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Synthesis, characterization and biological activity of polymeric ligand

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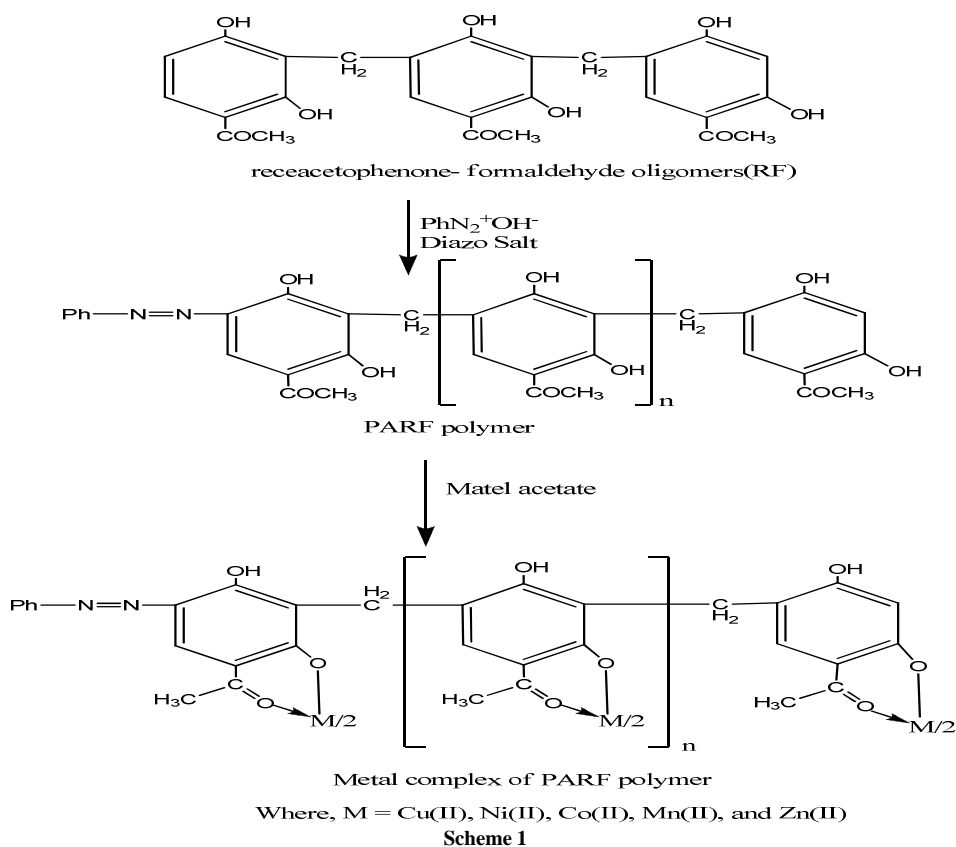
ABSTRACT

Novel ligand based on phenylazo of resorciacetophenone-Formaldehyde polymer was synthesized by diazotization reaction of resorciacetophenone-Formaldehyde polymer with phenyl diazonium salt. Co-ordination polymers of this ligand were prepared with Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) metal ions. All of these coordination polymers and the ligand were characterized by elemental analyses by IR, NMR, number-average molecular weights (\overline{Mn}), magnetic susceptibilities and by thermogravimetry. The biological activity of all the samples has also been monitored against plant pathogens.

Keywords: Bis(bidentate) ligand, Coordination polymers, Number average molecular weight (\overline{Mn}), IR, Thermogravimetric analysis (TGA), magnetic moment and Antifungal activities.

INTRODUCTION

Phenolic resins are commodity materials for wide applications [1,2]. Metal Containing polymers have important applications in medical sciences [3-5]. The presence of metals in polymeric materials leads to new physical properties and potential applications. Several different possible types of metal-containing polymer structures exist depending on where the metal atoms are incorporated and the nature of the linkages between them. A major subdivision of linear polymers involves a consideration of the location of the metal centers. Coordination polymers are light in weight and possess high thermal stability. Polymeric metal complexes have a variety of geometries that are not observed in organic polymers, some combine the properties of anisotropy with photo responsive behaviour that give rise to applications in areas such as optical storage, optical switching, diffractive optical elements, non-linear optical devices, liquid crystal displays (LCD's) etc.[6-8]. Metal complex dyes comprise an important class of chromophores. These dyes have been deeply investigated since antiquity [9] and have been widely used in many practical applications; textile dyeing, colouring polyamide fibers, are typical traditional uses [10, 11]. Hence the present article describes the synthesis and characterization of a novel ligand phenylazo of resorciacetophenone-Formaldehyde polymer and its coordination polymers with Cu(II), Co(II), Ni(II), Mn(II), and Zn(II) metal ions. The synthetic route is shown in scheme 1.



MATERIALS AND METHODS

Materials

All chemicals used were of analytical pure grade.

Synthesis of azo coupling of phenyl diazonium salts to resorciacetophenone-Formaldehyde polymer (PARF)

The resorciacetophenone-Formaldehyde polymer was prepared by method reported in literature [12].

Diazonium salt of Benzene solution (0.1mole) was slowly added to an alkaline solution of resorciacetophenone-Formaldehyde polymer (RF) (0.1mole) at pH 8.5-9.0 and below 0-5°C. The resultant solution was stirred for 3hr. The dye was precipitated by lowering the pH to 6.0. The precipitated dye (PARF) was filtered off, wash with water and air-dried. The yield of PARF was 68% and m.p.216-219°C (uncorrected). The predicted structure and formation of polymeric ligand is shown in Scheme-1.

Analysis of PARF: $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_9$ (584)

	C%	H%	N%
Calculated:	65.75	4.83	4.79
Found:	65.7	4.8	4.7

IR Spectral Features (cm^{-1}): 3030, 1520, 1640 (Aromatic), 1720 (CO), 3450-3160(OH), 2890, 2940(CH_2).

Preparation of Coordination Polymers

All coordination polymers were synthesized by using metal acetate by the method described below.

A warm clear solution of PARF (0.01 mol) in 20% aqueous formic acid (200 ml) was added to a solution of metal acetate (0.01 mol) in 50% aqueous formic acid (50 ml) with constant stirring. After complete addition of the metal salt solution, the pH of the reaction mixture was adjusted to about 5 with dilute ammonia solution. The Co-

ordination polymers thus separated out in the form of a suspension was digested on a water bath for 1 h and eventually filtered, washed with hot water followed by acetone and dimethyl formamide (DMF) and then dried in air at room temperature. The yields of all coordination polymers were almost quantitative.

Table 1 Analytical data of coordination polymers of PARF (H₂L)
^aMagnetic moment; D is diamagnetic.

Ligand/ Co-ordination polymers	Empirical Formula (Formula Weight)	Yield (%)	Elemental analysis Calc. / (Found)				μ_{eff}^a (B.M)	$(\overline{Mn})_{60} \pm$	\overline{Dp}
			C	H	N	M			
PARF	C ₃₂ H ₂₈ N ₂ O ₉ (584)	68	65.75 (65.7)	4.83 (4.8)	4.79 (4.7)	-	-	-	
[CuPARF(H ₂ O) ₂] _n	Cu.C ₆₄ H ₅₄ N ₄ O ₁₈ .2H ₂ O (1267.54)	87	60.60 (60.58)	4.58 (4.55)	4.42 (4.39)	5.16 (5.14)	1.9	7662	
[CoPARF(H ₂ O) ₂] _n	Co.C ₆₄ H ₅₄ N ₄ O ₁₈ .2H ₂ O (1260.94)	83	60.91 (60.88)	4.60 (4.57)	4.44 (4.41)	4.67 (4.65)	3.7	6368	
[NiPARF (H ₂ O) ₂] _n	Ni.C ₆₄ H ₅₄ N ₄ O ₁₈ .2H ₂ O (1260.71)	89	60.92 (60.90)	4.60 (4.58)	4.44 (4.42)	4.66 (4.64)	3.1	6342	
[MnPARF(H ₂ O) ₂] _n	Mn.C ₆₄ H ₅₄ N ₄ O ₁₈ .2H ₂ O (1256.94)	86	61.10 (61.08)	4.61 (4.58)	4.46 (4.44)	4.37 (4.35)	5.7	7586	
[ZnPARF(H ₂ O) ₂] _n	Zn.C ₆₄ H ₅₄ N ₄ O ₁₈ .2H ₂ O (1267.98)	91	60.60 (60.58)	4.58 (4.56)	4.42 (4.39)	5.16 (5.15)	D	6398	

MESUREMENTS

Elemental analyses of PARF and its coordination polymers were carried out on a Thermofingan flash 1101EA (Italy). The metal content of the coordination polymers were performed by decomposing a weighed amount of coordination polymer followed by complexometric titration with EDTA (disodium ethylene diamine tetra acetate) [13]. Infrared (IR) spectra of all the samples were scanned on a Nicolet-760 FTIR spectrophotometer in KBr and ¹H NMR spectrum of PARF was recorded in DMSO with TMS as internal standard on Bruker spectrophotometer at 400 MHz. The number average molecular weight (\overline{Mn}) of all the coordination polymers were determined by method reported in earlier communications [14].

Magnetic susceptibility measurements of all the coordination polymers were carried out at room temperature by the Gouy method. Mercury tetrathio cynato cobaltate (II) Hg[Co(NCS)₄], was used as a calibrant Molar susceptibilities were corrected for diamagnetism of component atoms using Pascal's Constant [15]. The solid diffuse reflectance spectra of all the coordination polymers samples were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

Table 2 Thermogravimetric analysis of PARF ligand and its co-ordination polymers

Ligand/ Co-ordination polymers	% Weight loss at different temperature(°C)						
	100	200	300	400	500	600	700
PARF	-	8.87	9.32	23.42	28.08	31.44	34.12
[Cu PARF(H ₂ O) ₂] _n	1.12	8.68	11.82	26.45	30.54	33.42	37.16
[Co PARF(H ₂ O) ₂] _n	1.73	12.62	24.47	38.3	52.13	64.52	67.24
[Ni PARF (H ₂ O) ₂] _n	2.66	15.4	18.52	36.6	52.64	65.49	68.03
[MnPARF(H ₂ O) ₂] _n	2.34	9.96	13.66	34.4	53.22	66.07	68.52
[Zn PARF(H ₂ O) ₂] _n	6.65	15.25	31.3	36.6	55.34	66.11	69.54

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

Antifungal activities

The fungicidal activity of all the compounds was studied at 1000 ppm concentration in vitro. Plant pathogenic organisms used were *penicillium expansum*, *Botrydepladia thiobromine* and *Nigrospora Sp.*. The antifungal activity of ligand and its coordination polymers (1a-e) 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:

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

Where, X = Area of colony in control plate

Y = Area of colony in test plate

Table 3 Antifungal Activity of co-ordination polymers

Compounds	Zone of Inhibition at 1000 ppm (%)		
	<i>Penicillium Expansum</i>	<i>Botrydepladia Thiobromine</i>	<i>Nigrospora Sp.</i>
[Cu PARF(H ₂ O) ₂] _n	71	63	74
[Co PARF(H ₂ O) ₂] _n	62	71	66
[Ni PARF (H ₂ O) ₂] _n	70	69	75
[MnPARF(H ₂ O) ₂] _n	71	72	68
[Zn PARF(H ₂ O) ₂] _n	57	62	71

RESULTS AND DISCUSSION

The synthesis of the bidentate ligand phenylazo of resorciacetophenonel-Formaldehyde polymer has been not reported previously. It was prepared by diazotization reaction of resorciacetophenonel-Formaldehyde polymer with phenyl diazonium salt. The ligand PARF was isolated in form of a light brown powder. It is soluble in organic solvents such as dioxane, DMSO and DMF. The results of elemental analyses of the PARF ligand (Table-1) are agreed with those predicted on the basis of formula.

The IR spectrum of PARF shows a broad band extending from 3400-3100 cm⁻¹ with maximum at 3330 cm⁻¹ attributed to -OH group. The weak bands at 2932cm⁻¹and 2850cm⁻¹ are attributed to asymmetric and symmetric stretching vibrations of methylene groups. The band at 1720 cm⁻¹ due to CO group.

The coordination polymers derived from PARF and metal ions Cu(II), Co(II), Ni(II), Mn(II) and Zn(II) vary in color from light red to brown, These polymers do not melt upto 360°C. On the basis of the proposed structure shown in Scheme1, the molecular formula of the PARF ligand is C₃₂H₂₈N₂O₉, which, upon chelation coordinates with one central metal atom at four coordination sites and two water molecules. Therefore, the general molecular formula of the resulting coordination polymer is given by [M(PARF)₂.2H₂O] as shown in scheme 1. This has been confirmed by the results of elemental analyses of all of the five coordination polymers 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 coordination polymers. Examination of data of the metal content in each polymer (Table I) revealed a 1:2 metal:ligand (M/L) stoichiometry in all of the coordination polymers.

One of the significant differences to be expected between the IR spectrum of the parent ligand and that of its metal coordination polymers is the presence of much broader bands in the region of 3000-3600cm⁻¹ for the coordination polymers, as the oxygen of the O-H group of the ligand forms a coordination bond with the metal ions. This is explained by the fact that water molecule could have strongly coordinated to the polymer samples during its formation. Another noticeable difference is that the band at 1600 cm⁻¹ in IR spectrum of PARF due to the C=N stretching is shifted toward lower frequency. The band at 1420cm⁻¹ in the IR spectrum of PARF assigned to in-plane -OH deformation [16] is shifted toward higher frequency in the spectra of the coordination polymers indicating formation of metal-oxygen bond. This further confirmed by a weak band at 1110 cm⁻¹ corresponding to C-O-M band [16]. All of these features suggest that the structure of the coordination polymers is shown in scheme 1.

The value of the degree of polymerization of all the coordination 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 coordination polymers are given in Table 1. Examination of these data reveals that all coordination polymers except Zn (II) metal ion polymer are paramagnetic while that of Zn(II) metal ion polymer is diamagnetic.

The diffuse electronic spectrum of the [CuPARF(H₂O)₂] coordination polymers shows two broad bands around 15,977 cm⁻¹ and 22,795 cm⁻¹ due to the 2_{T_{2g}} → 2_{E_g} transition while the second may be due to charge transfer, respectively. This suggests a distorted octahedral structure for the [CuPARF(H₂O)₂] polymer. The higher value of μ_{eff} of the [CuPARF(H₂O)₂] polymer supports this view [17,18]. The [NiPARF(H₂O)₂] coordination polymer gave two absorption bands at 15,607 cm⁻¹ and 22,994 cm⁻¹ due to 3_{A_{2g}} → 3_{T_{1g}} (F) and 3_{A_{2g}} → 3_{T_{1g}} (P) respectively. The [CoL(H₂O)₂] polymer shows two absorption bands, at 19,622 and 22,931 cm⁻¹ corresponding to 4_{T_{1g}} (F) → 4_{T_{2g}} and 4_{T_{1g}}(F) → 4_{T_{2g}}(F) transitions, respectively [14]. Thus, the absorption bands of the diffuse reflectance spectra and the values of the magnetic moments (μ_{eff}) indicate an octahedral configuration for the [Ni PARF (H₂L)₂] and [CoPARF(H₂O)₂] polymers [15,19]. The spectrum of [MnPARF(H₂O)₂] shows weak bands at 16,484, 17,699, and 23,159 cm⁻¹ assigned to the transitions 6_{A_{1g}} → 4_{T_{1g}}(4G), 6_{A_{1g}} → 4_{T_{2g}}(4G) and 6_{A_{1g}} → 4_{A_{1g}}, 4_{E_g} respectively, suggesting an octahedral structure for the [MnPARF(H₂O)₂] polymer [19]. As the spectrum of the [ZnPARF(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. This may be due to accelerating by metal oxide which forms in situ. Each polymer lost about 53% of its weight when heated up to 700°C. Inspection of the thermograms of all coordinated polymer samples revealed that all samples suffered appreciable weight loss in the range 150 to 280°C. This may be due to the presence of coordinated water molecules.

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



The antimicrobial activity of PARF and its coordination polymers are presented in Tables 3. The data suggest that all the samples are toxic to fungus. The data also suggest that the % age of fungus is inhibited in the range of 60 to 75% depending upon the biospecies and coordination polymers.

CONCLUSION

The present paper describes the novel bis-ligand having phenylazo of resorciacetophenone-formaldehyde polymer moieties. The bis-ligand afforded the coordination polymers with metal ions. The polymers have moderate thermal stability. All the polymers have good microbicidal activity.

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