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Synthesis, characterization and antimicrobial activity studies of 5,5'-(6-(4-bromophenoxy)-1,3,5-triazine-2,4-diyl)bis(azanediyl)diquinolin-8-ol and their co-ordination polymers

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ABSTRACT

Co-ordination polymers containing a novel bis ligand namely 5,5'-(6-(4-bromophenoxy)-1,3,5-triazine-2,4-diyl) bis (azanediyl)diquinolin-8-ol (PBDQ-3) has been prepared and characterized. The coordination polymers based on this bis ligand with transition metal ions like Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) were prepared and studied for their metal: ligand (M/L) ratio, IR and reflectance spectroscopies, magnetic properties, thermogravimetry. The microbicidal activities of all the samples have been monitored against plant pathogens.

Keywords: 5-Amino 8-hydroxyquinoline, antibacterial and antifungal activities, coordination polymers, IR, NMR, reflectance spectra and TGA.

INTRODUCTION

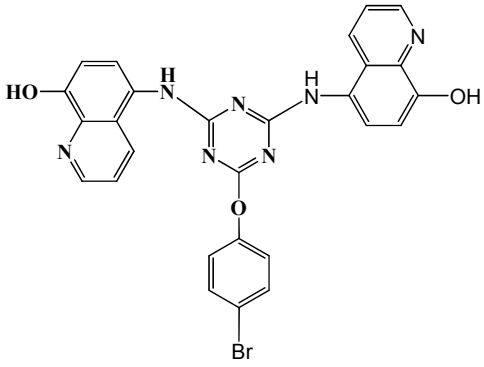
In recent years, the study on Co-ordination polymer has made much progress[1-3]. 8-quinolinol is well known as an analytical reagent [4,5]. Its various derivatives are very useful in pharmaceuticals [6]. Several azo dyes based on 8-quinolinol are also reported for dyeing of textiles as well as their chelating properties [7,8]. A promising method has 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 with bridge, usually at the 5,5'-position [9–11]. The 5–Amino 8-hydroxy quinolinol is the easiest preparable precursor for the preparation of bis-ligand and thus bis-ligands based on 5–Amino 8–hydroxyquinoline have been reported for coordination polymers [11,12]. Ion exchange resins have also been prepared from 5–amino 8–hydroxyquinoline and amino or hydroxyl functionalized polymers [13,14]. We are also synthesized compound of PBDQ-3. Hence, In this paper, we report newly compound of in continuous of this work [15-17] the present paper deals with synthesis, characterization and chelating properties of ligand (PBDQ-3) and its co-ordination polymers are shown in **Scheme 1**.

MATERIALS AND METHODS

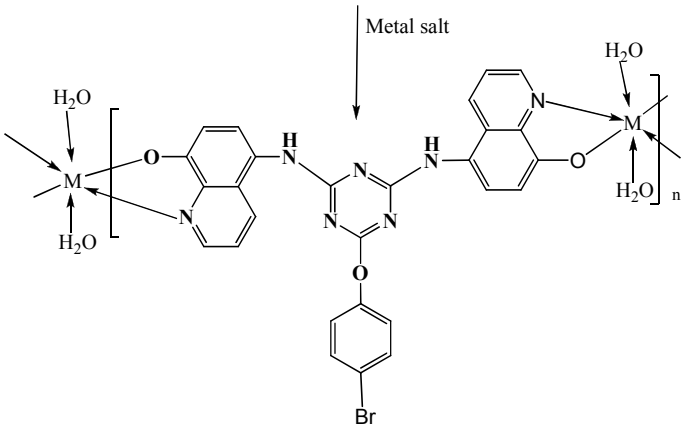
Materials:
All the chemicals used were of pure grade. The synthesis 5,5'-(6-(4-bromophenoxy)-1,3,5-triazine-2,4-diyl) bis(azanediyl)diquinolin-8-ol (PBDQ-3) was carried out in two steps. 5–Amino 8 –hydroxyl quinoline was prepared according to a literature method [18].

Synthesis of 5,5'-(6-(4-bromophenoxy)-1,3,5-triazine-2,4-diyl) bis(azanediyl)diquinolin-8-ol (PBDQ-3)
To a suspension of 5–amino 8-hydroxyquinoline (3.2 g, 0.02 mol), 2,4-dichloro-6-(4-bromophenoxy)-1,3,5-triazine (3.19 g, 0.01 mol) in an acetone–water mixture was added. Then K_2CO_3 (0.02 mol) was added as an acid accepted [19]. The resulting mixture was refluxed for 3 hr with occasional shaking. The resulting suspension, which

contained a precipitate, was neutralise and then filtered. The solid product was collected and dried to give PBDQ-3 (69% yield). The product melted with decomposition at above 242^{0}C (uncorrected).



5,5'-(6-(4-bromophenoxy)-1,3,5-triazine-2,4-diyl)bis(azanediyl)diquinolin-8-ol



$(PBDQ\text{-}3\text{-}M^{+2})_n$ polymers

where,M= Cu(II),Mn(II),Ni(II),Co(II),Zn(II)

Synthesis of coordination polymer

A solution of metal (0.01 mol) in aqueous formic acid was added drop wise to a solution of PBDQ-3 (0.01 mol) in aqueous formic acid with stirring. The reaction mixture was heated on a water bath for 0.5 hr. The reaction mixture was made alkaline by the addition of dilute aqueous ammonia until the precipitation was completed. The polymer separated out in the form of a suspension and was digested on a boiling water bath for about 1 hr. Finally, the resultant solid was collected by filtration and washed with hot water, dimethylformamide (DMF), and then acetone. The polymer [PBDQ-3-M^{+2}] (resultant product) was air-dried.

Antimicrobial Activities

Antibacterial activity and antifungal activities of PBDQ-3 ligand and its coordination polymers were studied against gram-positive bacteria (*Bacillus subtilis* and *staphylococcus aureus*) and gram-negative bacteria (*E.coli, salmonella typhi* and *klebsiella promioe*) and plant pathogenic organisms used were *Aspergillus niger, Candida albicans, Trichoderma harsianum., Mucor mucedo.*, and *Botrytis cinerea* at a concentration of 50 μg/ml by agar cup 520 plate method. The methanol system was used as control in this method. The area of inhibition of zone was measured in mm.

MEASUREMENT

The C, H, N contents of metal were determined by TF-Flash-1101 EA. The metals contents of metal chelates were determined volumetrically by Vogel's method [20]. To a 100mg chelate sample, 1ml of HCl, H_2SO_4 and $HClO_4$ each were added and then 1 gm of $NaClO_4$ was added. The mixture was evaporated to dryness and the resulting salt was dissolved in double distilled water and diluted to the mark. From this solution the metal content was determined by titration with standard EDTA solution. Infrared spectra of the synthesized compounds were recorded on Nicolet 760 FT-IR spectrometers. NMR spectrum of ligand was recorded on a Brucker spectrophotometer at 400 MHz. Magnetic susceptibility measurement of the synthesized coordination polymer was carried out on Gouy Balance at

room temperature. The electronic spectra of coordination polymer in solid were recorded at room temperature. MgO was used as a reference. Antimicrobial activity of all the samples was monitored against various gram positive(+) and gram negative(-) organisms, following the method reported in the literature [21,22].

RESULTS AND DISCUSSION

The synthesis bis-ligand of 5,5'-(6-(4-bromophenoxy)-1,3,5-triazine-2,4-diyl) bis(azanediyl) diquinolin-8-ol (PBDQ-3) was performed by a simple nucleophilic substitution reaction of ,4-dichloro-6-(4-bromophenoxy)-1,3,5-triazine and 5-amino 8-hydroxy quinoline. The resulting PBDQ-3 ligand was an amorphous colour powder. The ligand is characterized by elemental analysis as well as ^{1}H NMR and IR spectroscopic techniques as given below.

Elemental Analysis

The analytical and physical properties of the ligand and its coordination polymers are listed in Table-1. The metal and C, H, N contents of bis-ligand and coordination polymer (its coordination polymer) are shown in Table-1 and are also consistent with the predicted structure. The results show that the metal: ligand (M: L) ratio for all divalent metal chelate is 1:1.

Table-1:Analysis of PBDQ-3 ligand and its metal chelates

Empirical Formula	Mol. Cal g/mol	Yield %	Elemental Analysis (%) Found(Calcd)			
			C	H	N	M
$C_{27}H_{18}N_7O_3Br$	568	69	57.04(57.0)	3.17(3.1)	17.25(17.2)	--
$C_{27}H_{16}N_7O_3Br\ Cu^{+2}.2H_2O$	665.5	66	48.68(48.60)	3.00(3.00)	14.72(14.70)	9.54 (9.50)
$C_{27}H_{16}N_7O_3Br\ Ni^{+2}.2H_2O$	657	70	49.31(49.3)	3.04(3.00)	14.91(14.90)	8.37 (8.30)
$C_{27}H_{16}N_7O_3Br\ Co^{+2}.2H_2O$	661	78	49.01(49.0)	3.02(3.00)	14.82(14.80)	8.93 (8.90)
$C_{27}H_{16}N_7O_3Br\ Mn^{+2}.2H_2O$	661	72	49.01(49.0)	3.02(3.00)	14.82(14.82)	8.93(8.90)
$C_{27}H_{16}N_7O_3Br\ Zn^{+2}.2H_2O$	667	77	48.57(48.50)	2.99(2.90)	14.69(14.60)	9.74(9.7)

Table-2: Spectral feactures and magnetic moment of metal chelates

Metal Chelates	μ_{eff} BM	Electronic Spectral Data cm^{-1}	Transitions	IR spectral feactures Common for all cm^{-1}
PBDQ-3 -Cu^{+2}	1.73	24385 15622	C.T $^2Eg \rightarrow {}^2T_2g$	1602 Quinoline Moiety 1508, 1427, 1481 3450, 3550 -NH 3800-2600 broad OH-phenolic 1090, 1280 C-O-M **(Stretching)** 1220 O-M 550 M-N 490
PBDQ-3 -Ni^{+2}	2.82	24116 15192 8000	$^3A_2g \rightarrow {}^3T_1g(P)$ $^3A_2g \rightarrow {}^3T_1g(F)$ $^3A_2g \rightarrow {}^3T_2g$	
PBDQ-3 -Co^{+2}	4.87	24125 19720 8669	$^4T_1g(F) \rightarrow {}^4A_2g$ $^4T_1g(F) \rightarrow {}^4T_1g(P)$ $^4T_1g(F) \rightarrow {}^4T_2g$	
PBDQ-3 -Mn^{+2}	5.91	23975 17644 15468	$^6A_1g \rightarrow {}^6A_1g\ (^4Eg)$ $^6A_1g \rightarrow {}^4T_2g(^4G)$ $^6A_1g \rightarrow {}^4T_1g(^4G)$	
PBDQ-3 -Zn^{+2}	Diamagnetic		-----	

IR Analysis

The important infrared spectral bands and their tentative assignments for the synthesized ligand H_2L and its coordination polymers were recorded as KBr disks and are shown in Table-2.

IR spectrum of ligand of PBDQ-3 show a broad band extended from 3800 to 2600 cm^{-1} which might be responsible to phenolic -OH group bonded to N atom of 8-hydroxyquinoline moieties[23].

Several bands appeared between 1500 and 1600 cm^{-1} region may arised from aromatic breathing and 3450 to 3550 cm^{-1} for –NH group. The IR band at 1580 cm^{-1} (C=N of 8-quinolinol system) of PBDQ-3 ligand shifted to higher frequency side 1600 cm^{-1} in the spectra of the metal complexes indicating involvement of nitrogen in the complexes formation[24], whereas the band at 1220 cm^{-1} in the IR spectrum of PBDQ-3 assigned to in-plane –OH deformation was shifted towards higher frequency in the spectra of the coordination polymer due to the formation of the M–O bond [25]. This was further confirmed by a weak band at 1090 cm^{-1} corresponding to C–O–M stretching, while bands around 550 and 490 cm^{-1} correspond to the M→ N vibration [26].

^{1}H NMR Analysis

The structural analysis of the ligand (PBDQ-3) was determined by ^{1}H NMR spectrum.

NMR(DMSO)

6.8 – 8.8 ppm (14H)	Multiplet Aromatic
5.3 ppm (1H)	Singlet (OH)
4.0 ppm (1H)	Singlet (NH)

Magnetic Measurements

Magnetic moments of coordination polymers are given in Table-2. The diffuse electronic spectrum of Cu^{+2} complex shows two broad bands 15622 and 24385cm^{-1}. The first band may be due to a $^2Eg \rightarrow {}^2T_2g$ transition, while the second band may be due to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the Cu^{+2} metal complex [27,28]. The Co^{+2} metal complex gives rise to two absorption bands at 21270 cm^{-1}, 18700 cm^{-1} and 11500 cm^{-1} which can be assigned $^4T_1g(F) \rightarrow {}^4A_2g$, $^4T_1g(F) \rightarrow {}^4T_1g(P)$ and $^4T_1g(F) \rightarrow {}^4T_2g$ transitions, respectively. These absorption bands and the μ_{eff} value indicate octahedral configuration of the Co^{+2} metal complex [29,30]. The spectrum of Mn^{+2} polymeric complex comprised three bands at 24125cm^{-1}, 19720cm^{-1} and 8669 cm^{-1}. These bands may be assigned to $^6A_1g \rightarrow {}^6A_1g(^4Eg)$, $^6A_1g \rightarrow {}^4T_2g(^4G)$ and $^6A_1g \rightarrow {}^4T_1g(^4G)$ transitions, respectively. The high intensity of the bands also suggests that they may have some charge transfer character. The magnetic moment is found to be lower than normal range. In the absence of low temperature measurement of magnetic moment, it is difficult to attach any significance to this. As the spectrum of the metal complex of Ni^{+2} show three distinct bands at 24116cm^{-1}, 15192cm^{-1} and 8000 cm^{-1} are assigned as $^3A_2g \rightarrow {}^3T_1g(P)$, $^3A_2g \rightarrow {}^3T_1g(F)$ and $^3A_2g \rightarrow {}^3T_2g$ transition, respectively, suggesting the octahedral environment for Ni^{+2} ion. The observed μ_{eff} values in the range 1.73–5.91 B.M are consistent with the above moiety [31,32].

Thermal Studies

The TGA data for the Co-ordination polymers samples at different temperatures indicate that the degradation of the co-ordination polymers is noticeable beyond 390^0 C. The rate of degradation becomes a maximum at a temperature between 410 and 490^0 C. This may be due to acceleration by metal oxides, which form in situ. Each polymer lost about 60% of its weight when heated up to 700^0 C. Inspection of the thermograms of all coordinated polymer samples revealed that all samples suffered appreciable weight loss in the range of 150 to 290^0 C. This may be due to the presence of a coordinated water molecule.

Antimicrobial Activities

The antibacterial and antifungal data obtained from analysis are shown in Table-3 and Table-4, respectively. The increase in antimicrobial activity may be considered in light of Overtone's concept [33] and Tweedy's chelation theory[34]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage only of lipid-soluble materials due to which liposolubility is an important factor controlling the antimicrobial activity. On complexation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of -electrons over the whole chelate ring and enhances the lipophilicity of the coordination polymers. This increased lipophilicity enhances the penetration of the coordination polymer into lipid membranes and blocks the metal binding sites in the enzymes of microorganisms. These coordination polymers also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organisms.

Table-3:Antibacterial activity of coordination Polymers

Compounds	Gram +ve		Gram –ve		
	Bacillus Subtilis	*Staphylococcus Aureus*	*klebsiella promioe*	*Salmonella Typhi*	*E. coli*
PBDQ-3	22	23	25	20	21
(Cu PBDQ-3 $(H_2O)_2)_n$	32	34	30	30	28
(Co PBDQ-3 $(H_2O)_2)_n$	32	26	24	20	24
(Ni PBDQ-3 $(H_2O)_2)_n$	30	26	26	25	26
(Mn PBDQ-3 $(H_2O)_2)_n$	30	32	24	26	25
(Zn PBDQ-3 $(H_2O)_2)_n$	28	32	30	32	25

Coordination polymers exhibit higher biocidal activity as compared with the free ligands; from the comparative analysis shown in Table-3 and Table-4, respectively, it is observed that all the coordination polymer are more potent biocidals than the free ligands. From the data obtained it is clear that Cu (II) is highly active among the coordination polymer of the respective metal.

Table-4:Antifungal activity of coordination Polymers

Compounds	Zone of Inhibition at 1000 ppm (%)				
	Aspergillus Niger	*Candida albicans*	*Trichoderma harsianum*	*Mucor mucedo*	*Botrytis cinerea*
PBDQ-3	32	25	28	23	25
(Cu PBDQ-3 $(H_2O)_2)_n$	44	30	36	39	25
(Co PBDQ-3 $(H_2O)_2)_n$	25	32	32	28	31
(Ni PBDQ-3 $(H_2O)_2)_n$	30	27	30	27	24
(Mn PBDQ-3 $(H_2O)_2)_n$	32	27	32	26	30
(Zn PBDQ-3 $(H_2O)_2)_n$	30	22	32	24	28

CONCLUSION

The present work in the conclusions with coordinaly polymer based of bis-8HQ has been performed successfully. Through bis-8HQ versatile pharmaceutical active molecule. A series of coordination polymers from these bis-ligands with transition metals have been prepared and characterized for their spectral and magnetic properties. All the synthesized coordination polymers were monitored for their antimicrobial activity. The coordination polymers are toxic for gram-negative bacteria (*E.coli*, *samonella typhi* and *klebsiella promioe*) and gram-positive bacteria (*Bacillus subtilis* and *staphylococcus aureus*), and plant pathogenic organisms (fungi) used were *Aspergillus niger, Candida albicans, Trichoderma harsianum, Mucor mucedo,* and *Botrytis cinerea* microorganisms. It is found that the coordination polymers were more toxic for one or more bacterial strains, thus introducing a novel class of metal-based bactericidal agents. The information as octahedral geometry of the coordination polymer was obtained from their electronic and magnetic moment values.

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