass using conventional methods like osmometry, viscometry etc. These Polymeric chelates do not melt up to 360^oC.

On the basis of the proposed structure shown in scheme-1, the molecular formula of the SPH-PF ligand is $C_{11}H_{10}O_4$, 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 $[M(SPH-PF)_2.2H_2O]$ as shown in scheme-1. This has been confirmed by the results of elemental analyses of all of the five Polymeric chelates and their parent ligand. The data of elemental analyses reported in Table-1 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 SPH-PF and those of the Polymeric chelates reveals certain characteristic differences. The broad band at 3400-3100 cm^{-1} for SPH-PF has almost disappeared for the spectra of polymers. However, the weak bands around 3200 cm^{-1} in the spectra of PH-PF-Co^{2+}, PH-PF-Ni^{2+}, PH-PF-Mn^{2+} 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 frequency [14].The band at 1435 cm^{-1} in the IR spectrum of SPH-PF is attributed to the in-plane OH deformation [14]. The band is shifted towards higher frequency in the spectra of the polymers indicating formation of metal-oxygen bond. These feature suggest that the structure of the co-ordination polymer.

The value of the degree of polymerization of all the polymeric chelates 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 PH-PF-Cu^{2+} Polymeric chelates shows two broad bands around 15,385 cm^{-1} and 22,732 cm^{-1}.The first bands may be due to $^2T_{2g} \rightarrow ^2E_g$ transition. While the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the PH-PF-Co^{2+} polymers. The higher value of μ_{eff} of the PH-PF-Cu^{2+} polymer support this view [15-17]. The PH-PF-Ni^{2+} and SPH-PF -Co^{2+} 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 $^4T_{1g} \rightarrow ^2T_{2g}$, $^4T_{1g} \rightarrow ^4T_{1g(P)}$ transitions. These absorption bands and the values of μ_{eff} indicate an octahedral configuration for the PH-PF-Ni^{2+} and PH-PF-Co^{2+} polymers [18].The spectrum of [Mn(PH-PF)$_2$(H$_2$O)$_2$] show weak bands at 16,470, 17,689 and 23,166 cm^{-1} assigned to the transitions $6_{A1g} \rightarrow 4_{T1g}$(4G), $6_{A1g} \rightarrow 4_{T2g}$(4G) and $6_{A1g} \rightarrow 4_{A1g}, 4_{Eg}$ respectively, suggesting an octahedral structure for the [Mn(HQ-EPF)$_2$(H$_2$O)$_2$] polymer. As the spectrum of the [Zn (PH-PF)$_2$(H$_2$O)$_2$] 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 PH-PF-Co^{2+},PH-PF-Mn^{2+} and PH-PF-Ni^{2+} samples revealed that these samples suffered appreciable weight loss in the range 150 to 280°C. This may 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 Polymeric chelates may be arranged in order in increasing stability as:

<div align="center">

Cu < Ni < Co < Mn

</div>
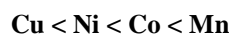
This trend also coincides with the stability order already reported for the metal oxinates [14] and for Polymeric chelates of SPH-PF [18].

 The antimicrobial activity of SPH-PF and its Polymeric chelates 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.

<div align="center">

CONCLUSION

</div>

The investigation described in the present article revels the following conclusion:
Polycondensation of succinic anhydride and phenol-formaldehyde resin (EPF) yielded a novel oligomeric ligand PH-PF. The applicability of the polymeric ligand was explored by preparing polymeric chelates using different divalent metal ion indicating that the SPH-PF polymeric ligand has good chelating property and high thermal stability.

Further, the polymeric ligand is thermally more stable than its polymeric chelates. Among the five polymeric chelates, M-SPH-PF chelate is least stable, whereas M-SPH-PF 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 comparison of the thermal stability of the present polymeric chelates with those of succinic anhydride and phenol-formaldehyde (PF) as parent groups of polymeric chelates revels that the SPH-PF 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.

<div align="center">

REFERENCES

</div>

[1] J. R. Patel; K. S. Nimavat and K. B.Vyas, *Der Pharma Chemica*, **2011**, 3 (4),102.
[2] J. R. Patel; K. S. Nimavat and K. B.Vyas, *J. Chem. Pharm. Res.,***2011**, 3(6),483.

[3] A. D. Kushwaha, V. V. Hiwase andA. B. Kalambe,*Der Chemica Sinica*, **2012**,3(4),794.

[4] R.Yadav, P.Awasthi, D.Srivastava, *Jour. of app.poly.science*, **2009,**114 (3), 1471.

[5] R. Yadav and D.Srivastava,*Chemistry & Chemical Tech*., **2008,**2(3),173.

[6] D.T. Masram, K.P. Kariya and N.S. Bhave, *Advances in Applied Science Research*, **2011**, 2 (4),156.

[7] D. R. Gosai1, K. S. Nimavat and K. B. Vyas, *Archives of Applied Science Research,***2012, 4 (3),1395**.

[8] D. R. Gosai, K. S. Nimavat and K. B. Vyas, *J. Chem. Pharm. Res*., **2011**,3(6),490..

[9] Vogel, A. I. A Text book of Quantitative Inorganic Analysis, 5th ed.,(Longman, London), **1989,**pp. 584.

[10] Vogel, A. I. A Text book of Quantitative Inorganic Analysis, 5th ed., (Longman, London), **1989,**pp. 1248.

[11] H.S.Patel, R.B.Dixit and T.B.Shah, *Int. J. Polym. Material*., **2001,**49,27.

[12] T. B.Shah, H. S.Patel, R. B.Dixit and B. C.Dixit, *Int. J. of Polym.Anal. and Charact*., **2003,**8, 369.

[13] R M.Silverstein,*Spectrometric Identification of organic compounds*,5th Ed. John   wiley**1991**.

[14] W.Kemp,*Organic Spectroscopy*,ELBS.(Macmillan'UK),**1998**.

[15] R.N.Carlin and A. J.Van Dryneveldt, *Magnetic properties of Transition Metal   Compound,*Springe-Berlag,NY,**1997**.

[16] D.Oza, K. N.Kaul and R. K. Mehta, *Indian J. Chem*., **1996,**7, 927.

[17] D.K.Patel and A.Singh, *E-Journal of Chemistry*,**2009,** 6(4), 1017.

[18] R.Purohit and S.Devi, *Analyst.*, **1991,**116, 825.