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Synthesis, characterization and applications of coordination polymers of Ln(III)

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The resin was synthesized by condensation of 2-hydroxy-4-ethoxybenzophenone with 1,4-butane diol in presence of polyphosphoric acid as a catalyst at 155 °C for 10 h. The synthesized resin was used to get polychelates of 4f-block elements. The resin and its polychelates were characterized on the basis of elemental analyses, electronic spectra, magnetic susceptibilities, FTIR, NMR and thermogravimetric analyses. Morphological study of resin and polychelates were carried out by scanning electron microscope. The number average molecular weight ($\overline{M}_n$) was determined using a vapor pressure osmometry method. The catalytic activity of selected polychelates was examined for organic synthesis. It is observed from the study that polychelates give excellent results. They were found to be efficient and effective catalysts and antimicrobial agents. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: polychelates; thermal study; catalysts; antimicrobial study; morphology

Introduction

Metal-containing polymer chemistry is a growing field, in which the synthetic materials are anticipated to offer unique properties due to presence of organic and inorganic components. Novel and fascinating types of entanglements of individual moieties are exhibited in coordination network polymers.[1] The incorporation of metals into the polymer chain offers potential for the preparation of processable materials with various applications, which differ significantly from those of conventional organic polymers. The diverse nature of the coordination and geometry of the elements offer the possibility of accessing polymers with unusual conformational, mechanical and morphological characteristics.[2,3]

It is well known that the lanthanides, as well as most of their compounds, are highly paramagnetic and fluorescent. Therefore, they have many scientific and industrial applications in optical or magnetic devices, as radiotherapeutic drugs,[4] in fluoroimmunoassay,[5] in hetero- and homogeneous catalysis[6,7] and as components of permanent magnetic materials,[8] since the addition of lanthanides to polymeric networks is of considerable interest for both scientific and technological purposes.[9] The possibility of the incorporation of a wide range of rare earth ions into the host polymers provides opportunities to obtain some polymers having different physicochemical as well as biological properties than those of general organic polymers. Lanthanides are nontoxic for humans, even though they possess good antimicrobial activity against microorganisms.[10]

An attempt has been made to synthesize polymer-metal complexes of phenolic resin with lanthanide (III) metal ions, and their characterization and thermal, catalytic and antimicrobial properties studied. Compared with polychelates, resin possesses good thermal stability. The applicability of polymer–metal complexes as catalysts in organic synthesis has also been studied. Polymer–metal complexes show good bactericidal activity compared with the parent polymeric ligand, because of the introduction of the metal ion into their polymeric backbone. Thus, looking at their effective and efficient behavior, lanthanide polychelates can be used as bactericidal agents and catalysts.

Experimental

Materials Required

The chemicals used were 2,4-dihydroxy benzophenone (DHBP, Aldrich), K_2CO_3 (anhydrous), *n*-bromo ethane (Aldrich), 1,4-butane diol (BD, Aldrich), polyphosphoric acid (PPA, Lancaster), methanol, ethanol, acetone, dimethyl sulfoxide (DMSO), benzaldehyde, 4-hydroxybenzaldehyde, 4-chlorobenzaldehyde, vanillin, urea, acetoacetic ester and acetyl acetone (AR-grade), hydrated metal acetates of lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium and dysprosium (Merck), nutrient-broth (Hi-media, M 002) and MGYP media (Hi-media).

Synthesis of Monomer

2,4-Dihydroxy benzophenone (14.98 g, 0.07 mol) was dissolved in 60 ml of acetone. Then anhydrous K_2CO_3 (19.32 g, 0.14mol) was added to it and stirred well. To this mixture, *n*-bromo ethane (5.18 ml, 0.07 mol) was added slowly with stirring. The reaction mixture was then refluxed at boiling temperature for 24 h. After 24 h, anhydrous K_2CO_3 (9.66 g, 0.07 mol) was added and further refluxed for 24 h. The reaction mixture was then allowed to cool, then poured on crushed ice. The pale yellow solid was separated out. It was collected by filtration and washed with cold water and recrystallized from acetone. The product was pale yellow in color, m.p. 58 °C, yield 13.23 g (88%).

Synthesis of Resin

To a well-stirred and ice-cooled mixture of 2-hydroxy-4-ethoxy benzophenone (14.52 g, 0.06 mol) and 1,4 butane diol (5.32 ml,

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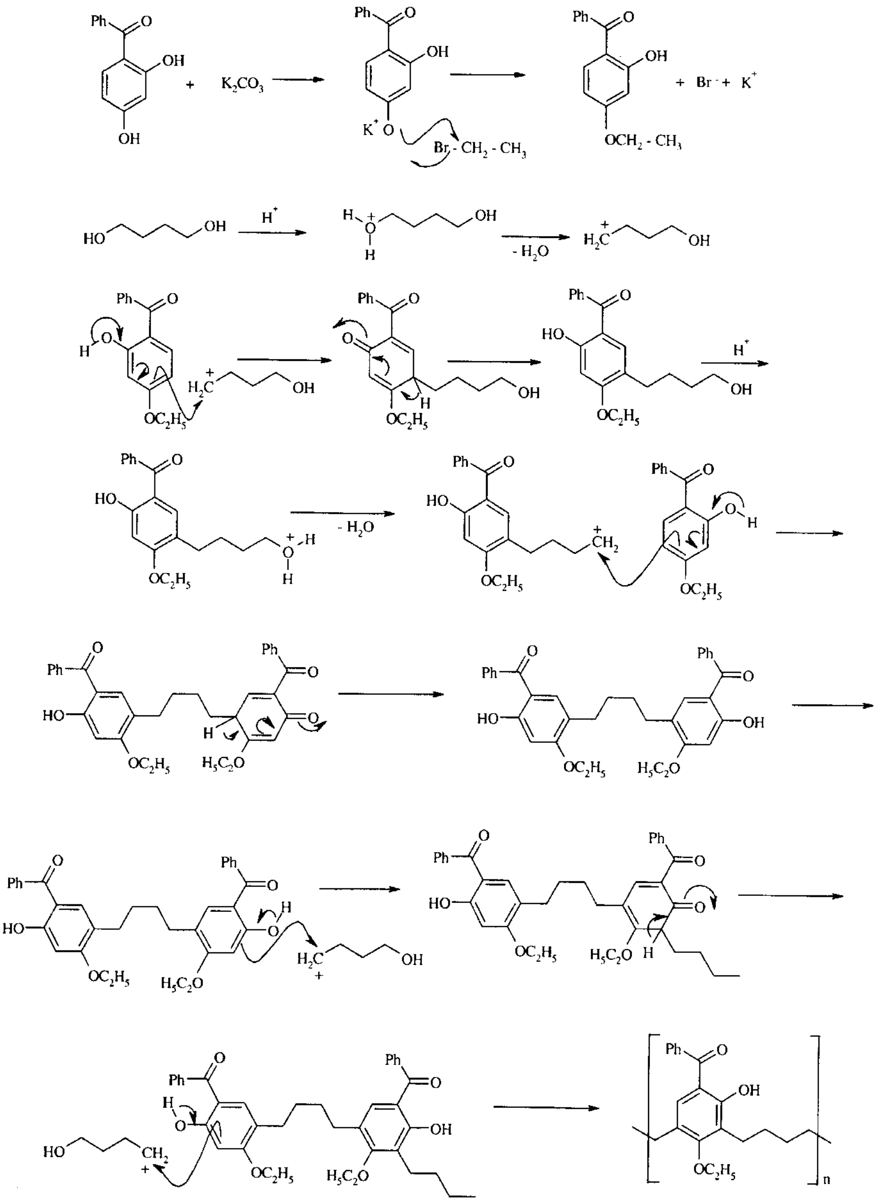


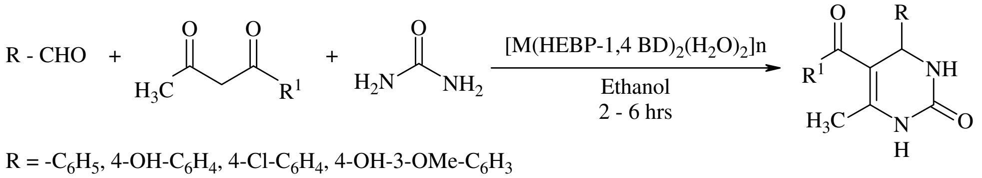
Scheme 1. Synthesis of monomer and resin.

0.06 mol), polyphosphoric acid (PPA) (20 g) was added slowly with stirring as a catalyst. The reaction mixture was left at room temperature for half an hour and condensed on an oil bath at 155 °C for 10 h. The reaction mixture was then cooled, poured on crushed ice and left overnight. A blackish-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 three times and dried at 60 °C. The synthesized resin is soluble in dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF). The polymer was yellowish brown in color, d.p. >280 °C, yield 8.37 g (57.65%). The reaction is shown in Scheme 1.

Synthesis of Polychelates

All the polychelates of hydrated metal acetates of lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium and dysprosium were synthesized as in an earlier reported method.[11] The polymeric ligand 2-hydroxy-4-ethoxybenzophenone-1,4 butylene (HEBP-1,4-BD; 2.96 g, 0.01 mol) was dissolved in DMSO (50 ml). The lanthanum acetate (1.72 g, 0.005 mol) was dissolved in DMSO (25 ml). The hot and clear solution of the lanthanum acetate was added with constant stirring to the hot and clear solution of ligand. A reddish-brown colored product separated out immediately. The suspension was digested on a water bath for 2 h and then filtered. The solid was washed with cold DMSO to remove unreacted metal acetate. Finally, the polychelate formed was washed with acetone and dried at 60 °C for 24 h.

A similar procedure was applied for the synthesis of Pr (III), Nd (III), Sm (III), Gd (III), Tb (III) and Dy (III) polychelates. All the polychelates are soluble in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). The yield obtained was in the range of 60–80%.



R = $-C_6H_5$, 4-OH-C_6H_4, 4-Cl-C_6H_4, 4-OH-3-OMe-C_6H_3

R^1 = $-OC_2H_5$, $-CH_3$

M = Nd (III), Sm (III)

Scheme 2. Synthesis of 3,4-dihydropyrimidine-2(1H)-ones.

Synthesis of Substituted 3,4-Dihydropyrimidin-2(1H)-ones

All substituted 3,4-dihydropyrimidin-2(1H)-ones were synthesized by the following method. Benzaldehyde, 4-hydroxybenzaldehyde, 4-chlorobenzaldehyde, vanillin, urea, acetoacetic ester and acetyl acetone were used to synthesize 3,4-dihydropyrimidin-2(1H)-ones.

In a typical experimental reaction a solution of β-ketoester (0.1 mol), aldehyde (0.1 mol) and urea (0.1 mol) in ethanol (40 ml) was refluxed in presence of metal polychelate as a catalyst, to give 3,4-dihydropyrimidin-2(1H)-ones, as shown in Scheme 2. The reaction mixture was then allowed to cool; the crude product obtained was separated by filtration. The crude product was dissolved in ethanol and filtered to remove insoluble catalyst and recrystallized. The separated catalyst can be used again using a simple water treatment and drying.

Preparation of Microbial Culture

The antimicrobial activity of resin and its polychelates was checked against *Escherichia coli, Bacillus subtilis, Staphylococcus aureus* and yeast strains *Saccharomyces cerevisiae*. The antimicrobial effect of the compound was investigated by standard microbiological parameters using the agar diffusion method.[12] The concentration of the compound tested for the antimicrobial activity was 500 ppm during the experiment. The bacterial culture was maintained on N-agar (N-broth, 2.5% w/v agar). The yeast culture was maintained on MGYP in 3% (w/v) agar.

For inocula developments of bacterial and yeast culture, 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. 1×10^8 cells/ml).

Sterile, melted N-agar was initially inoculated with respective cultures and poured into a sterile empty Petri plate and allowed to solidify. Two troughs was prepared using a sterile scalpel at opposite ends, with one for control (solvent without compound) and the other for the test sample. To find the minimum inhibitory concentration, all the cultures were tested for different concentrations of compound ranging from 50 to 1000 ppm. Then the plates were transferred to the refrigerator for 10 min to allow the sample diffuse out of the trough and into the agar before organisms started growing, followed by incubation at 37 °C for 24 h. On the next day the distance in millimeters from the trough was measured as a parameter of inhibition.

Media Composition

For the growth and testing of bacteria and yeast, N-broth and MGYP media were used. The compositions were as shown below:

- *N-broth* – peptone 0.6% (6.0 g), NaCl 0.15% (1.5 g) and beef extract 0.15% (1.5 g) were dissolved in l l distilled water and the 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.

Analytical Procedures

Elemental analysis of carbon, hydrogen and nitrogen was carried out on a Coleman C, H, N analyzer (Table 1). The metal content was determined by complexometric titrations with standard Na_2EDTA[13] after decomposing the polychelates with a mixture of concentrated hydrochloric, sulfuric and perchloric acids in a 5 : 2 : 3 ml ratio, respectively. Magnetic susceptibilities were measured using the Gouy method at room temperature. FTIR spectra were recorded over the 4000–400 cm^{-1} range on a

Table 1. Analytical data of the polymeric ligand and its polychelates

Compound	Formula weight of repeating unit	Yield, g (%)	Percentage found (calculated)			μ_{eff} (BM)
			M	C	H	
$(HEBP\text{-}1,4\text{-}BD)_n$ $[C_{19}H_{20}O_3]_n$	296	8.37 (57.65)	–	77.13 (77.03)	6.85 (6.76)	–
$[La(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$ $[C_{38}H_{42}O_8La]_n$	765	2.14 (72.30)	18.25 (18.17)	59.67 (59.61)	5.59 (5.49)	Diamagnetic
$[Pr(HEBP\text{-}1,4\text{-}BD)_2(H_2O_2)]_n$ $[C_{38}H_{42}O_8Pr]_n$	767	2.12 (71.62)	18.48 (18.38)	59.55 (59.45)	5.54 (5.48)	3.67
$[Nd(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$ $[C_{38}H_{42}O_8Nd]_n$	770	2.06 (69.59)	18.81 (18.70)	59.32 (59.22)	5.56 (5.45)	3.61
$[Sm(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$ $[C_{38}H_{42}O_8Sm]_n$	776	2.22 (75.00)	19.44 (19.33)	58.84 (58.76)	5.50 (5.41)	1.72
$[Gd(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$ $[C_{38}H_{42}O_8Gd]_n$	783	2.16 (72.97)	20.14 (20.05)	58.32 (58.24)	5.44 (5.36)	7.88
$[Tb(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$ $[C_{38}H_{42}O_8Tb]_n$	785	2.11 (71.28)	20.34 (20.25)	58.17 (58.09)	5.43 (5.35)	9.46
$[Dy(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$ $[C_{38}H_{42}O_8Dy]_n$	788	2.18(73.65)	20.65 (20.56)	57.96 (57.87)	5.42 (5.33)	10.61

HEBP-1,4-BD, poly[(2-hydroxy-4-ethoxybenzophenone)1,4-butylene].

Perkin Elmer infrared spectrophotometer model 938 using KBr pellets. ^{1}H-NMR spectra were recorded on Brucker 400 MHz NMR spectrometer. Thermal measurements were carried out using a Du Pont thermal analyzer in nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The number average molecular weight ($\overline{M}_n$) of polymeric ligand (resin) sample was measured with a Knaur Germany vapor pressure osmometry method (VPO) using DMF as solvent at 90 °C and polystyrene (PS) as a calibrant.

Results and Discussion

Chemistry

HEBP-1,4-BD resin was synthesized by polycondensation of 2-hydroxy-4-ethoxy benzophenone and 1,4 butane diol in acidic medium as shown in Scheme 1. The structures of the ligand and its polychelates were determined by FTIR (Fig. 1), ^{1}H-NMR and elemental analysis. The geometry of the central metal ion was confirmed by electronic spectra (UV–visible) and magnetic susceptibility measurements. Micro-analytical data of the polymeric ligand and its polychelates are presented in Table 1. The slight deviation in the elemental analysis results may have been due to the polymeric nature of the compounds, as the value of the end groups were not taken into account for the theoretical calculations. The analysis of the resin indicates that the molar ratio of 2-hydroxy-4-ethoxy benzophenone and 1,4 butane diol is 1 : 2. The micro-analytical data showed that the HEBP-1,4-BD and metal acetates were in a 1 : 2 ratio in all the polychelates. The nature of the ligand, its high thermal stability, metal – ligand ratio (1 : 2) and insolubility of chelates in common organic solvent suggest their polymeric nature.[14] It was observed from the analytical data that all the polychelates were coordinated with two water molecules, which is supported by the thermo gravimetric analysis.

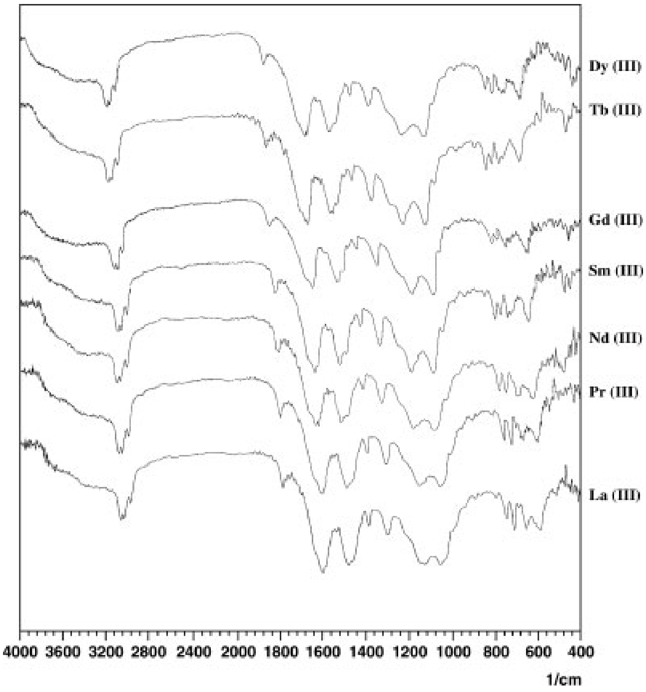


Figure 1. IR spectra of polychelates of HEBP-1,4-BD resin.

FTIR and ^{1}H NMR Spectra

The important FTIR bands and proton signals of monomer, resin and its polychelates with their assignments are discussed below. The –C=O stretching frequency in the resin was observed around 1645–16450 cm^{-1} and appeared at a lower frequency of 15–30 cm^{-l} in all the polychelates (Table 2), which suggests –C=O → M coordination. In polychelates the bands observed around 460–475 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 geometry of the polymeric ligand is shown in Scheme 3.

HEBP

IR(KBr): 3200–3400, 2730, 1590, 1560, 1525, 1490, 1345, 1266, 890, 690 cm^{-1}; ^{1}H NMR (DMSO-d$_6$): δ 12.73 (s, phenolic OH), 4.11 (q, 2H), 1.44 (t, 3H), 6.53–7.66 (8H, Ar– H).

HEBP-1,4-BD

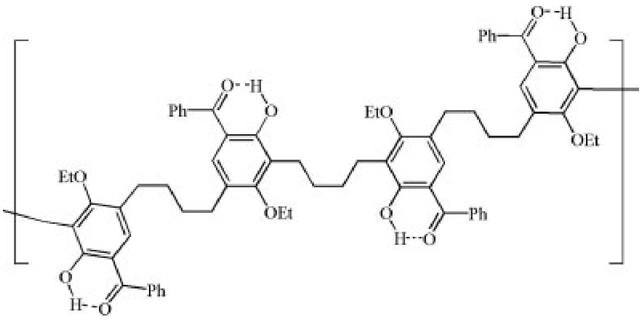
IR(KBr): 3200–3400, 2950–2880, 2735, 1590, 1560, 1525, 1495, 1345, 1260, 995, 690 cm^{-1}; ^{1}H NMR (DMSO-d$_6$): δ 12.029 (s, phenolic OH), 3.91 (q, 2H), 1.38 (t, 3H), 1.57 (q, 2H), 1.80 (q, 2H), 2.57 (q, 2H, bridge), 2.77 (q, 2H, bridge), 7.23–7.66 (6H, Ar– H).

$M[(HEBP\text{-}1,4\text{-}BD)_2 \cdot 2H_2O]_n$

IR(KBr): 3100–3400, 2950–2880, 1600–1645, 1520–1480, 1440–1600, 1350–1340, 1265 ± 10, 960–1000, 700–720,, 670–650, 565, 459–480 cm^{-1}; ^{1}H NMR (DMSO-d$_6$): δ 4.01–3.94 (q, 2H), 1.43–1.39 (t, 3H), 1.54–1.60 (q, 2H, bridge), 1.81–1.85 (q, 2H, bridge), 2.59–2.64 (q, 2H, bridge), 2.79–2.85 (q, 2H, bridge), 7.31–7.72 (6H, Ar– H).

Table 2. Water content at 25 °C and cumulative weight loss data of polychelates at 100, 150 and 200 °C

			Found					
	H_2O at 25 °C		100 °C		150 °C		200 °C	
Compound	g	%	g	%	g	%	g	%
$[La(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	36.00	4.70	18.07	2.36	33.16	4.33	55.30	7.22
$[Pr(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	36.00	4.69	16.19	2.11	32.54	4.24	57.33	7.47
$[Nd(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	36.00	4.67	16.88	2.19	32.06	4.16	65.06	8.44
$[Sm(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	36.00	4.64	22.81	2.94	33.98	4.38	51.82	6.67
$[Gd(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	36.00	4.59	14.90	1.90	28.47	3.63	49.09	6.26
$[Tb(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	36.00	4.58	9.19	1.17	22.63	2.88	43.78	5.57
$[Dy(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	36.00	4.56	9.07	1.15	22.50	2.85	43.18	5.47



Scheme 3. Proposed structure of the polymeric ligand.

5-(Ethoxycarbonyl) 4-phenyl-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR(KBR): 3234, 3106, 2928, 1730, 1646, 1598, 1464, 1417, 1339, 1315, 1288 cm^{-1}; ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 1.17 (t, 3H), 2.33 (s, 3H), 4.05 (q, 2H), 5.29 (d, 1H), 5.69 (s, 1H, NH), 7.20–7.49 (5H, Ar–H), 9.22 (s, 1H, NH).

5-(Ethoxycarbonyl)-4-(4-Chlorophenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3460, 3253, 3126, 2977, 2926, 1720, 1716, 1653, 1577, 1497, 1465, 1383 cm^{-1}; ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 1.18 (t, 3H), 2.26 (s, 3H), 2.33 (s, 3H), 4.06 (q, 2H) 5.44 (d, 1H), 6.44 (s, 1H, NH), 7.20–7.43 (4H, Ar–H), 8.55 (s, 1H, NH).

5-(Ethoxycarbonyl)-4-(4-Hydroxyphenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3441, 3290, 3127, 2920, 1700, 1653, 1617, 1493, 1424, 1387, 1364, 1312, 1260, 1236, 1141, 1090, 1014, 963, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 1.07 (t, 3H) 2.53 (s, 3H), 2.33 (s, 3H), 4.06 (q, 2H) 5.47 (d, 1H), 8.27 (s, 1H phenolic OH), 6.26 (s, 1H, NH), 6.80–7.27 (4H, Ar–H), 8.20 (s, 1H, NH).

5-(Ethoxycarbonyl)-4-(4-hydroxy-3-methoxphenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3442, 3291, 3128, 2923, 1705, 1640, 1622, 1493, 1427 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.26 (s, 3H), δ 1.11 (t, 3H), 3.99 (q, 2H), 3.76 (s, 3H, OCH_3) 5.23 (d, 1H), 6.84–7.12 (3H, Ar–H), 7.58 (s, 1H, NH), 9.45 (s, 1H, NH), 8.36 (s, 1H phenolic OH).

5-Acetyl-4-phenyl-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3284, 3127, 2919, 1702, 1644, 1620, 1495, 1429, 1387, 1363, 1317, 1275, 1236, 1146, 1097, 1019, 966, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 2.11 (s, 3H), 2.28 (s, 3H), 5.26 (d, 1H), 5.26 (s, 1H, NH), 7.21–7.45 (5H, Ar–H), 9.21 (s, 1H, NH).

5-Acetyl-4-(4-chlorophenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3441, 3291, 3127, 2915, 1703, 1643, 1621, 1494, 1427, 1389, 1366, 1316, 1264, 1238, 1144, 1095, 1017, 964, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.27 (s, 3H), 2.34 (s, 3H), 5.07 (d, 1H), 7.37 (s, 1H, NH), 7.24–7.61 (4H, Ar–H), 9.25 (s, 1H, NH)

5-Acetyl-4-(4-hydroxyphenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3372, 3255, 3115, 2964, 2921, 1703, 1680, 1667, 1607, 1447, 1426, 1389, 1366, 1315, 1265 cm^{-1}; ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 2.17 (s, 3H), 2.31 (s, 3H), 5.05 (d, 1H), 7.37 (s, 1H, NH), 7.07–7.39 (4H, Ar–H), 9.29 (s, 1H, NH), 8.64 (s, 1H).

5-Acetyl-4-(4-Hydroxy-3-Methoxphenyl)-6-methyl-3-4-dihydropyrimidin-2 (1H)-one

IR (KBr): 3441, 3292, 3127 2923 1706 1642 1623 1490 1427 m^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.06 (s, 3H), 2.33 (s, 3H), 3.81 (s, 3H, OCH_3), 5.21 (d, 1H), 6.67–6.86 (3H, Ar–H), 8.67 (s, 1H, NH), 7.24 (s, 1H, NH), 8.96 (s, 1H phenolic OH).

Vapor pressure osmometry

The number average molecular weight ($\overline{M}_n$) of the polymeric ligand (HEBP-1,4-BD) samples were estimated by VPO.[15] Dilute solutions of polymer samples were prepared to determine $\overline{M}_n$. Four concentrations 2.21, 4.42, 6.63 and 8.84 g mol^{-1} were prepared in DMF. The VPO experiment was carried out for each concentration and the corresponding bridge output reading in millivolts was noted as 21.00, 43.00, 65.00 and 83.00 respectively. The plot of millivolts vs concentration was drawn. With the help of the slope (9.77) and the VPO constant K (1.15×10^4), the $\overline{M}_n = 1177$ g mol^{-1} value of the polymer was calculated.

Thermogravimetric analyses

The percentage weight loss at various temperatures and the characteristic percentage weight left at 700 °C for HEBP-1,4-BD resin and its metal polychelates were studied. In the present study no sharp weight loss was observed in the TG curve of the polychelates, which indicates their polymeric nature. After 1–2% weight loss of lattice/absorbed water/solvent molecules, the polychelates gradually degraded. In case of two-step degradation, the first step was rapid than the second step. This may be due to the fact that the noncoordinate part of the ligand decomposes first, while the coordinated part decomposes later.[16] In case of all the polychelates, the curve showed a 4–7% weight loss corresponding to two coordinated water molecules in the temperature range of 150–200 °C. According to Nikolaev *et al.*,[17] water eliminated above 150 °C may be due to coordination with the metal ion. The water molecules observed in polychelates is water of coordination. The presence of water molecules in the polychelates has also been supported by IR studies. For the resin, a steady and regular loss of weight was observed and at 300 °C the weight loss was about 18%. The rate of decomposition was then quite rapid between 400 and 600 °C, and maximum decomposition of the resin was observed at 770 °C. In the case of polychelates, the rate of decomposition of the polychelate is higher than that of the parent resin, suggesting that there may be strong intramolecular hydrogen bonding. The absence of such hydrogen bonding in chelates favors a reduction in the thermal stability of polychelates compared with the parent resin.[18] It seems that metal ions accelerate the decomposition of polychelates. The absence of such hydrogen bonding in polychelate favors the reduction in thermal stability of polychelates compared with the parent resin. The thermal stability of the ligand and metal chelates is in the order: ligand > polychelates. Between 600 and 700 °C the resin decomposes to about 70–75%, whereas the polychelates decomposed almost completely. This result revealed that the resin shows better heat-resistance characteristics than all the polychelates. This is supported by the cumulative percentage weight loss and thermal data presented in Table 2.

Scanning Electron Microscopy of HEBP-1,4-BD Resin and its Polychelates

Scanning electron microscopy (SEM) of pure resin and polychelate was carried out to understand the inner morphology and pore structure. The morphology of the fracture surface for the resin is quite different from that of the polychelate. It is clear from the SEM that the resin [Fig. 2(a)] is porous in nature.

The pores of the resin samples are filled after interaction of metal ions with the resin. This is clear from the SEM of polychelate

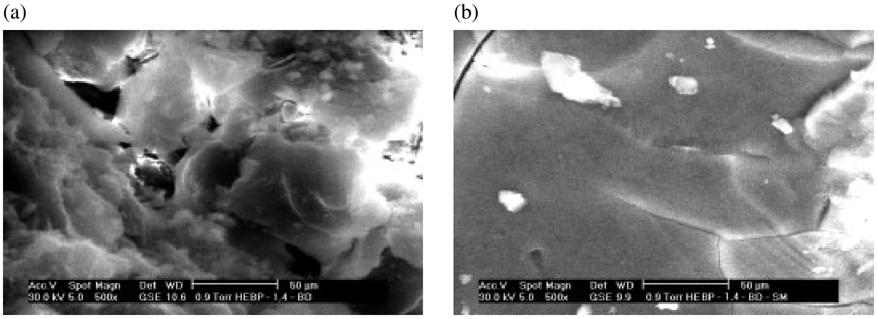


Figure 2. SEM of (a) HEBP-1,4-BD resin and (b) HEBP-1,4-BD-Sm polychelate.

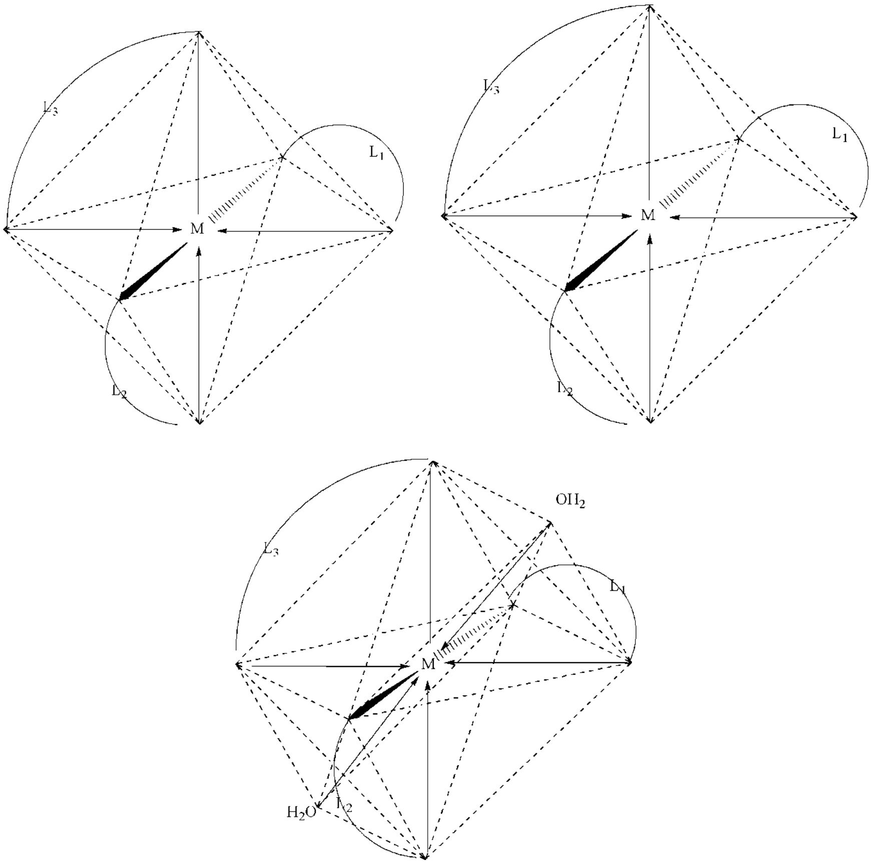


Figure 3. Possible geometries of polychelates.

[Fig. 2(b)]. The surface of the polychelate is quite uniform, but some holes and cracks are observed, which may be due to air.

Electronic Spectra and Magnetic Measurements

The electronic spectra of all the polychelates exhibited two additional bands in the region 260–300 and 445–465 nm. The first band occurs in the spectra of the polymeric ligand, and is assigned to the type $\pi \rightarrow \pi_1{}^*$ and $\pi \rightarrow \pi_2{}^*$.[19] The second band is assigned to the polymeric ligand → Ln(III) transitions in all the polychelates. The La (III) polychelates were found to be diamagnetic in nature, as expected for six-coordinated octahedral geometry. The electronic spectra of Pr(III), f^3, polychelates exhibit absorption at 21 324, 20 865, 19 458 and 17 715 cm^{-1}, assigned to $^3H_4 \rightarrow {}^3p_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3p_o$ and $^3H_4 \rightarrow {}^1d_2$ transitions of Pr(III) in a octahedral environment, due to large crystal field with magnetic moment 3.67 BM. The Nd (III) polychelates are paramagnetic as expected for the f^4 system. Bands were obtained at 18 970, 17 645, 14 273 and 9885 cm^{-l} for $^4I_{9/2} \rightarrow {}^2G_{9/2}$, $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^4I_{9/2} \rightarrow {}^2S_{3/2}$, and $^4I_{9/2} \rightarrow {}^4F_{5/2}$ transitions of Nd (III) in octahedral geometry. In addition, the bands at 23 168, 22 920 and 23 880 cm^{-1} for polychelates were 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 octahedral geometry due to large crystal field splitting. All the polychelates are paramagnetic in nature. The magnetic moment 1.72 BM was obtained as expected. The Gd (III) and Tb (III) polychelates were found to be paramagnetic in nature: 7.88 and 9.46 B.M. as expected for six-coordinated octahedral polychelates. The electronic spectra of Dy (III) f^{10} polychelates exhibited absorption at 27 750 cm^{-l} assigned to $^6H_{15/2} \rightarrow {}^6H_{13/2}$ transition of Dy (III) in octahedral geometry due to large crystal field splitting.

Proposed Geometry of Polychelates

The following geometries are possible for synthesized lanthanide polychelates (Fig. 3): I, $[M{\cdot}L_3]$; II, $[M{\cdot}L_2{\cdot}(H_2O)_2]$; and $[M{\cdot}L_3.(H_2O)_2]$. The elemental analysis, TGA-analysis and magnetic properties data correspond to two monomer units and two water molecules. Hence molecular formula II, $[M{\cdot}L_2{\cdot}(H_2O)_2]$ is acceptable.[11] In this geometry equilibrium is established between the metal ion, two ligand molecules and two water molecules, where the minimum steric hindrance results. Owing to steric hindrance, the coordination tendency of ligand always decreases with decreasing ionic radius along the series.[20] In a similar manner, an increase in the size of the ligand results in decreases in the coordinating tendency of the ligand with lanthanide ions.[21] Therefore, equilibrium is established between metal ion and ligands, where the system experiences minimum steric hindrance.

Considering all the above facts, elemental analysis, TGA-analysis, magnetic properties data and electronic spectrum data, the proposed the geometry II, $[M{\cdot}L_2{\cdot}(H_2O)_2]$ (Scheme 4a and b), is most appropriate and acceptable.

Catalytic Study

3,4-Dihydropyrimidin-2(1H)-ones and their derivatives are an important class of compounds due to their diverse therapeutic and pharmacological applications. Many functionalized derivatives of 3,4-dihydropyrimidin-2(1H)-ones are known to act as antihypertensive agents, α-antagonists and nueropeptide-Y (NPY) antagonists and also serve as integral backbones of several calcium channel blockers.[22] Several marine alkaloids containing the 3,4-dihydropyrimidin-2(1H)-ones units are found to exhibit diverse biological activities as antiviral, antibacterial, antitumor and anti-inflammatory agents.[23,24] The most simple and straightforward procedure, reported by Biginelli in 1893, involves one-pot condensation of ethyl acetoacetate, benzaldehyde and urea under strongly acidic conditions.[25] However, one serious drawback of Biginelli's reaction is low yield in the case of substituted aromatic and aliphatic aldehydes.[26] This has led to the development of multistep strategies to produce higher yield, but lack of simplicity was observed in one-pot, one-step synthesis.[23,26] Biginelli's reaction to synthesize 3,4-dihydropyrimidin-2(1H)-ones has received renewed interest and several improved procedures have recently been reported.[23,27,28] However, some of the methods involve strong protic acids such as HCl,[29] AcOH[30] and H_2SO_4,[31] or Lewis acids such as BF_3,[30] and additives.[30] Consequently, there is a scopes for further renovation toward milder reaction conditions, variations of substituents in all three components and better yields. Recently, indium (III) chloride has emerged as a powerful Lewis catalyst imparting high regio- and chemoselectivity in various chemical transformations.[32]

Under the increasing pressure of environmental problems caused by the chemical industry, solid-phase catalysis is recognized to play a leading part in the development of green chemistry.

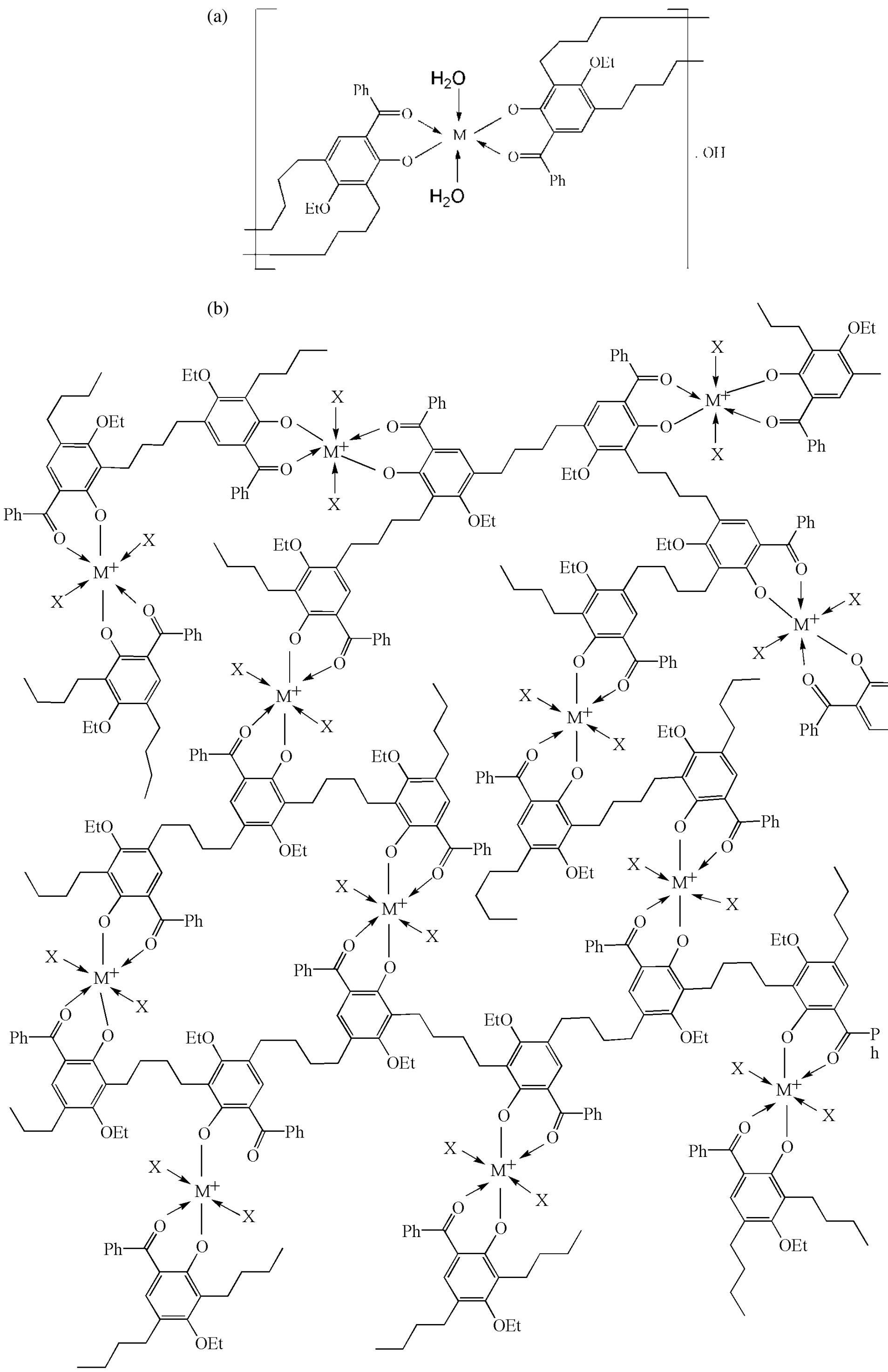
Hence, we have developed efficient, practically viable, environmentally benign and high-yield method for the Biginelli three-component, one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones using only selected Nd (III) and Sm (III) polymer–metal complexes.

Table 3. Nd (III) polychelate catalyzed synthesis of substituted 3,4-dihydropyrimidin-2(1H)-ones

Product	R	R^1	Time (h)	Yield (%)	m.p. (°C)	
					Found	Reported
a	C_6H_5	OEt	2	91	201	202–204
b	4-OH-C_6H_5	OEt	4	88	199	199–200
c	4-OH-3-OMe-C_6H_5	OEt	6	90	208	208–211
d	4-Cl-C6H_4	OEt	5	87	213	213–214
e	C_6H_5	Me	2	89	234	234–235
f	4-OH-C_6H_5	Me	4	88	209	210–211
g	4-OH-3-OMe-C_6H_5	Me	6	91	245	246–248
h	4-Cl-C_6H_4	Me	5	89	216	215–216

Table 4. Sm (III) polychelate catalyzed synthesis of substituted 3,4-hydropyrimidin-2(1H)-ones

Product	R	R^1	Time (h)	Yield (%)	m.p. (°C)	
					Found	Reported
a	C_6H_5	OEt	2	89	200	202–204
b	4-OH-C_6H_5	OEt	4	87	199	199–200
c	4-OH-3-OMe-C_6H_5	OEt	6	90	207	208–211
d	4-Cl-C6H_4	OEt	5	89	213	213–214
e	C_6H_5	Me	2	89	234	234–235
f	4-OH-C_6H_5	Me	4	90	210	210–211
g	4-OH-3-OMe-C_6H_5	Me	6	91	245	246–248
h	4-Cl-C_6H_4	Me	5	89	214	215–216



Scheme 4. (a) Proposed geometry of the polychelate. M = La (III), Pr (III), Nd (III), Sm (III), Gd (III), Tb (III) and Dy (III); X = H_2O. (b) Proposed cluster of the polychelates.

To study the efficiency and effectiveness of the catalyst, selected reactions were studied using Nd (III) and Sm (III) polymer–metal complexes under similar conditions to synthesize the 3,4-dihydropyrimidin-2(1H)-ones and results are summarized in Tables 3 and 4. It was found that Nd (III) and Sm (III) polymer–metal complexes give excellent results for all the syntheses studied. The yield obtained is ≥90%, the time required for completion of the reaction is low and the melting point of the product is the same or very close to reported values, which is acceptable as per the present standard.

Antimicrobial Activity of Resin and Polychelates

The polymeric ligand and their metal complexes were studied for their antimicrobial activity against standard bacterial strains

Table 5. Antimicrobial activity data of the polymeric ligand and its polychelates

Ligand/polychelats	Zone of inhibition[a] (mm)			
	E. coli	*B. substilis*	*S. aureus*	*S. cerevisiae*
$(HEBP\text{-}1,4\text{-}BD)_n$	–	–	–	10
$[La(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	16	18	19	19
$[Pr(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	17	19	20	20
$[Nd(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	18	19	20	19
$[Sm(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	20	18	21	19
$[Gd(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	19	19	17	20
$[Tb(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	18	18	20	19
$[Dy(HEBP\text{-}1,4\text{-}BD)_2(H_2O)_2]_n$	17	18	19	20
DMSO[b]	–	–	–	–

[a] 16–23 mm = significantly active; 10–15 mm = moderately active; <10 mm = weakly active. [b] Solvent (negative control).

of *Escherichia coli, Bacillus subtilis, Staphylococcus aureus* (bacteria) and *Saccharomyces cerevisiae* (yeast). The compounds were tested at different concentrations ranging from 50 to l000 ppm to find the minimum concentration of the ligand and polychelates to inhibits the microbial growth. The minimum concentration 500 ppm was found. The inhibition of growth from the trough was measured in millimeters and the results are shown in Table 5. The polymeric ligand was found biologically active and their polychelates showed significantly enhanced antibacterial activity against one or more bacterial species, in comparison to the uncomplexed polymeric ligand. It is known that chelation tends to make the ligands act as more potent bactericidal agents than the parent ligand. The antimicrobial activity of the compounds is increased after chelation with metal ion. Chelation reduces the polarity of the central metal ion by partial sharing of its positive charge with the donor groups,[33] increasing the lipophilic nature of the central metal ion, which in turn favors its permeation to the lipid layer of the membrane. Other factors, viz. stability constant, molar conductivity, solubility and magnetic moment, are also responsible for increasing the antimicrobial activity of the complexes.[34]

Conclusion

HEBP-1,4-BD resin was synthesized by the condensation of 2-hydroxy-4-ethoxybenzophenone and 1,4-butane-diol in acidic medium and its metal polychelates were synthesized with hydrated metal acetates in good yield and characterized by various physicochemical methods. Resin and polychelates were soluble in DMF and DMSO but insoluble in chloroform, acetone, ethanol and benzene. It was observed that the coordinaion of the metal ion to the polymeric backbone decreases the thermal stability because of the breaking of an intramolecular hydrogen bond present in the polymeric ligand. Thus intramolecular hydrogen bond plays an important role in thermal stability.

Insertion of the metal ion enhances the antimicrobial activity significantly. Thus, polychelates can be used as antifungal and antifouling coatings. The results revealed that, the resin can be used as an ion-exchanger for 4f-block elements and polychelates are found as an efficient and effective catalyst.

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