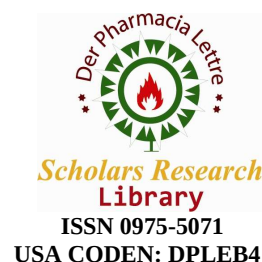




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Studies of the Coordination Polymers Based on Divalent Transition Metal Ion with Bis ligands

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ABSTRACT

The bisligand namely, 5,5'-(2,2'-(p-tolylazanediyl) bis (ethane-2,1-yl) bis (oxy) bis (methylene)) diquinolin-8-ol (TBEQ) was synthesized by facile and fast procedure, which further underwent for its co-ordination polymerization with Cu^{+2} , Zn^{+2} , Co^{+2} , Mn^{+2} and Ni^{+2} metal ions. The bis-ligand and co-ordination polymers were characterized by elemental analyses, IR spectral and diffuse reflectance spectral studies, their thermal stability were evaluated by thermogravimetric analyses. In addition, all these coordination polymers have been characterized by their magnetic susceptibilities. All these compounds were also monitored for antimicrobial activity.

Keywords: Coordination polymers, Elemental Analysis, Infrared Spectra, Electronic Spectra, Magnetic measurements, Thermo gravimetric Analysis

INTRODUCTION

The study of co-ordination polymers has made much progress [1]. These polymers are useful in waste water treatment for metal recovery, in protective coating, as antifouling paints, and anti fungal properties [1,2]. Such co-ordination polymers are mostly used for bi-chelating ligands in which metal ions and chelating agents are arrayed alternatively. Most of bichelating ligands are derived from well known chelating agents like 8-hydroxy quinoline and salicylic acid etc [3,6]. The joining segment of these two similar ligands are mainly $-\text{N}=\text{N}-$, SO_2 , $-\text{CH}_2-$, $-\text{O}-$ [3-9]. The interest in the construction of coordination polymers by linking transition metal ions with ligand has been constantly growing over the past years [10-16]. Coordination polymers are defined as materials in which metal ions are linked together with di or polyfunctional ligands. The design of new coordination supramolecules and polymers based on transition metal compounds and multidentate organic ligands has attracted much interest in recent years [17-21]. The literature survey reveals that the reaction of CMQ with 2,2'-(p-tolylazanediyl)diethanol derivatives has not been reported so far. Hence it was thought to under take such study. The present paper deals with synthesis, characterization and chelating properties of bisligand (TBEQ) and its co-ordination polymers is shown in Scheme-1 and Scheme-2.

MATERIALS AND METHODS

Materials

The starting compounds, 5-chloromethyl-8-hydroxyquinoline hydrochloride **1** and 2,2'-(p-tolylazanediyl)diethanol **2** were synthesized by previously reported routes [22, 23]. All the other necessary chemicals were of analytical grade and purchased from Merck, Fluka and localize companies.

Preparation of 5-(chloromethyl)quinolin-8-ol hydrochloride **1**

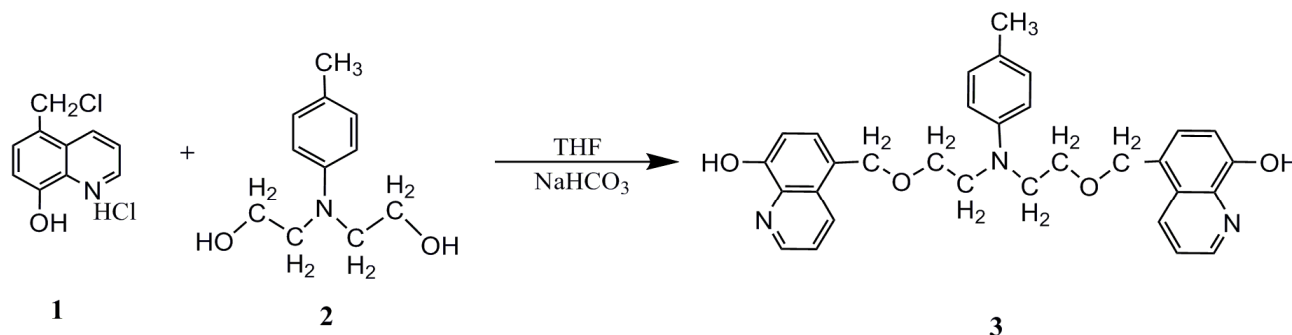
5-(chloromethyl)quinolin-8-ol hydrochloride was synthesized, purified and characterized by previously reported routes. [22]

Preparation of 2,2'-(p-tolylazanediyl)diethanol **2**

2,2'-(p-tolylazanediyl)diethanol was also synthesized, purified and characterized by previously reported routes. [23]

Preparation of 5,5'-(2,2'-(p-tolylazanediyl)bis(ethane-2,1-diyl)bis(oxy)bis(methylene))diquinolin-8-ol (TBEQ) **3**

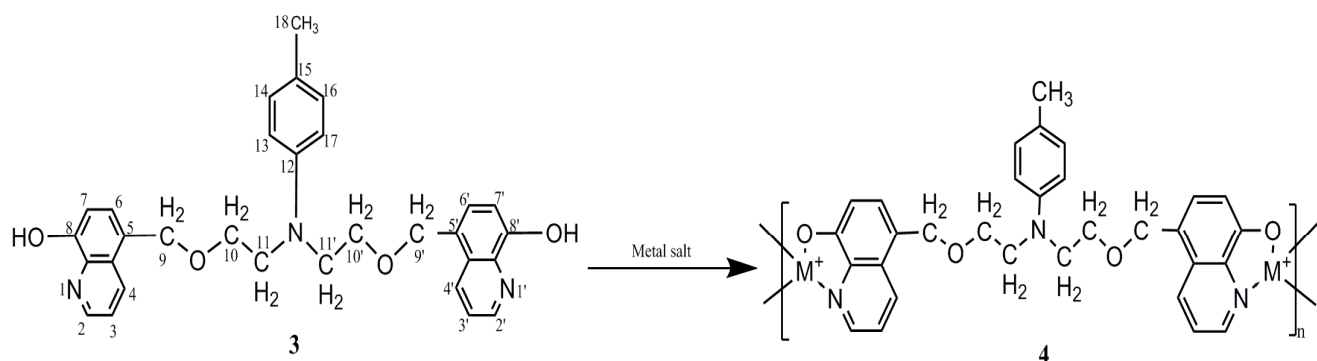
TBEQ was prepared according to the method reported for CMQ-alcohol reaction [24]. To a suspension of 5-chloromethyl-8-hydroxyquinoline hydrochloride (4.6 g, 0.02 mol), 2,2'-(p-tolylazanediyl)diethanol (1.95 g, 0.01 mol) in an acetone-water mixture was added. The resulting mixture was refluxed for 3 hr with occasional shaking. The resulting suspension, which contained of a green precipitate was made alkaline with dilute aqueous ammonia and then filtered. The solid product was collected and dried to give TBEQ (78% yield). The product melted with decomposition at 230-242 °C (uncorrected).



Scheme- 1. Synthetic route for 5,5'-(2,2'-(p-tolylazanediyl)bis(ethane-2,1-diyl)bis(oxy)bis(methylene))diquinolin-8-ol (TBEQ)

Preparation of Coordination Polymers **4**

A solution of metal ion (0.01 mol) in aqueous formic acid was added dropwise to a solution of TBEQ (0.005 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 boiling water bath for about 1 hr. Finally, the resultant solid green was collected by filtration and washed with hot water, dimethylformamide (DMF) and then acetone. The polymer [TBEQ-M⁺²] was air-dried. The TBEQ-Cu (II), TBEQ-Co (II), TBEQ-Ni (II), TBEQ-Mn (II), and TBEQ-Zn (II) polymers were almost yield quantitatively.



Scheme-2. Synthetic route for preparation of coordination polymers

Where $M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II) .

Antibacterial Activities

Antibacterial activity and Antifungal activities of TBEQ ligand and its coordination polymers were studied against gram-positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative bacteria (*E.coli*, *Samonella typhi* and *Klebsiella promioe*) and Plant pathogenic organisms used were *Penicillium expansum*, *Botrydepladia thiobromine*, *Nigrospara Sp.*, *Trichothesium Sp.*, and *Rhizopus nigricum*. at a concentration of 50 $\mu\text{g/ml}$ by agar cup plate method. Methanol system was used as control in this method. The area of zone of inhibition measured in mm.

Measurements

The elemental contents of C, H, N were determined by TF-Flash-1101 EA. Infrared spectra of the synthesized compounds were recorded on Nicolet 760 FT-IR spectrometers. $^1\text{H-NMR}$ spectrum of ligand was recorded on a Bruker spectrophotometer at 400MHz. Magnetic susceptibility measurement of the synthesized complexes was carried out on Gouy Balance at room temperature. The electronic spectra of complexes in solid were recorded on at room temperature, MgO was used as reference. The metals contents of metal chelates were determined volumetrically by Vogel's method [25]. To a 100 mg chelate sample, each 1 ml of HCl, H_2SO_4 and HClO_4 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. Antimicrobial activity of all the samples was monitored against various grampositive(+) and gramnegative(−) organism, following the method reported in literature [26,27].

RESULTS AND DISCUSSION

The synthesis of the bis bidentate ligand, 5,5'-(2,2'-(p-tolylazanediyl) bis(ethane-2,1-diyl) bis(oxy) bis(methylene)) diquinolin-8-ol (TBEQ) has not been reported in the literature. The ligand TBEQ was isolated in the form of a green powder. It was soluble in organic solvents such as in dioxane, dimethyl-sulfoxide (DMSO) and DMF etc. The bis-ligand is characterized by Elemental analysis as well as $^1\text{H NMR}$ and IR spectroscopic techniques as given below.

Elemental Analysis

The metal and C, H, N contents of bis ligand and co-ordination polymers are shown in Table 1 and also consistent with the predicted structure. The results show that the metal: ligand (M: L) ratio for all divalent metal chelate is 1:2.

Table 1: Analysis of TBEQ ligand and its Co-ordination polymers

Empirical Formula	Mol.Cal. g/mol	Yield %	Elemental Analysis			
			%C	%H	%N	%M
			Calc./Found	Calc./Found	Calc./Found	Calc./Found
C ₃₁ H ₃₁ N ₃ O ₄	509	86	73.10/73.08	8.29/8.25	6.13/6.09	–
C ₃₁ H ₂₉ N ₃ O ₄ Ni ₂ .2H ₂ O	663	73	56.15/56.10	6.35/6.33	4.40/4.37	18.11/18.09
C ₃₁ H ₂₉ N ₃ O ₄ Mn ₂ .2H ₂ O	653	69	56.98/56.96	6.46/6.43	4.47/4.44	16.88/16.84
C ₃₁ H ₂₉ N ₃ O ₄ Co ₂ .2H ₂ O	661	76	56.30/56.27	6.36/6.35	4.40/4.38	17.87/17.85
C ₃₁ H ₂₉ N ₃ O ₄ Zn ₂ .2H ₂ O	673	71	55.28/55.27	6.24/6.27	4.33/4.30	19.35/19.31
C ₃₁ H ₂₉ N ₃ O ₄ Cu ₂ .2H ₂ O	671	75	55.45/55.43	6.29/6.25	4.35/4.32	19.10/19.07

IR Analysis

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

The IR spectrum of comprises the important bands due to 8-quinolinol. The bands were observed at 1623, 1575, 1461, and 754 cm⁻¹. The broad band in ligands at 3800-2700 cm⁻¹ is due to the presence of –OH group. In this band the inflections are observed at 2940, 2930 and 2860 cm⁻¹. While the latter two might be attributed to asymmetric and symmetric vibration of - CH₂ group of CMQ [28].

In the investigated coordination polymers, the bands observed in the region 3430–3480, 1280–1320, 870–890 and 722–724cm⁻¹ are attributed to OH stretching, bending, rocking and wagging vibrations, respectively due to the presence of water molecules [29]. The presence of rocking band indicates the coordination nature of the water molecule [30]. Another noticeable difference is that the band due to the C=N stretching vibration of 8-HQ at around 1620 cm⁻¹ in the IR spectrum of TBEQ was shifted to lower frequency, whereas the band at 1410 cm⁻¹ in the IR spectrum of TBEQ assigned to in plane -OH deformation was disappeared in the spectra of the coordination polymer due to the formation of the M–O bond [28]. This was further confirmed by a weak band at 1120 cm⁻¹ corresponding to C–O–M stretching, while bands around ~710 and ~560 cm⁻¹ correspond to the M → N vibration [31].

¹H NMR Analysis

The structure of the ligand (TBEQ) was characterized by ¹H NMR spectrum in DMSO- *d*₆ system. The ligand shows a signal at δ = 4.54 ppm (s, 4H, H₉ and H₉' protons) is assigned to two –CH₂- protons. Two triplet, one at δ = 3.72 ppm (t, 4H, H₁₀ and H₁₀' protons) and second at 4.16 ppm (t, 4H, H₁₁ and H₁₁' protons) is assigned to two ethyl (CH₂-CH₂) groups. The signal at δ = 2.40 ppm (s, 3H, -CH₃ protons) is assigned to aromatic methyl protons. A sharp signal at δ = 9.5 ppm (s, 2H, -OH protons) is assigned to two aromatic hydroxyl protons [32], which are confirmed by D₂O exchange experiment. Aromatic protons observed at 7.06 (d, 2H, H₁₄, H₁₆), 6.66 (d, 2H, H₁₃, H₁₇), 7.24 (d, 2H, H₆, H₆'), 7.12 (d, 2H, H₇, H₇'), 8.52 (d, 2H, H₂, H₂'), 7.40 (dd, 2H, H₃, H₃'), 8.23(d, 2H, H₄, H₄').

Magnetic Measurements

Magnetic moments of metal complexes are given in Table 2. The diffuse electronic spectrum of Cu²⁺ complex shows two broad bands at 15850 and 23320 cm⁻¹. The first band may be due to a ²B_{1g}→²A_{1g} 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 [33,34]. The Co^{2+} metal complex gives rise to two absorption bands at 22632 and 15165 cm^{-1} , which can be assigned ${}^4\text{T}1\text{g}(\text{F}) \rightarrow {}^4\text{T}2\text{g}(\text{F})$, ${}^4\text{T}1\text{g}(\text{F}) \rightarrow {}^4\text{T}2\text{g}$ transitions, respectively. These absorption bands and the μ_{eff} value indicate octahedral configuration of the Co^{2+} metal complex [35,36]. The spectrum of Mn^{2+} polymeric complex comprised two bands at 18240 cm^{-1} and 23600 cm^{-1} . These bands may be assigned to ${}^6\text{A}1\text{g} \rightarrow {}^4\text{T}2\text{g}$ (4G) and ${}^6\text{A}1\text{g} \rightarrow {}^6\text{A}2\text{g}$ (4Eg) 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 two distinct bands at 22500 and 15287 cm^{-1} are assigned as ${}^3\text{A}1\text{g} \rightarrow {}^3\text{T}1\text{g}(\text{P})$ and ${}^3\text{A}1\text{g}^3 \rightarrow \text{T}1\text{g}(\text{F})$ transition, respectively suggested the octahedral environment for Ni^{2+} ion. The observed μ_{eff} values in the range 2.12-5.49 B.M are consistent with the above moiety [37,38].

Table 2: Spectral features and magnetic moment of metal chelates

Metal Chelates	μ_{eff} BM	Electronic Spectral data cm^{-1}	Transition	IR spectral features common for all cm^{-1}
TBEQ- Cu^{2+}	2.12	23320 15850	Charge transfer ${}^2\text{B}1\text{g} \rightarrow {}^2\text{A}1\text{g}$	1659 Quinoline 1563 Moiety 1515 1439
TBEQ- Ni^{2+}	3.32	22500 15287	${}^3\text{A}1\text{g} \rightarrow {}^3\text{T}1\text{g}(\text{P})$ ${}^3\text{A}1\text{g}^3 \rightarrow \text{T}1\text{g}(\text{F})$	2920 CH_2 2854 1456
TBEQ- Co^{2+}	4.58	22632 15165 8893	${}^4\text{T}1\text{g}(\text{F}) \rightarrow {}^4\text{T}2\text{g}(\text{F})$ ${}^4\text{T}1\text{g}(\text{F}) \rightarrow {}^4\text{T}2\text{g}$ ${}^4\text{T}1\text{g}(\text{F}) \rightarrow \text{T}2\text{g}(\text{P})$	1110 C-O-M & 510 O-M Bands
TBEQ- Mn^{2+}	5.49	23600 18240 16726	${}^6\text{A}1\text{g} \rightarrow {}^6\text{A}2\text{g}$ (4Eg) ${}^6\text{A}1\text{g} \rightarrow {}^4\text{T}2\text{g}$ (4G) ${}^6\text{A}1\text{g} \rightarrow {}^4\text{T}1\text{g}(\text{PG})$	720 Ar-Cl 750
TBEQ- Zn^{2+}	Dimg.	-	-	-

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 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 57% of its weight when heated up to 700°C. Figure 1 is typical. Inspection of the thermograms of all coordinated polymer samples revealed that all samples suffered appreciable weight loss in the range 152 to 287 °C. This may be due to the presence of a coordinated water molecule.

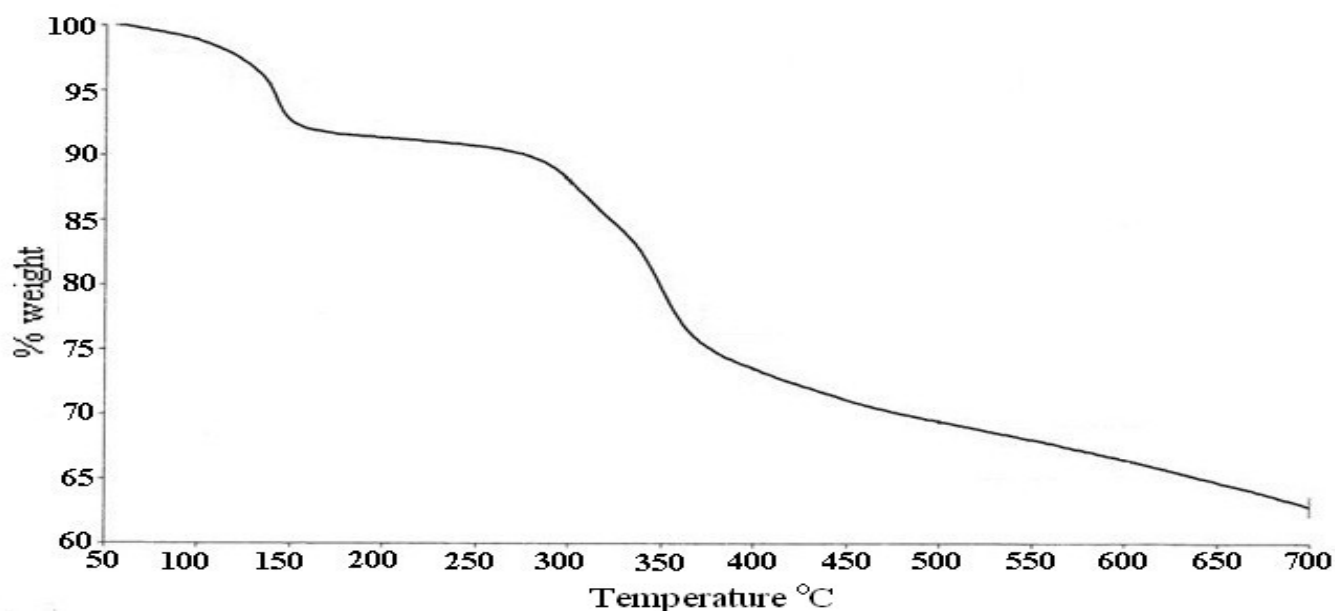


Figure 1: TG thermogram of (Cu TBEQ(H₂O)_n)

Antibacterial 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 [39] and Tweedy's chelation theory [40]. 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 π -electrons over the whole chelate ring and enhances the lipophilicity of the complexes. 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 complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organisms.

Coordination polymer 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 metal complexes are more potent biocidals than the free ligands. From the data obtained it is clear that Cu (II) is highly active among the complexes of the respective metal.

Table 3: Antibacterial activity of coordination polymers

Compounds	Zone of inhibition at 1000 ppm (%)				
	Gram +ve			Gram -ve	
	<i>Bacillus Subtilis</i>	<i>Staphylococcus Aureus</i>	<i>Klebsiella Promioe</i>	<i>Samonella Typhi</i>	<i>E.Coil</i>
TBEQ	09	12	09	08	07
(Cu TBEQ(H ₂ O) ₂) _n	27	26	25	28	24
(Co TBEQ(H ₂ O) ₂) _n	23	20	18	19	19
(Ni TBEQ(H ₂ O) ₂) _n	20	25	21	23	22
(Mn TBEQ(H ₂ O) ₂) _n	21	24	23	26	21
(Zn TBEQ(H ₂ O) ₂) _n	19	21	16	18	18

Table 4: Antifungal Activity of Coordination polymers

Compounds	Zone of Inhibition at 1000 ppm (%)				
	<i>Penicillium Expansum</i>	<i>Botrydepladia thibromine</i>	<i>Nigrospara Sp.</i>	<i>Tichothesium Sp.</i>	<i>Rhizopus nigricum</i>
TBEQ	12	09	11	07	10
(Cu TBEQ(H ₂ O) ₂) _n	27	28	25	24	25
(Co TBEQ(H ₂ O) ₂) _n	23	19	19	19	23
(Ni TBEQ(H ₂ O) ₂) _n	22	22	20	22	21
(Mn TBEQ(H ₂ O) ₂) _n	17	21	23	21	20
(Zn TBEQ(H ₂ O) ₂) _n	13	23	21	17	19

CONCLUSIONS

The results obtained in this study allow the following conclusions. The design and synthesis of new bis-ligand have been successfully demonstrated. FT-IR, ¹H-NMR spectral studies. We have synthesized a series of some novel coordination polymers with bis-ligand derivative with transition metals and characterized their properties. All the synthesized compounds were screened for their bioassay. The complexes exhibited strong activities against Gram-negative bacteria and Gram-positive bacteria and plant pathogenic microorganisms. In comparison with the ligand complexes were more active against one or more bacterial strains, thus introducing a novel class of metal-based bactericidal agents. The information regarding geometry of the complexes was obtained from their electronic and magnetic moment values. The magnetic moment values indicate an octahedral geometry.

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REFERENCES

- [1] T. Kaliyappan, P. Kannan, *Prog, Polym. Sci.*, **2000**, 25(3), 343.
- [2] G.P. Gooding, *Chemical Review*, **1975**, 95, 108.
- [3] H. Horowitz, J.P. Perrors, *J. Inorg Nucle. Chem.*, **1964**, 26, 139.
- [4] R.D. Patel, H.S. Patel, S.R. Patel, *Eur. Polym. J.*, **1987**, 23, 229.
- [5] A.M. Karampurwala, R.P. Patel, J.R. Shah, *Angew. Makromol. Chem.*, **1980**, 87, 87.

- [6] A.K. Rana, N.R.Shah, A.M. Karampurwala, J.R. Shah, *Makromol. Chem.*, **1981**, 182, 3387.
- [7] K.D. Patel, S.C. Panchani, *Ulter of Phy. Science.*, **2003**, 15, 195.
- [8] H.S. Patel, R.B. Dixit, T.B. Shah, *Int. J. Polym. Material.*, **2001**, 49, 27.
- [9] D.C. Patel, PhD. *Thesis HNGU, Patan*, **2007**.
- [10] S. R Batten, R. Robson, *Chem. Int. Ed.*, **1998**, 37, 1460.
- [11] O. M. Yaghi, M.O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim., *Nature.*, **2003**, 423, 705.
- [12] S. Kitagawa, R. Kitaura, S.I. Noro, *Chem. Int. Ed.*, **2004**, 43, 2334.
- [13] S. Kitagawa, K. Uemura, *Chem. Soc. Rev.*, **2005**, 34, 109.
- [14] H. W. Roesky, M. Andruh, *Coord. Chem. Rev.*, **2003**, 236, 91.
- [15] C. Janiak, *J. Chem. Soc., Dalton Trans.*, **2003**, 14, 2781.
- [16] N. H. Patel, K. N. Patel, M. N. Patel, *Synth. React Inorg. Met.-Org. Chem.*, **2002**, 32, 1879.
- [17] B. Moulton, M. J. Zaworotko, *Chem. Rev.*, **2001**, 101, 1629.
- [18] G.-Q. Zhang, G.-Q. Yang, J.-S. Ma., *Cryst. Growth Des.*, **2006**, 6, 357.
- [19] A. K. Ghosh, D., Ghoshal, J. Ribas, G. Mostafa, N. R. Chaudhuri, *Growth Des.*, **2006**, 6, 36.
- [20] S.-Q., Zang, Y. Su, Y.-Z..Li, H.-Z. Zhu, Q.-J., *Inorg. Chem.*, **2006**, 45, 2972.
- [21] Y. Xu, D. Yuan, B. Wu, L.Han, M.Wu, F. Jiang, M. Hong., *Cryst. Growth Des.*, **2006**, 6, 1168.
- [22] K. D. Patel, S.C. Pachani, R. B. Dixit, *Int. J. Inorganic and orgeno metallic Polmers*, **2003**.
- [23] A. B. Shivarkar, S. P. Gupte, R. V. Chaudhari, *Ind. Eng. Chem. Res.*, **2008**, 47, 2484.
- [24] H.S. Patel, V.K. Patel., *Indian J. Hetrocycl Chem.*, **2003**, 12, 253.
- [25] Vogel. A I. Textbook of Quantitative Chemical Analysis, (ELBS 4th Edn. London) **1978**.
- [26] P.R.Murrey, E.J.Baran M.A. Pfuller, F.C. Tenovov, R.H. Yolken, *An antimicrobial agent And susceptibility testing Americal Soc. Microbiology, Washington DC*, **1995**, 1327.
- [27] B.A. Arthinton, M D.Motley, W Warnoek, C.J. Morrison, *J.Clin. Microbiology*, **2000**, 38, 1254.
- [28] R.G. Charles, H. F. Frieser, R. Priedel, L. E. Hilliand, R. D. Johnston, *Spectrochem. Acta* , **1956**, 8, 1.
- [29] H.M. Parekh, P.K. Panchal, M.N. Patel, *J. Therm. Anal. Cal.* **2006**, 86, 803.
- [30] M.S. Masoud, M.F. Amira, A.M. Ramadan, G.M. El-Ashry, *Spectrochim. Acta, Part A*, **2008**, 69, 230.
- [31] K. C. Satpathy, A. K. Pande, R. Mishra, I. Panda, *Synth. React. Inorg. Met. Org. Chem.*, **1991**, 21, 531.
- [32] J. Kidri, D. Hadi, D. Kocjan, *et al. Org. Magnet. Reson.*, **2004**, 15, 280.
- [33] B.J. Hathway, A.G. Tomilson A, *Coord Chem Rev.*, **1980**, 5, 1.
- [34] H.B. Pancholi, M. M. Patel, *J Polym Mater.*, **1996**, 13, 261.
- [35] R. Papplardo, *J Chem Phys.*, **1960**, 33, 613.
- [36] J. Lewis, R. S. Wilkins, *Modern Coordination Chemistry, New York*, p., **1960**, 90.
- [37] C. Furlani, G. Morpurgo, *Theoret Chim Acta.*, **1965**, 1, 1181.
- [38] C.K. Jorgenson, *Acta Chem Scand.*, **1955**, 9, 1362.
- [39] H. M. Parekh, P. B. Pansuriya, M. N. Patel, *Polish J. Chem.*, **2005**, 79, 1843.
- [40] B. G. Tweedy, *Phytopathology*, **1964**, 55, 910.