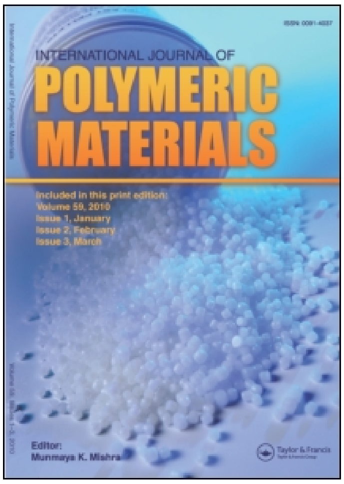

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Coordination Polymers Based on Bis-Ligand-Containing Indole and 8-hydroxyquinoline Moieties

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The novel bis-(bidentate)-ligand 5,5′-(3,3′-(phenyl methylene)bis(1H-indole-3,1-diyl)bis (methylene)diquinolin-8-ol) (PBIQ) was synthesized by condensation of 5-chloromethyl-8-hydroxyquinoline hydrochloride with 3,3′-(phenyl methanediyl) bis (1H-indole) in the presence of a base catalyst. Coordination polymers of this PBIQ bis-ligand were prepared with Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) metal ions. All of these coordination polymers and the PBIQ parent ligand were characterized by elemental analyses, IR, NMR, diffuse reflectance and fluorescence spectral studies, number-average molecular weights ($\overline{Mn}$), magnetic susceptibilities, and by thermogravimetry. The microbicidal activity of all the samples has also been monitored against plant pathogens.

Keywords antibacterial and antifungal activities, bis(bidentate)-ligand, coordination polymers, fluorescence spectral studies, IR, magnetic moment, NMR, number average molecular weight ($\overline{Mn}$), reflectance, thermogravimetric analysis (TGA)

INTRODUCTION

The coordination polymers based on 8-hydroxyquinoline and its derivatives have received attention due to their application in various areas such as in

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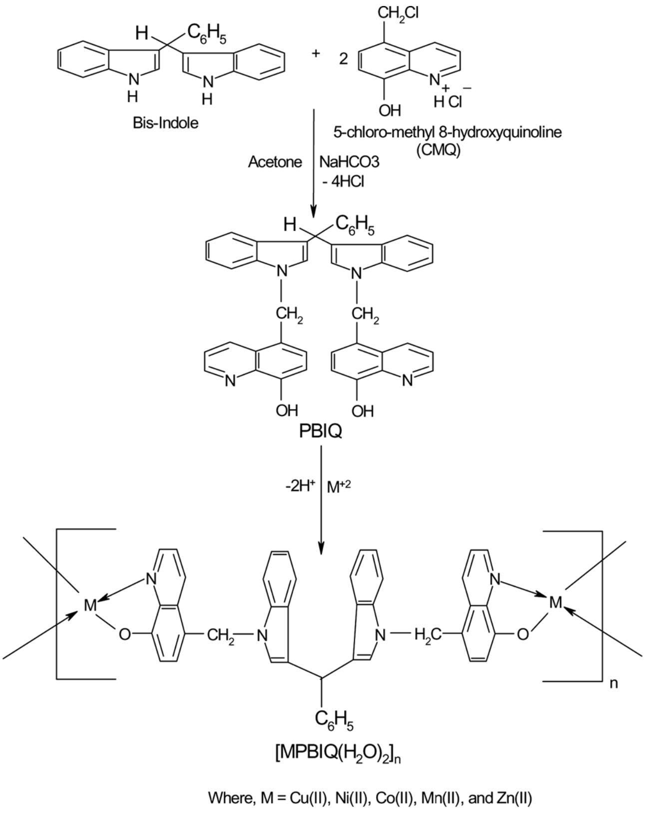
wastewater treatment for metal recovery, in proactive coating, and their potential biological activity [1–9]. A promising method has also been reported for the formation of coordination polymers of enhanced chelating ability by using a bidentate 8-hydroxyquinoline moiety in which two 8-hydroxyquinolinyl end groups are joined by a linear aliphatic bridge, usually at the 5,5′-position [10–12]. The 5-chloromethyl-8-hydroxy quinolinol (CMQ) is the easiest preparable precursor for the preparation of bis-ligand and thus several bis-ligands based on CMQ have been reported for coordination polymers [12,13]. Ion-exchange resins have also been prepared from CMQ and amino or hydrogen functionalized polymers [14,15]. Looking to easy derivatization of CMQ, it is thought worthwhile to prepare the ligand containing both indole and 8-hydroxyquinoline in one molecule. This may afford the compound having not only the metal gripping potentiality but may also have good biological efficacy due to indole moiety [16,17]. Hence, the present article describes the synthesis and characterization of the novel bis(bidentate)-ligand 5,5′-(3,3′-(phenyl methylene) bis (1H-indole-3,1-diyl)bis(methylene)diquinolin-8-ol (PBIQ) and its



Scheme 1: The synthetic route for the coordination polymers.

coordination polymers with Cu(II), Co(II), Ni(II), Mn(II), and Zn(II) metal ions. The synthetic route is shown in Scheme 1.

EXPERIMENTAL

Materials

All chemicals used were of Analar or chemically pure grade.

Procedure

Synthesis of 5,5′-(3,3′-(phenyl methylene)bis(1H–indole-3,1-diyl)bis (methylene)diquinolin-8-ol (PBIQ)

The 5-chloromethyl-8-hydroxyquinoline hydrochloride (m.p. 280°C) was prepared by a method reported in the literature [18]. 3,3′-(phenyl methanediyl) bis (1H-indole) (BI) was also prepared by a method reported in the literature [19,20].

PBIQ was prepared by following a method reported for N-alkylmethylene-8-quinoline [18]. According to this method, a mixture of 5-chloromethyl-8-hydroxyquinoline hydrochloride (23 g, 0.1 mole) and bis indole (32.2 g, 0.1 mole) was refluxed at 75–80°C for 2.5 h with occasional stirring. The resulting solution was then made alkaline with dilute ammonia to precipitate out the PBIQ ligand, which was then filtered and air-dried. The yield was 70% and its melting point was 234–236°C (uncorrected).

Preparation of Coordination Polymers

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

A warm clear solution of PBIQ (4.04fg, 0.01 mol) in 20% aqueous formic acid (200 ml) was added to a solution of copper acetate (1.99 g, 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 coordination polymers thus separated out in the form of a suspension were 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.

MEASUREMENTS

Elemental analyses of PBIQ and its coordination polymers were carried out on a Thermofingan flash 1101EA (Italy). The metal contents of the coordination polymers were determined by decomposing a weighed amount of each coordination polymer followed by complexometric titration with EDTA (disodium ethylenediaminetetraacetate) [21]. Infrared (IR) spectra of all the samples were scanned on a Nicolet-760 FTIR spectrophotometer in KBr. ^{1}H NMR spectrum of PBIQ was recorded in DMSO with TMS as the internal standard on a Brucker spectrophotometer at 400 MHz. The number average molecular weights ($\overline{\mathrm{Mn}}$) of all the coordination polymers were determined by a method reported in earlier communications [13].

Magnetic susceptibility measurements of all the coordination polymers were carried out at room temperature by the Gouy method. Mercury tetrathiocynatocobaltate(II) $Hg[Co(NCS)_4]$, was used as a calibrant. Molar susceptibilities were corrected for diamagnetism of component atoms using Pascal's Constant [22]. The solid diffuse reflectance spectra of all the coordination polymer samples were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

The fluorescence spectral measurement during the addition of metal acetate solution in DMSO to the solution of PBIQ in DMSO was carried out at room temperature on a Hitachi F-4500 fluorophotometer. To prevent any nonlinearity of the fluorescence intensity, isobestic points (256 or 258) of the absorption spectra of PBIQ were chosen as the excitation wavelength.

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

Antibacterial Activities

The antibacterial activity of PBIQ ligand and its coordination polymers was studied against gram-positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative bacteria (*E. coli, Salmonella typhi* and *Klebsiella promioe*) at a concentration of 50 μg/ml, by agar cup plate method. The methanol system was used as a control in this method. The area of the inhibition zone was 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, Botrydepladia thiobromine, Nigrospora sp., Trichothesium sp.*, and *Rhizopus nigricum*. The antifungal activity of the ligand and its coordination polymers were measured for each of these plant pathogenic strains on a potato dextrose agar (PDA) medium. Such a PDA medium contained 200 g potato, 20 g dextrose, 20 g agar, and one liter water. Five-day-old cultures were employed. The compounds to be tested were suspended

(1000 ppm) in a PDA medium and autoclaved at 120°C for 15 min at 15 atm pressure. These media were poured into sterile petri dishes and the organisms were inoculated after cooling the petri dishes. 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 dish.
Y = area of colony in test dish.

RESULTS AND DISCUSSION

The synthesis of the bidentate ligand 5,5′-(3,3′-(phenyl methylene)bis(1H-indole-3,1-diyl)bis(methylene)diquinolin-8-ol) (PBIQ) has been not reported previously. It was prepared by condentation of CMQ and bis-indole. The ligand PBIQ was isolated in the form of a light green powder. It is soluble in organic solvents such as dioxane, DMSO (dimethyl sulfoxide), and DMF. The results of elemental analyses of the PBIQ ligand (Table 1) agree with those predicted on the basis of formula.

The IR spectrum of PBIQ shows a broad band extending from 3400–3100 cm^{-1} with maximum at 3330 cm^{-1} attributed to –OH group. The weak bands at 2932 cm^{-1} and 2850 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of methylene groups (-CH_2-). The bands around at 1420, 1480, 1588, and 1600 cm^{-1} are due to the 8-hydroxyquinoline moiety [23]. In addition to these bands, the IR spectrum of PBIQ has many characteristic absorption bands identical to those that occurred in 5,5′-methylene(8-hydroxyquinoline) (MBQ) [11], as well as bis-indole [19,20]. The ^{1}H NMR (δ ppm) spectrum of PBIQ also show the signals 5.58 (4H, s, CH_2); 5.48 (1H, s, CH); 11.24 (2H, s, OH); and 8.30–6.67 (17H, m, Ar-H,); 8.86–7.6 (6H, s, pyridine ring-H). These features confirm the proposed structure of ligand PBIQ.

The coordination polymers derived from PBIQ and metal ions Cu(II), Co(II), Ni(II), Mn(II), and Zn(II) vary in color from light green to brown. These polymers do not melt up to 360°C. On the basis of the proposed structure shown in Scheme 1, the molecular formula of the PBIQ ligand is $C_{43}H_{32}N_4O_2$, 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 $[M(PBIQ)_2 \cdot 2H_2O]$ as shown in Scheme 1. This has been confirmed by the results of elemental analyses of all 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

Table 1: Analytical data of coordination polymers of PBIQ.

Ligand/ Coordination polymers	Empirical formula	Formula weight	Yield (%)	Color	Elemental analysis Calc. / (Found)				μ_{eff}[a] (B.M)	$(\overline{Mn})$ ± 60	$(\overline{Dp})$
					C	H	N	M			
PBIQ	$C_{43}H_{32}N_4O_2$	636.25	70	Light green	81.10 (81.00)	5.02 (4.95)	8.80 (8.75)	—		—	
(Cu PBIQ($H_2O)_2$)n	$Cu \cdot C_{43}H_{30}N_4O_2 \cdot 2H_2O$	732.79	87	Green	70.41 (70.30)	4.09 (4.00)	7.64 (7.60)	11.53 (11.50)	2.0	4367	6
(CoPBIQ($H_2O)_2$)n	$Co \cdot C_{43}H_{30}N_4O_2 \cdot 2H_2O$	729.18	83	Brown	70.76 (70.70)	4.11 (4.10)	7.67 (7.60)	12.37 (12.35)	3.8	3626	5
(Ni PBIQ ($H_2O)_2$)n	$Ni \cdot C_{43}H_{30}N_4O_2 \cdot 2H_2O$	728.15	89	Green	70.78 (70.75)	4.11 (4.05)	7.68 (7.65)	12.41 (12.40)	3.3	3680	5
(MnPBIQ($H_2O)_2$)n	$Mn \cdot C_{43}H_{30}N_4O_2 \cdot 2H_2O$	725.19	86	Light green	71.15 (71.10)	4.18 (4.15)	7.72 (7.70)	13.19 (12.15)	5.9	4325	6
(Zn PBIQ($H_2O)_2$)n	$Zn \cdot C_{43}H_{30}N_4O_2 \cdot 2H_2O$	735.62	91	Pale yellow	70.14 (70.10)	4.07 (4.00)	7.61 (7.55)	11.25 (11.25)	D	4149	5

[a] Magnetic moment; D is diamagnetic.

ligand as well as coordination polymers. Examination of data of the metal content in each polymer (Table 1) revealed a 1:1 metal:ligand (M/L) stoichiometry in all the coordination polymers. The IR spectra of all of the coordination polymers of PBIQ resemble each other in their general shape. Comparison of the IR spectrum of the parent ligand PBIQ with those of the coordination polymers reveals certain characteristic differences. The broad band at 3400–3100 cm^{-1} for PBIQ has virtually disappeared from the spectra of the polymers. However, the weak band around 3200 cm^{-1} in the spectra of polymers indicates the presence of coordinated water molecules.

One of the significant differences to be expected between the IR spectrum of the parent ligand and those of its metal coordination polymers is the presence of much broader bands in the region of 3000–3600 cm^{-1} for the coordination polymers, as the oxygen of the OH group of the ligand forms a coordination bond with the metal ions. This is explained by the fact that the water molecules could have strongly coordinated with the polymer samples during their formation. Another noticeable difference is that the band at 1600 cm^{-1} in IR spectrum of PBIQ, due to the C=N stetching, is shifted toward lower frequency. The band at 1420 cm^{-1} in the IR spectrum of PBIQ, assigned to in-plane –OH deformation [23], is shifted toward a higher frequency in the spectra of the coordination polymers indicating the formation of a metal-oxygen bond. This is further confirmed by a weak band at 1110 cm^{-1} corresponding to a C-O-M band [23]. All 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 suggests 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 the Zn(II) metal ion polymer are paramagnetic while that of the Zn(II) metal ion polymer is diamagnetic.

The diffuse electronic spectrum of the [CuPBIQ(H_2O)$_2$] coordination polymers shows two broad bands around 15,973 cm^{-1} and 22,791 cm^{-1}. The first is due to the $2_{T2g} \rightarrow 2_{Eg}$ transition while the second may be due to charge transfer. This suggests a distorted octahedral structure for the [CuPBIQ(H_2O)$_2$] polymer. The higher value of μ_{eff} of the [CuPBIQ(H_2O)$_2$] polymer supports this view [24,25]. The [NiPBIQ(H_2O)$_2$] coordination polymer gave two absorption bands, at 15,603 cm^{-1} and 22,990 cm^{-1} due to $3_{A2g} \rightarrow 3_{T1g}$ (F) and $3_{A2g} \rightarrow 3_{T1g}$ (P), respectively. The [CoL(H_2O)$_2$] polymer shows two absorption bands, at 19,618 and 22,927 cm^{-1} corresponding to $4_{T1g}(F) \rightarrow 4_{T2g}$ and $4_{T1g}(F) \rightarrow 4_{T2g}(F)$ transitions, respectively [13]. Thus, the absorption bands of the diffuse reflectance spectra and the values of the magnetic moments (μ_{eff}) indicate an octahedral configuration for the [NiPBIQ(H_2O)$_2$] and [CoPBIQ(H_2O)$_2$] polymers [22,26]. The spectrum of [MnPBIQ(H_2O)$_2$] shows weak bands at

16,484, 17,695, and 23,155 cm^{-1} assigned to the transitions $6_{\mathrm{A1g}} \rightarrow 4_{\mathrm{T1g}}(4\,\mathrm{G})$, $6_{\mathrm{A1g}} \rightarrow {}_{\mathrm{4T2g}}(4\,\mathrm{G})$ and $6_{\mathrm{A1g}} \rightarrow 4_{\mathrm{A1g}},4_{\mathrm{Eg}}$, respectively, suggesting an octahedral structure for the $[\mathrm{MnPBIQ(H_2O)_2}]$ polymer [26]. As the spectrum of the $[\mathrm{ZnPBIQ(H_2O)_2}]$ polymer is not well resolved, it is not interpreted, but its μ_{eff} value shows that it is diamagnetic as expected.

The 8-hydroxy quinoline gives a fluorescence activity [27]. So when fluorescence spectra were determined a very weak fluorescence was observed for PBIQ at $\lambda_{\max} = 434$ nm. When Co(II), Ni(II), Cu(II), Mn(II), and Zn(II) were added to an DMSO solution of PBIQ, the fluorescence spectra were not or slightly changed. However the fluorescence intensity of PBIQ changed greatly with the addition of Zn(II): the fluorescence spectra for metal complexes were observed to be red-shifted at $\lambda_{\max} = 550$ nm. The fluorescence spectra of PBIQ in the presence of several concentration Zn(acetate) are shown in Figure 1.

The TGA data for the polymer samples at different temperatures indicate that the degradation of the polymers is noticeable beyond 300°C. The rate of degradation becomes a maximum at a temperature between 400 and 500°C. This may be due to acceleration by metal oxides which form in situ. Each polymer lost about 55% of its weight when heated up to 700°C. Figure 2 is typical. 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 a coordinated water molecule.

The antimicrobial activity of PBIQ and its coordination polymers are presented in Tables 2 and 3. The data suggest that all the samples are toxic to bacteria or fungus. The data also suggest that the percentage of bacteria or fungus is inhibition is in the range of 55 to 90%, depending upon the biospecies and coordination polymers.

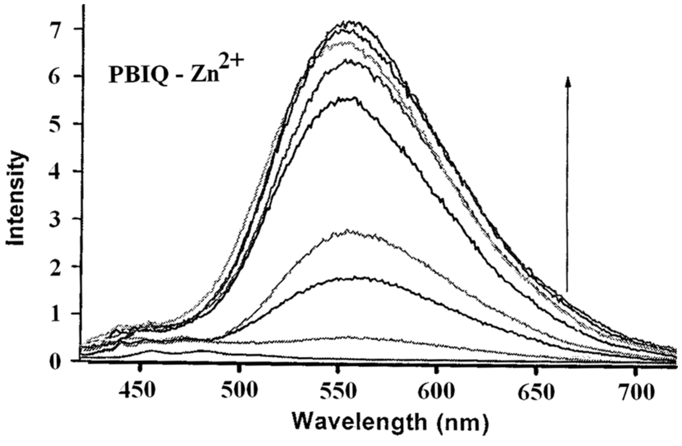


Figure 1: Fluorescence spectra of PBIQ and $\mathrm{Zn^{2+}}$ complexes when excited at 258 nm. (PBIQ) = 1×10^{-5} mol $\mathrm{dm^{-3}}$. ($\mathrm{Zn^{2+}}$) = 0, 1×10^{-6}, 5×10^{-6}, 1×10^{-5}, 2×10^{-5}, 5×10^{-5}, 1×10^{-4}, 2×10^{-4}, 5×10^{-4}, 1×10^{-3} and 1×10^{-2} mol $\mathrm{dm^{-3}}$.

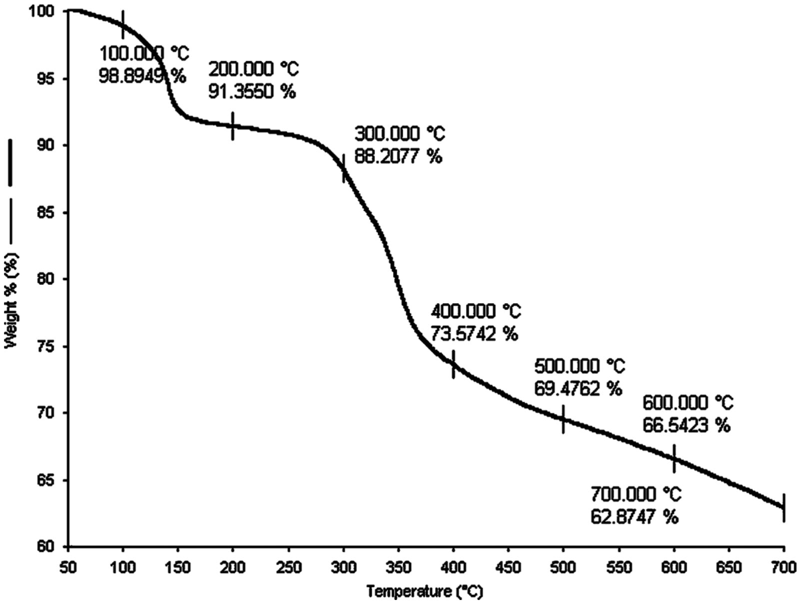


Figure 2: TG thermogram of $(CuPBIQ(H_2O)_2)_n$.

Table 2: Antibacterial activity of coordination polymers.

	Zone of inhibition				
	Gram +ve		Gram −ve		
Compounds	***Bacillus subtilis***	***Staphylococcus aureus***	***Klebsiella promioe***	***Salmonella typhi***	***E. coli***
$(Cu\ PBIQ(H_2O)_2)n$	56	58	56	55	66
$(Co\ PBIQ(H_2O)_2)n$	58	67	58	58	68
$(Ni\ PBIQ\ (H_2O)_2)n$	62	69	72	69	82
$(MnPBIQ(H_2O)_2)n$	73	77	74	84	85
$(Zn\ PBIQ(H_2O)_2)n$	66	62	66	65	64

Table 3: Antifungal activity of coordination polymers.

	Zone of inhibition at 1000 ppm (%)				
Compounds	***Penicillium expansum***	***Botrydepladia thiobromine***	***Nigrospora sp.***	***Trichothesium sp.***	***Rhizopus nigricum***
$(Cu\ PBIQ(H_2O)_2)n$	74	62	71	58	55
$(Co\ PBIQ(H_2O)_2)n$	65	72	65	60	72
$(Ni\ PBIQ\ (H_2O)_2)n$	73	70	77	67	68
$(MnPBIQ(H_2O)_2)n$	72	69	66	81	74
$(Zn\ PBIQ(H_2O)_2)n$	58	59	72	66	70

CONCLUSION

The present paper describes a novel bis-ligand having indole and 8-quinolin moieties. The bis-ligand formed coordination polymers with metal ions. The polymers have moderate thermal stability. All the polymers have good microbicidal activity. The Zn(II) polymer displays an intensive fluorescence spectrum.

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