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Discovery

Polychelates of Selected Lanthanides: La Pr Nd Sm Gd Tb Dy. with 2,4–dihydroxybenzophenone resin and their behavior as an antimicrobial agents

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ABSTRACT

The polymeric ligand (resin) was prepared from 2,4-dihydroxybenzophenone with 1,3-butane diol in presence of polyphosphoric acid as a catalyst at 160°C for 13 h. The poly[(2,4-dihydroxybenzophenone) 1,3-butylene] H(DHBP-1,3-BD) forms, 1:2 metal:ligand chelates with La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), and Dy(III). The polymeric ligand and its polychelates were characterized on the basis of elemental analyses, electronic spectra, magnetic susceptibilities, thermogravimetric analysis, and results of NMR and IR spectroscopy. The molecular weight was determined using number average molecular weight ($\overline{Mn}$) by the vapour pressure osmometry (VPO) method. All the polychelates are paramagnetic in nature. The resin and their polychelates were tested for antimicrobial activity against *E. coli, B. substilis, and S. aureus* (bacteria) and *S. cerevisiae* (yeast). It is found that the synthesized polychelates can be used as antibacterial agents.

Key words: poly[(2,4-dihydroxybenzophenone),1,3-butylene]; lanthenides (III); polychelates; thermal study; antimicrobial activity.

Abbreviation: B.M.-Bohr magneton; DHBP- 2,4-dihydroxybenzophenone; [DHBP-1,3-BD]n- poly[(2,4-dihydroxybenzophenone)butylene]; DMF- Dimethyl formamide; DMSO- dimethyl sulphoxide; IR-infrared; MHz- megahertz; NMR-nuclear magnetic resonance; $[\overline{Mn}]$ number average molecular weight; THF- tetrahydrofuran; VPO- vapour pressure osmometry. TGA-thermogravymetric analysis.

1. INTRODUCTION

The first study on metallo-polymer compounds was carried out by Arimoto and Haven in 1955 [Arimoto and Haven, 1995]. These researchers synthesized vinyl ferrocine by free radical polymerization. Recently, several coordination polymers have been prepared from aromatic and aliphatic polymers containing pendant functional groups which act as a chelating group in binding polyvalent metal ions [Joshi J.D., Patel N.B., 2006]. Chelating polymers have gained more interest, due to their applications in bioinorganic industry, water purification and selective removal of waste materials in nuclear plants [Mizuta T., Onishi M.,2000, Rivas B L., Maturana H.A.,1998, Tusa H., Paavola A.,2001], pollution control [Orazzhanova L.K., Yashkarova M.G.,2003], selective removal of metals from dilute solutions [Atia A.A., Donia A.M.,2005, Jacob A.M., Yizhak M.,1997], as protective coatings on metal surfaces, as a priming layer or coating on paper, fibre, and fabrics, and selective binding of enzymes [Geckeler K.E., Rongnong Z.,1994, Alelah A., Moet A.,1990]. The chelates of phenols possess interesting activities in microbial growth inhibition or acceleration. The metal polychelates depending on their structures can be used as catalysts, high-temperature and flame resistant fibers, semi conductors, ion exchanging resins, and in agricultural purposes [Vankrevelen D.W, 1972, Dentini M., Santis P.,1974, Patel M.N., Patel J.B.,1983]. In general, organic polymers have some limitations; therefore, their applications are also limited to some extent. When organic polymers are used as adhesive coatings and exposed to the atmosphere, can be broken down on heating in air most of the time and some of them may be infected by microorganisms such as bacteria and fungi [Nho Y.C., Park J.S., 1993]. These problems can be solved by the addition of metal ions in the polymeric system [Jayakumar R., Rajkumar M., 2002], which changes the physicochemical, as well as, biological properties of the polymers [Belfiore L.A., Curdie M.P. M., 2001]. Transition and inner transition metal ions form coordination polymers which are thermally stable and impart both high flexibility due to presence of the organic moiety and thermal stability due to the presence of the inorganic elements in the same polymeric skeleton. Therefore, due to their superiority over organic polymers, coordination polymers are widely used in scientific and industrial applications. Polymeric coordinating reagents are the novel types of substances possessing a combination of physical properties of a polymer and chemical properties of the attached reagent. In the present work, synthesis, characterization, thermal, and antimicrobial studies of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) polychelates with poly[(2,4-dihydroxybenzophenone) 1,3-butylene] have been carried out. It is observed that the polychelates are thermally less stable than the polymeric ligands but show good bactericidal activity compared to the parent polymeric ligand. Thus, looking into the very effective behaviours of lanthanide polychelates may prove some of their excellent antibacterial capabilities. This helps us to guide the basic user to the effects of these metal ions in chemical, biological, soil, and marine systems.

2. MATERIALS AND METHODS

2,4-diHydroxybenzophenone (DHBP, Aldrich), 1,3-butanediol(PG, Aldrich), polyphosphoric acid (Lancaster) (PPA), methanol, (ARGrade), hydrated metal acetates of lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium and dysprosium (Merck).

Synthesis of resin

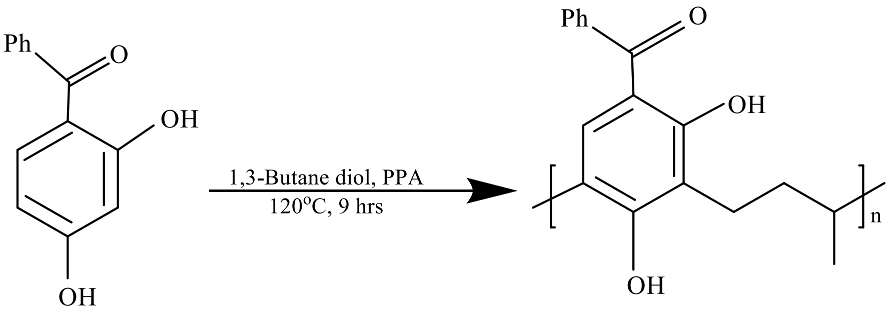
To a well stirred and ice-cooled mixture of 2,4 dihydroxy benzophenone(12.84 gm, 0.06 mol) and 1,3-butane diol (5.32 mL, 0.06 mol), polyphosphoric acid (PPA) (20 gm) was added slowly with stirring as a catalyst (Scheme 1). The reaction mixture was left at room temperature for half an hour and condensed on an oil bath at 155°C for 10 hrs. The reaction mixture was then cooled, poured on crushed ice and left overnight. A brown solid was separated out. It was collected by filtration and washed with cold water and methanol to remove unreacted acid and monomer. The synthesized resin was further purified by reprecipitation from dimethyl formamide with water for three times and dried at 60°C temperature. The purified resin was brown in color. D.P.>Yield 40.50.%.

Synthesis of polychelates

All polychelates were synthesized as reported earlier [Joshi J.D., Patel N.B., 2006]. Lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium, and dysprosium acetates (BDH) of AR grades were used in the preparation of the polychelates. The polymeric ligand (2.68 g, 0.01 mol) was dissolved in DMSO (50 mL). The metal acetate (0.005 mol) was also dissolved in DMSO (25 mL). The hot and clear solution of the metal acetate was added with constant stirring to the hot and clear solution of ligand. A dark red coloured product separated out immediately. The suspension was digested on a water bath at 90 °C for 2 h and then filtered. The solid was washed with hot DMSO to remove unreacted metal acetate. Finally, the product was washed with acetone and dried at 60°C for 24 h. The yield of each polychelate obtained was between 60-80%.

Analytical Procedures

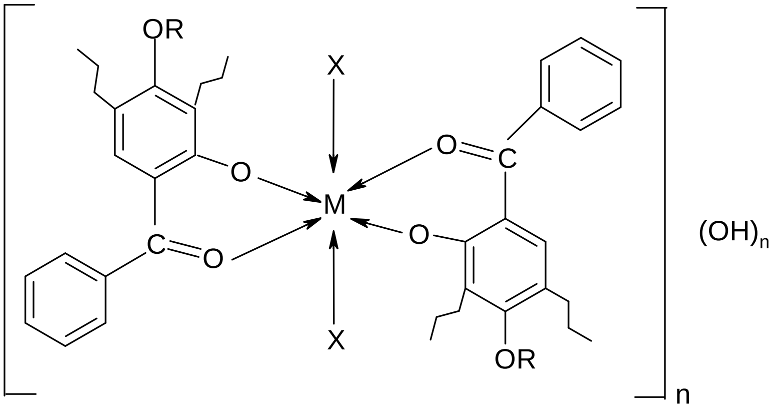
Carbon and hydrogen were analyzed with a Coleman C, H, N analyzer (Table 1). The metal content was determined by titration with standard EDTA after decomposing the polychelates with a mixture of concentrated hydrochloric acid, sulphuric acid and perchloric acid in a 5:2:3 mL ratio, respectively. Magnetic susceptibilities were measured by the Gouy method at 25 °C. The IR spectra of the samples in KBr pellets were recorded on a model 938 Perkin Elmer Spectrophotometer. Thermal measurements were performed using a Du Pont thermal analyzer at heating rate of 10°C min-1. 1HNMR spectra were determined in DMSO-d6 by FTNMR spectrophotometer using TMS as an internal reference. The number average molecular weight ($\overline{Mn}$) of polymeric ligand (resin) sample was measured by a VPO (Knaur, Germany) using DMF as a solvent at 90°C and polystyrene (PS) as a calibrant.



DHBP

DHBP-1,3 BD

Scheme 1
Synthesis of DHBP-1,3 BD resin



Scheme 2
Proposed geometry of polychelates M=La^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Tb^{III}, Dy^{III}; X=H_2O ; R=H

Table 1

Analytical Data of DHBP- 1,3 BD resin and its Polychelates

Compound	Formula weight of Repeating unit	% Found (Calculated)			μ$_{eff}$ (B.M)
		M	C	H	
(DHBP-1,3 BD)$_n$ [$C_{17}H_{16}O_3$]$_n$	268		76.18 (76.10)	6.07 (6.01)	
{[La(DHBP-1,3 BD)$_2$(H_2O)$_2$].OH}$_n$ [$C_{34}H_{35}O_9La$]$_n$	726	19.14 (19.11)	56.15 (56.20)	4.80 (4.85)	
{[Pr(DHBP-1,3 BD)$_2$(H_2O)$_2$].OH}$_n$ [$C_{34}H_{35}O_9Pr$]$_n$	728	19.30 (19.34)	56.01 (56.05)	4.81 (4.84)	
{[Nd(DHBP-1,3 BD)$_2$(H_2O)$_2$].OH}$_n$ [$C_{34}H_{35}O_9Nd$]$_n$	731	19.60 (19.70)	55.75 (55.79)	4.85 (4.82)	
{[Sm(DHBP-1,3 BD)$_2$(H_2O)$_2$].OH}$_n$ [$C_{32}H_{31}O_9Sm$]$_n$	738	20.36 (20.37)	55.35 (55.33)	4.80 (4.78)	
{[Gd(DHBP-1,3 BD)$_2$(H_2O)$_2$].OH}$_n$ [$C_{34}H_{35}O_9Gd$]$_n$	744	21.15 (21.11)	54.90 (54.82)	4.75 (4.73)	
{[Tb(DHBP-1,3 BD)$_2$(H_2O)$_2$].OH}$_n$ [$C_{34}H_{35}O_9Tb$]$_n$	746	21.36 (21.28)	54.62 (54.69)	4.70 (4.72)	
{[Dy(DHBP-1,3 BD)$_2$(H_2O)$_2$].OH}$_n$ [$C_{34}H_{35}O_9Dy$]$_n$	750	21.60 (21.66)	54.50 (54.43)	4.72 (4.70)	

DHBP-1,3 BD = poly[(2,4dihydroxyenzophenone)1,3-butylene]

Table 2

Infrared spectra of the polymeric ligand and its polychelates (cm-1)

Compound	V (O-H)	V- (-CH2) Bridge	V (C=O) Chelate	V (C=C) Aromatic	V (Ar-O-R) Ether linkage	V Penta substituted-Ph Ring	(M-OH)
(DHBP-1,3-BD)n	3200-3400 (b)	2930 (w)	1655 (s)	1490 (m)	1270 (m)	890 (m) _	___
[La(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	3200-3400 (b)	2925 (s)	1625 (s)	1500 (m)	1265 (m)	900 (m)	465 (w)
[Pr(DHBP -1,3-BD) $_2$ (H2O)$_2$]n	3200-3400 (b)	2925 (w)	1635 (m)	1480 (m)	1265 (m)	900 (m)	470 (w)
[Nd(DHBP -1,3-BD) $_2$ (H2O)$_2$]n	3200-3400 (b)	2930 (w)	1620 (s)	1495 (m)	1260 (m)	890 (m)	470 (w)
[Sm(DHBP -1,3-BD) $_2$ (H2O)$_2$]n	3200-3400	2925 (w)	1630 (s)	1480 (m)	1265 (m)	890 (m)	465 (w)

	(b)						
[Gd(DHBP -1,3-BD)$_2$(H2O)$_2$]n	3200-3400 (b)	2925 (w)	1625 (m)	1485 (m)	1270 (m)	895 (m)	465 (m)
[Tb(DHBP -1,3-BD)$_2$(H2O)$_2$]n	3200-3400 (b)	2935 (w)	1635 (m)	1480 (m)	1270 (m)	900 (m)	470 (m)
[Dy(DHBP -1,3-BD)$_2$(H2O)$_2$]n	3200-3400 (b)	2930 (w)	1610 (m)	1485 (m)	1265 (m)	895 (m)	465 (m)

3. RESULTS AND DISCUSSION

3.1. Infrared Spectra

Resin

The IR spectroscopy showed a broad band appearing in the range 3200-3400 cm-1 due to -O-H stretching in the polymeric compound. The presence of -O-H groups originate from the phenolic hydroxyl groups and water absorbed by resins. The major contribution to this particular band comes from the absorbed water. The band due to -OH stretching is less broad in the IR spectra of the polymer, which suggests the absence of absorbed water. Hence, this band may largely be due to the presence of hydroxyl groups. The strong band of -C=O around 1635-1655 cm-1 which suggests an orthohydroxy aryl compound (intramolecular hydroxy bonding) and a weak band of -OH at 2740 -2765 cm-1 indicates an intramolecular hydrogen bond. The band in the range of 1250 ±10 cm-1 is attributed to -OH in plane bendings. The bands observed around the 1480-1510 cm-1 region are attributed to -C=C stretching (aromatic) vibrations. The band in the region of 2940 10 cm-1 is attributed to the -CH2 groups. The band in the region 1020-1170 cm-1 is attributed to -C-H in plane bending. In the spectra of each of the resin, a band observed around 890 10 cm-1 is due to isolated hydrogen on the phenolic moiety repeating unit of the polymer chain. The band around 860 – 900 cm-l may be attributed to the l, 2, 3, 4, and 5-penta substituted phenyl ring, having only one isolated H atom. The strong bands observed around the 1265 10 cm-l region is attributed to the Ph-O-CH3 ether linkage. The presence of a band around 860-900 cm-1 suggests that the linkage in the resin chain occurs through 3 and 5 positions of the monomer. The important IR frequencies of the polymeric ligand and its polychelates are shown in Table 2.

Polychelate

The -C=O stretching frequency in all the polychelates is observed around 1655-1635 cm-1, appearing at a lower frequency of 20 to 40 cm-1, which suggests -C=O M coordination [Nursen S., Ebru K.,2006] as shown in Figure 1. In the polychelates the bands observed around 465-480 and 565 cm-1 indicate the M-O bond, suggesting that phenolic and carbonyl groups are involved in bond formation with the metal ion. The proposed structure of the polymeric ligand is shown in Scheme 3.

3.2. ^{1}H NMR Spectra

The ^{1}H NMR spectrum of 2,4-dihydroxybenzophenone (DHBP), poly[(2,4-dihydroxybenzophenone) 1,3-butylene] H(DHBP-1,3-BD) and polychelates (M-DHBP-1,3-BD) are presented in Table 3. DHBP shows signals at =12.48, 3.85, and 6.4- 7.51 ppm which are due to -OH group ortho to (Ar- C=O), and aromatic ring protons, respectively. H(DHBP-BD) shows signals at = 12.66, 3.85 and 6.50-7.65 ppm which are due to –OH groups ortho to Ar-C=O, Ar-C=O and aromatic ring protons, respectively [Silverstein R.M., Webster, F.X.,1998]. One broad signal at = 1.1-3.12 ppm appears as shown in Figure 2. In all the polychelates the signal of the –OH group is completely disappeared which suggests that the bond formation takes place through the -OH groups ortho to Ar-C=O. Also, aromatic protons were shifted downfield by 0.14-1.32 ppm in the NMR spectra of the polychelates due to the deshielding effect of the metal ion on the ligand protons.

3.3. Vapour Pressure Osmometry

The number average molecular weight ($\overline{Mn}$) of the polymeric ligand (resin) sample were estimated by vapour pressure osmometry (VPO) [Eliassi A., Modarress H., 2001] (Table 4). Dilute solutions of polymer samples were prepared to determine n. Four concentrations 2.21, 4.42, 6.63, and 8.84 g.kg^{-1} were prepared in DMF. The VPO experiment was carried out for each concentration and the corresponding bridge output reading in millivolts was noted. The plot of millivolts vs. concentration was drawn. With the help of the slope and the VPO constant K, the n value of the polymer was calculated and found as n = 1029 gmol^{-1}.

3.4. Thermogravimetric Analyses

Thermogravimetric analyses (TGA) data of the resin and polychelates are presented in Table 5. These data revealed that the rate of decomposition of the polychelate is higher than that of the parent resin, suggesting that there may be strong intramolecular hydrogen bonding in the polymer. The absence of such hydrogen bonding in polychelate favours the reduction in thermal stability of polychelates compared to the parent resin. It seems that metal ions accelerate the decomposition of the polychelates. The thermal stability of the ligand and metal chelates is in the order of ligand > polychelates. The presence of water molecules considered as the number of water coordination. According to Nikolaev et al. [Nikolaev V.A., Logvinenko L.T., 1969] water elimination above 150°C may be due to its coordination to the metal ion. The nature of the water molecules observed in the complexes is water of coordination, which is supported by cumulative weight loss percentage and thermal data presented in Table 5.

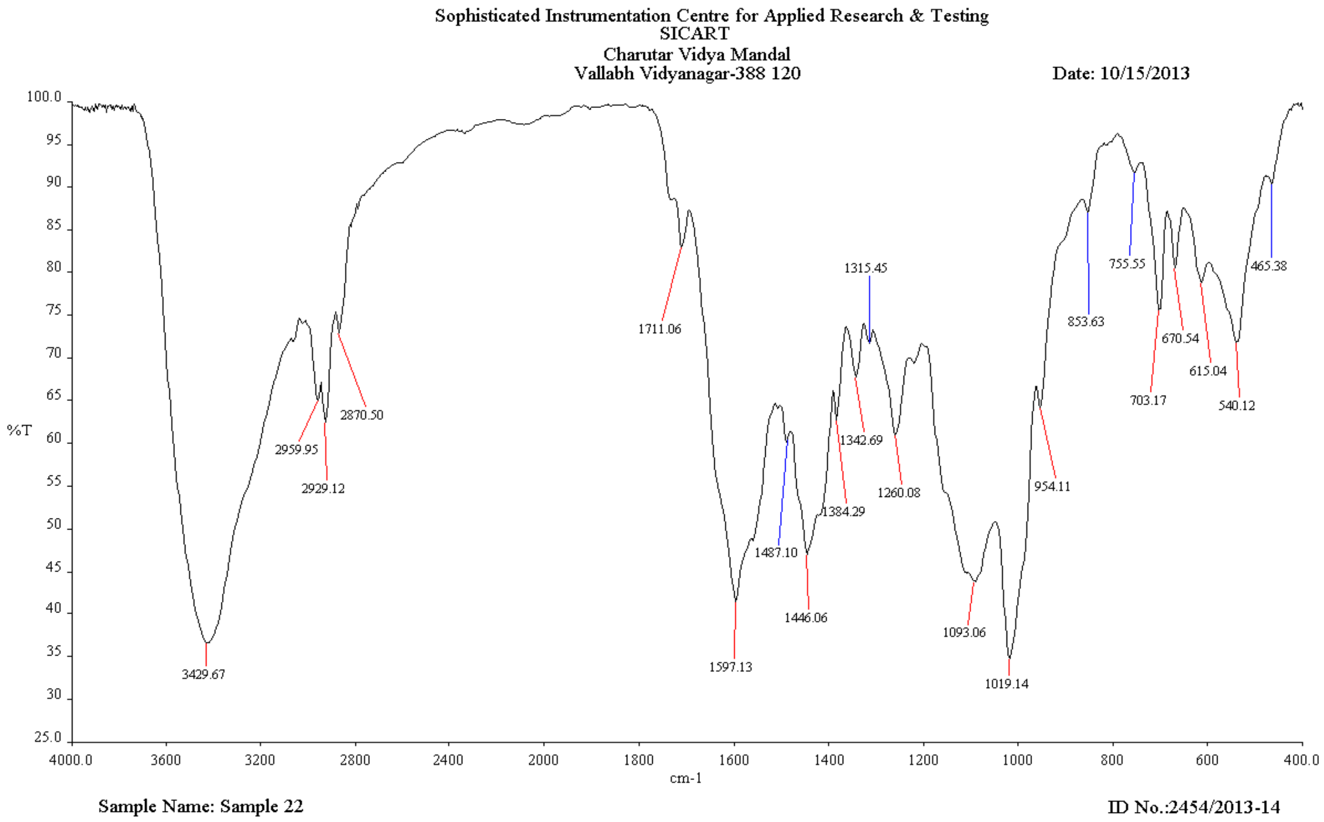


Figure 1

FTIR Spectrum of $\{[La(DHBP\text{-}1,3\text{-}BD)_2(H_2O)_2].OH\}_n$

3.5. Electronic Spectra and Magnetic Measurements

The electronic spectra of all the polychelates exhibited two additional bands in the region 280-290 nm and 450- 460 nm. The first band occuring in the spectra of the polymeric ligand, is assigned to the types $\pi \rightarrow \pi_1^*$ and $\pi \rightarrow \pi_2^*$ transitions [Kriza A., Reiss A., 2000]. The second band in all the polychelates is assigned to the polymeric ligand Ln(III) transition. The La(III) polychelates were found diamagnetic in nature as expected for six coordinated octahedral geometry. The electronic spectra of Pr(III), f3, polychelates exhibits absorption at 22,250, 21,000, 20,620, and 16,720 cm-1, assigned to $^3H_4 \rightarrow {}^3p_2$, $^3H_4 \rightarrow {}^3p_1$, $^3H_4 \rightarrow {}^3p_0$ and $^3H_4 \rightarrow {}^1D_2$ transitions of Pr(III) in an octahedral environment, due to the large crystal field with magnetic.

Moment 3.70 BM. The Nd(III) polychelates are paramagnetic as expected for f4 system. Bands were obtained at 19,210; 17,200; 13,250; and 10,222 cm-l for $^4I_{9/2} \rightarrow {}^2G_{9/2}$, $^4I_{9/2} \rightarrow {}^2G_{5/2}$, $^4I_{9/2} \rightarrow {}^2S_{3/2}$, and $^4I_{9/2} \rightarrow {}^4F_{5/2}$ transitions of Nd(III) in the octahedral geometry. In addition the bands at 24,720; 23,800; and 24,450 cm-1 for polychelates are assigned to $^4H_{5/2} \rightarrow {}^4F_{9/2}$, $^4H_{5/2} \rightarrow {}^6p_5$ and $^4H_{5/2} \rightarrow {}^4I_{11/2}$ transitions of Sm(III) in an octahedral geometry due to the large crystal field splitting and all the polychelates are paramagnetic in nature. The magnetic moment 1.75 BM is obtained as expected. The Gd(III) and Tb(III) polychelates were found paramagnetic in nature 7.89 BM and 9.52 BM as expected for the six coordinated octahedral polychelates. The electronic spectra of Dy(III) f10 polychelates exhibit absorption at 28,901 cm-l assigned to $^6H_{15/2} \rightarrow {}^6H1_{15/2}$ transition of Dy(III) in the octahedral geometry due to large crystal field splitting. From all the above study the proposed structure of polychelates is shown in Scheme III.

3.6. Antimicrobial Activity

The bacterial strains of *Escherichia coli*, *Bacillus substilis*, *Staphylococcus aureus* and Yeast strain *Sanccharomyces cerevisiae* were tested with the polymeric ligand and their polychelates. The effect of the compound in the growth media were investigated by standard microbiological parameters. The concentration of the compounds was kept at 500 ppm during the experiment. The bacterial culture was maintained on Nagar (N-broth, 2.5 % w/v agar). The yeast culture was maintained on MGYP in 3 % (w/v) agar agar, malt extract 0.3 % (w/v), glucose 1.0 % (w/v), yeast extract 0.3 % (w/v) and peptone 0.5 % (w/v) in distilled water and the pH was adjusted to 6.7-7.3. All were subcultured every fortnight and stored at 0-5oC.

3.7. Media Composition

For the growth and test of bacteria and yeast, the Nbroth and MGYP media were used. The composition used is as shown below. N-broth: Peptone 0.6 % (6.0 g), NaCl 0.15 % (1.5 g), beef extract 0.15 % (1.5 g) were dissolved in l L distilledwater and pH was adjusted to 6.7-7.3. MGYP: Malt extract (3.0 g), glucose (10.0 g), yeast extract (3.0 g) and peptone (5.0 g) were dissolved in l L distilled water and pH was adjusted to 5.5.

3.8. Inoculum Preparation

Bacterial and yeast cultures, a loop of cell mass from pregrown slants was inoculated into sterile N-broth tubes containing 15 mL medium and incubated on a shaker at 150 rpm and 37°C for 24 h, to obtain sufficient cell density (i.e., 1 * 108 cells/mL).

Table 3

^1H NMR data of the polymeric ligand and its polychelates (δ , ppm)

Compound	δ (ppm)		
	-OH	OH Aromatic protons	$-(CH_2)_2-CH(CH_2)-$
DHBP	12.48	6.40-7.51	-
(DHBP-1,3-BD)n	12.66	6.50-7.65	1.1-3.12
$[La(DHBP\ \text{-}1,3\text{-}BD)_2\,(H2O)_2]n$	-	6.65-7.8	1.1-3.12
$[Pr(DHBP\ \text{-}1,3\text{-}BD)_2\,(H2O)_2]n$	-	6.65-7.8	1.1-3.12
$[Nd(DHBP\ \text{-}1,3\text{-}BD)_2\,(H2O)_2]n$	-	6.65-7.8	1.1-3.12
$[Sm(DHBP\ \text{-}1,3\text{-}BD)_2\,(H2O)_2]n$	-	6.65-7.8	1.1-3.12
$[Gd(DHBP\ \text{-}1,3\text{-}BD)_2\,(H2O)_2]n$	-	6.65-7.8	1.1-3.12
$[Tb(DHBP\ \text{-}1,3\text{-}BD)_2\,(H2O)_2]n$	-	6.65-7.8	1.1-3.12

[Dy(DHBP -1,3-BD) 2 (H2O)2]n	-	6.65-7.8	1.1-3.12

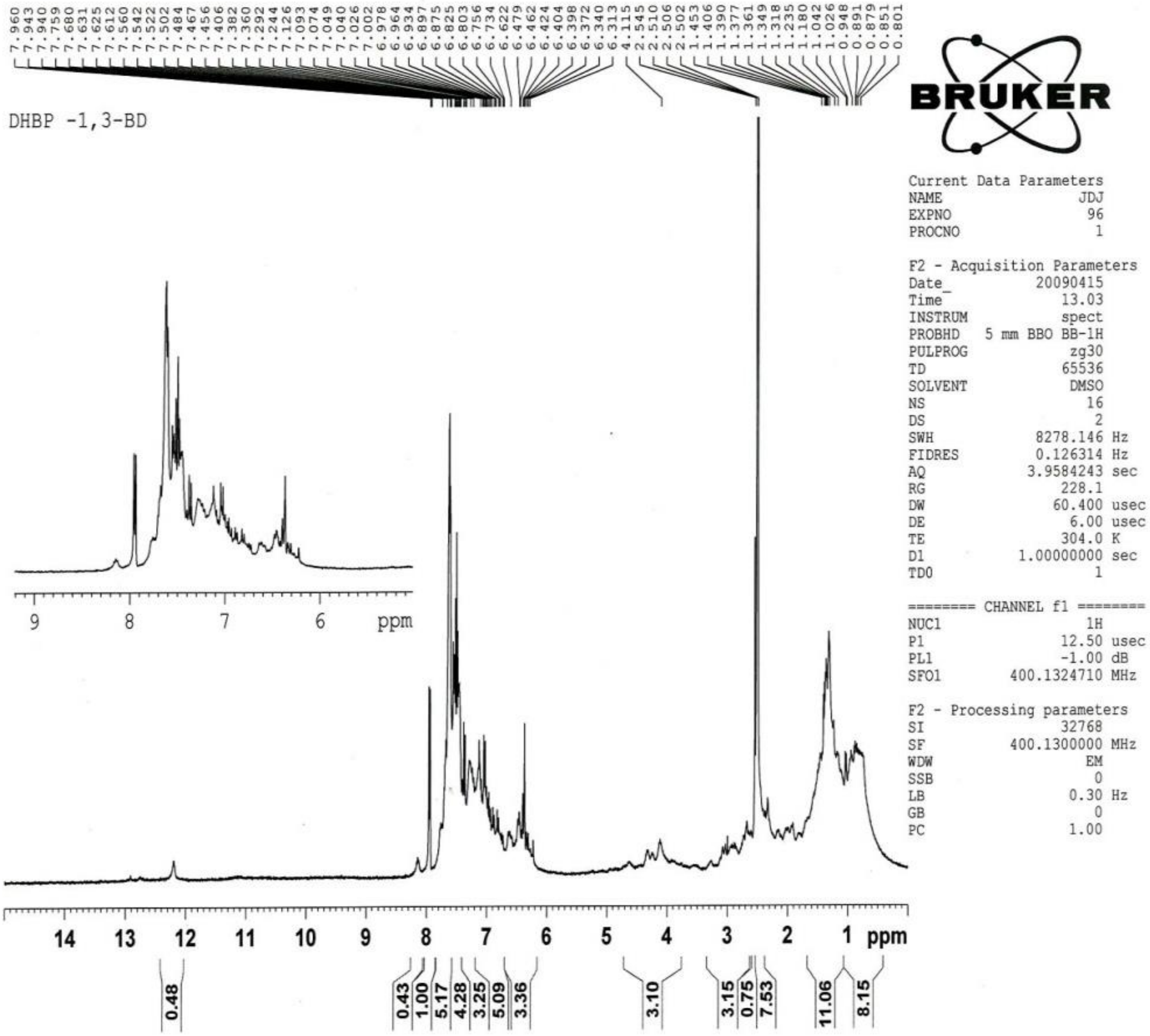


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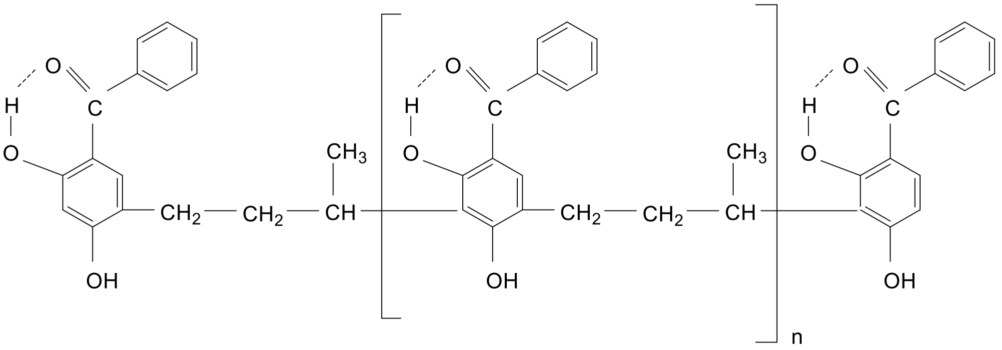
Figure 2

^{1}HNMR Spectrum of DHBP-1,3 BD Resins



Scheme 3

The proposed structure of the polymeric ligand

Table 4

Molecular Weight Determination of Resins by VPO Method

Resin	Conc. Gm.mol-1	S.D. Millivolts	Spole of Plot	$\overline{Mn}$ = K/slope g.mol^{-1}
	4.48	42.00		
DHBP-1,3 BD	6.63	61.00	8.93	1287
	8.84	82.00		
	2.21	21.00		
	4.48	43.00		

Table 5

Cumulative weight loss data of the polymeric ligand and its polychelates at various temperature

Compound	100 (°C)	150 (°C)	200 (°C)	250 (°C)	300 (°C)	350 (°C)	400 (°C)	450 (°C)	500 (°C)	550 (°C)	600 (°C)
(DHBP-1,3-BD)n	0.42	0.53	0.90	2.74	12.93	19.13	24.70	33.70	44.90	59.10	68.20
[La(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	1.20	2.85	10.40	23.16	30.31	32.10	35.06	37.09	40.11	47.90	50.10
[Pr(DHBP -1,3-BD) $_2$ (H2O)$_2$]n	1.79	2.89	9.88	17.98	26.64	28.19	32.10	34.10	39.10	45.03	49.00
[Nd(DHBP -1,3-BD) $_2$ (H2O)$_2$]n	1.96	2.30	9.59	16.65	20.12	24.09	28.12	31.10	34.40	38.17	42.10
[Sm(DHBP -1,3-BD) $_2$ (H2O)$_2$]n	1.30	2.86	9.30	15.10	19.65	26.10	32.40	35.10	39.10	46.77	55.23
[Gd(DHBP -1,3-BD) $_2$ (H2O)$_2$]n	1.99	2.20	9.98	14.84	20.19	27.19	30.10	33.19	38.45	46.49	53.10
[Tb(DHBP -1,3-BD) $_2$ (H2O)$_2$]n	1.26	2.30	12.75	17.98	24.16	28.90	32.18	34.90	39.45	40.10	41.48

[Dy(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	1.42	2.19	10.16	17.09	25.16	29.19	33.12	35.19	37.29	39.10	42.19

Table 6

Water content at 25°C and cumulative weight loss data of the polymeric ligand and its polychelates at 100, 150, and 200°C

Compound	H_2O at 25 (°C)		Found					
			100 (°C)		150 (°C)		200 (°C)	
	(g)	(%)	(g)	(%)	(g)	(%)	(g)	(%)
[La(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	36.00	4.89	8.83	1.20	20.97	2.85	76.54	10.40
[Pr(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	36.00	4.87	13.21	1.79	21.32	2.89	72.91	9.88
[Nd(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	36.00	4.85	14.54	1.96	17.06	2.30	71.15	9.59
[Sm(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	36.00	4.81	9.72	1.30	21.39	2.86	69.56	9.30
[Gd(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	36.00	4.76	15.02	1.99	16.61	2.20	74.34	9.98
[Tb(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	36.00	4.76	9.52	1.26	17.38	2.30	96.36	12.75
[Dy(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	36.00	4.73	10.79	1.42	16.64	2.19	77.21	10.16

Table 7

Antimicrobial activity data of the polymeric ligand and its polychelates

Ligand / Polychelates	Microbial species			
	E.coli	*B.substilis*	*S. aureus*	*S. cerevisiae*
(DHBP-1,3-BD)n	+	+	+	+
[La(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	+++	+++	+++	+++
[Pr(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	+++	+++	+++	+++
[Nd(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	+++	+++	+++	+++
[Sm(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	+++	+++	+++	+++
[Gd(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	+++	+++	+++	+++
[Tb(DHBP -1,3-BD)$_2$ (H2O)$_2$]n	+++	+++	+++	+++
Control (DMSO)	-	-	-	-

DHBP-1,3-BD = poly[(2,4-dihydroxybenzophenone)1,3-butylene]. Inhibition diameter in mm (% inhibition); +: 6-10 (27 - 45%); ++: 10-14 (45- 64%); +++: 14-18 (64-82%); ++++: 18-22 (82-100%). Percent inhibition values are relative to inhibition (22 mm) with 100% inhibition; _: No inhibition

3.9. Screening of Compounds for their Antimicrobial Activity

Antimicrobial activity was checked by the agar diffusion method [Stanier R.Y., 1986]. Sterile, melted N-agar was poured into a sterile empty Petri plate and allowed to solidify. A ditch was prepared with the help of a sterile scalpel on opposite ends, with one for control (solvent without compound) and the other for the test sample. The pre-grown cultures were streaked parallel from one ditch to another. Each ditch was filled with respective components dissolved in DMSO at concentrations ranging from 50 ppm to 1000 ppm. Then after, the plates were transferred into refrigerator for 10 min to allow the samples diffuse out from the ditch and into the agar before organisms start growing followed by incubation at 37°C for 24 h. Next day the distance in millimeter (mm) from the ditch was measured as a parameter of inhibition. The polymeric ligands and their metal complexes were studied for their antimicrobial activity against standard bacterial strains of *Escherichia coli*, *Bacillus substilis*, *Staphylococcus aureus* (bacteria) and *Sanccharomyces cerevisiae* (yeast). The compounds were tested at different concentrations ranging 50-l000 ppm to find out the minimum concentration of the ligand and the polychelates, which inhibits the microbial growth. The minimum concentration of 500 ppm was found. The inhibition of growth from the ditch was measured in millimeter (mm) and the results are shown in Table 7. The polymeric ligands were found biologically active and their polychelates showed significantly enhanced antibacterial activity against one or more bacterial species, in comparison to the uncomplexed polymeric ligands. It is found that chelation tends to make the ligands act as more potent bactericidal agents than the parent ligand. The increase in activity is due to formation of a chelate. It is suggested [Chohan Z. H., Kausar S., 2000] that, in the chelate, the positive charge of the metal is partially shared with the donor atoms of the ligands and there is -electron delocalization over the whole chelate ring. This, in turn, increases the lipophilic character of the metal and favours its permeation through the lipoid layers of the bacterial membrane. Besides this, other factors may also influence the antimicrobial activity. It is observed that diamagnetic as well as paramagnetic nature is equally effective as antibacterial and antiyeast agent. This property is increased by nearly more than 25% in polychelates. Other factors such as stability constant, molar conductivity, and solubility are also responsible for increasing the antimicrobial activity of the polychelates.

4. CONCLUSION

On the basis of elemental analysis, IR, thermogravimetric analysis, UV-visible and 1H NMR spectra, magnetic properties, and vapour pressure osmometry the proposed structure of the complex is determined. All the polychelates of lanthanides (III) with the polymeric ligands show good antimicrobial activity compared to free polymeric ligands. It is found that chelation is more effective for ligand to act as more potent bactericidal agents. The thermal stability of polychelates is less than the polymeric ligand.

SUMMARY OF RESEARCH

1. A novel phenolic polymeric resin was prepared from 2,4-dihydroxy benzophenone, an benzophenone derived monomer, which was used to synthesize polychelates of lanthanide(III) elements.
2. The resultant polychelates were characterized using IR, NMR, VPO, Electronic and magnetic measurements. The polychelates are behave as an antimicrobial agents.

FUTURE ISSUES

It would be definitely beneficial investigate the phsicochemical properties of the prepared polychelates, which may help to explore their potential for a variety of fields in Chemistry.

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REFERENCE

1. Arimoto F.S., HavenA.C., Derivatives of dicyclopentadienyliron, *J. Am. Chem. Soc.*, 77, 6295-6397, 1955.
2. Joshi J.D., Patel N.B., Patel S.D., Ion-exchange study of poly [(2,4-dihydroxy benzophenone)propylene]resin and its polychelates: Synthesis, characterization. *J. Macro. Molecular Sci. Part A, PAC.*, 43, 1179-1188, 2006.
3. Mizuta T., Onishi M., Miyoshi K., Photolytic ringopening polymerization of phosphorus–birdge. 1: Ferrocenophane coordinating to an organometallic fragment, *Organometallics*, 19, 5005-5009, 2000.
4. Rivas B L., Maturana H.A., Molina M.J., Gomej- Anton M.R., Rosa M., Pierola I.F., Metal ion binding properties of poly (N-vinylimidazole) hydrogels, *J. Appl. Polym. Sci.*, 67, 1109, 1998.
5. Tusa H., Paavola A., Harjula R., Letho J., 8th Int. Conf. of Radioactive Waste Management and Environmental Remediation, 3, 42, 2001.
6. Orazzhanova L.K., Yashkarova M.G., Bimendina L.A., Kudaibergenov S.E., Binary and ternary polymerstrontium complexes and the capture of radioactive strontium-90 from the polluted soil of the Semipalatinsk Nuclear Test site, *J. Appl. Polym. Sci.*, 87, 759-769, 2003.
7. Atia A.A., Donia A.M., Elwakeel K.Z., Selective separation of mercury (II) useing a synthetic resin containing amine and mercaptan as chelating groups, *Reacti. Funct. Polymer*, 65, 267-276, 2005.
8. Jacob A.M., Yizhak M., *Ion-Exchange and Solvent Extraction*, 13th Ed., Marcel & Dekker Inc., New York, 1997.

9. Geckeler K.E., Rongnong Z., Reaction products of amino or amide group containing polymer with compounds containing functional and linking groups, Ger. Offen. DE, 4227019, 1994; Chem. Abstr., 121, 10302f, 1994.
10. Alelah A., Moet A., *Functionalised Polymers and Applications*; Chapman and Hall, London, 93, 1990.
11. Vankrevelen D.W, New developments in the field of flame-resistance fibers, *Angew. Makromol. Chem.*, 22, 132, 1972.
12. Dentini M., Santis P., Vardin A., Formation properties and structures of bis(O-hydroxybenzylideneamine) copper(II) chelates of polypeptide ligands,*Macromol. Chem.*, 175, 327, 1974.
13. Patel M.N., Patel J.B., Chelateing polymers of phenolic resin, *J. Macromol. Sci. A Chem.*, 19, 193-199, 1983.
14. Nho Y.C., Park J.S., Jin J.H., Antibacterial activity of sulfonated styrene-grafted polypropylene fabric and its metallic salt, *J. Macro. Molecular Sci. Part A, PAC,* 36, 731 -740, 1993.
15. Jayakumar R., Rajkumar M., Nagendran R., Nanjundan S., Synthesis and characterization of metal-containing polyurethanes with antimicrobial activity, *J. Appl. Polym. Sci.*, 85, 1194 - 1206, 2002.
16. Belfiore L.A., Curdie M.P. M., Das P.K., Macromolecule-metal complexes: Ligand field stabilization and thermophysical property modification. *Polymer*, 42, 9995 - 10006, 2001
17. Nursen S., Ebru K., Bekir S., Aulin O., Synthesis of some polymer-metal complexes and elucidation of their structures, *J. Macro. Molecular Sci. Part A, PAC*, 43, 1227-1235, 2006.
18. Silverstein R.M., Webster, F.X., *Spectrometric Identification of Organic Compounds,* 6th Ed., John Wiley, New York, 1998.
19. Eliassi A., Modarress H., Water activities in binary and ternary aqueous system of poly(ethylene glycol), poly(propylene glycol) and dextran, *Euro. Polym. J.,* 37, 1487-1492, 2001.
20. Nikolaev V.A., Logvinenko L.T., Myachina L.T., *Thermal Analysis*, Academic; press New York., 779, 1969.
21. Kriza A., Reiss A., Florea S., Carproin T., Studies on complexes of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) with Schiff base derived from 3-aminodibenzofuran and salicylaldehyde, *J. Ind. Chem. Soc.*, 77, 207-208, 2000.
22. Stanier R.Y., *Introduction to the Microbial World,* 5th Ed., Prentice Hall, N.J., 16-20, 1986.
23. Chohan Z. H., Kausar S., Synthesis, characterization and biological properties of tridentate NNO, NNS, and NNN donor thiazole derived furnyl, thiophenyl and pyrollyl Schiff bases and their cobalt(II), copper(II), nickel(II) and zinc(II) metal chelates, *Met.- Based Drugs*, 7, 17-22, 2000.