Co-ordination polymers derived from pyromellitic diamic acid: synthetic, spectral, magnetic, thermal and biological aspects

Yogesh S. Patel and Hasmukh S. Patel
Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India.

ABSTRACT

The ligand 2,5-bis(phenylcarbamoyl)terephthalicacid (bpctpa) was synthesized and characterized. Novel co-ordination polymers were prepared by using ligand (bpctpa) and transition metal ions viz. Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). The co-ordination polymers and parent ligand were characterized by elemental analysis, spectral studies, thermogravimetry, number-average molecular weights ($\overline{Mn}$), diffuse reflectance spectral studies and magnetic susceptibilities. The biological activity of all the samples has also been monitored against plant pathogens.

© 2012 Elixir All rights reserved.

Introduction

The design of metal organic co-ordination polymeric materials have been deeply researched. In recent years, the studies of co-ordination polymers have made much progress. Such polymers are prepared by polymerization of bis ligand and metal ions. Most of the co-ordination polymers are reported based on bis-salicylic acid, bis-salicyaldehyde and bis-oxine.[1-6] One of the area in which the co-ordination polymer formation through bisamic acid has not been much developed except few instances. Bisamic acid based on maleic anhydride, [7-9] amic acid based on phthalic anhydride[10-13] are only such type of co-ordination compound / polymers based on amic acid. More particularly, multicarboxylate material i.e. 1,2,4,5-benzene tetra carboxylic acid has been shown to be good building blocks in the design of metal organic materials with desired topologies owing to their rich co-ordination modes. Therefore, the dianhydride of 1,2,4,5-benzenetetracarboxylic acid known as pyromellitic dianhydride–PMDA has been selected for the further work.

Literature survey also reviewed that, the co-ordination metal polyamide based on bisamic acid of pyromellitic dianhydride (PMDA) has not attracted any attention. Hence, the initial work in this direction has been reported by us recently. [14] This prompted us to extend our work by using other auxiliary ligand such as 2,5-bis (phenylcarbamoyl)terephthalicacid. Considering the special biological activity of these polymeric complexes along with their magnetic properties, thermo gravimetric analysis and polymeric property, we focused our work on this ligand by complexation using Cu(II), Co(II), Ni(II), Mn(II) and Zn(II) metal ions. The synthetic route is shown in Scheme-1.

Experimental details

Material

All the chemicals such as 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride-PMDA) (m.p. 397-400˚C) of Fluka Analytical-Japan , Aniline of SD fine chemicals-Mumbai and Cu(II), Co(II), Ni(II), Mn(II) and Zn(II) metal ions salt of Merck Laboratory and SD fine chemicals used

were of reagent grade. Solvents are dried and distilled before use according to standard procedures.

Measurements

Infrared (IR) spectra of all the samples were scanned on a Nicolet-760 FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded on Bruker spectrophotometer (400 MHz). Elemental analysis of ligand and its co-ordination polymers were carried out on a Thermofingan flash 1101EA (Italy). The metal content of the co-ordination polymers were performed by decomposing a weighed amount of co-ordination polymer followed by the complexometric titration with EDTA(disodiumethylenedi aminetetra acetate).[15] The number average molecular weight of polymers was determined by method reported.[16] Magnetic susceptibility measurements of polymers were carried out at room temperature by the Gouy method. Molar susceptibities were corrected for diamagnetism of component atoms using Pascal's Constant. [17] The solid diffuse reflectance spectra of polymers and ligand samples were recorded on a Beckman DK-2A spectrophotometer. Thermo gravimetric analysis was carried on Perkin Elmer TGA analyzer. Antibacterial activity of ligand and polymers were studied against gram-positive bacteria (*Bacillus subtilis and Staphylococcus aureus*) and gram-negative bacteria (*E.coli, and Salmonella typhi*). The fungicidal activity of all the compounds was studied at 1000 ppm concentration in vitro. Plant pathogenic organisms used were P*enicillium expansum, Botrydepladia thiobromine, Nigrospora Sp., Trichothesium Sp.*. The percentage inhibition for fungi was calculated after five days using the formula given

Percentage of inhibition = 100(X-Y) / X.

Where, X: Area of colony in control plate, Y: Area of colony in test plate

Preparation of 2,5-bis(phenylcarbamoyl)terephthalicacid (bpctpa)

The bpctpa was prepared by method reported.[18] According to this method, a mixture of 1,2,4,5-

benzenetetracarboxylic dianhydride (0.1 mole) and aniline (0.2 mole) was refluxed at 75-80 °C for 1 h with occasional stirring. Thus obtained light yellow precipitate was then filtered and washed. Lastly it was air dried. Molecualr formula $C_{22}H_{16}N_2O_6$ (m.p. 245-260(uncorrected), yield 70%, m.wt. 404.37, light yellow), Elemental analysis calculated: C, 65.34; H, 3.99; N, 6.93. Found C, 65.30; H, 3.99; N, 6.89%. ^{1}H NMR (δ ppm): 10.7 (2H, s, -COOH), 8.8(2H, s, -NH-CO-), 8.0 (2H, s, Ar.H), 7.30-7.63 (10H, m, Ar.H). ^{13}C NMR (δ ppm): 117, 119, 123, 126, 129, 132, 135, 167, 172. IR (KBr, cm^{-1}): 3530, 3254, 3021, 1740, 1700, 1652, 1575, 1450, 1034.

Preparation of co-ordination polymers

All co-ordination polymers were synthesized by using equimolar amount of ligand and metal salt. The yields of all co-ordination polymers were almost quantitative. The synthetic route for the co-ordination polymer is shown in Scheme-1.

$[Cu(bpctpa)(H_2O_2)]_n$ was prepared by neutralizing a warm clear solution of ligand (0.01 mol) in dimethyl sulphoxide-DMSO with 0.1 M sodium hydroxide solution and pH about 7-8 was maintained. A pasty mass was observed. It was diluted with water to make the solution clear and then added to a solution of copper salt (0.01 mol) with constant stirring. pH of the reaction mixture was adjusted to about 4-5. The Co-ordination polymers thus separated out in the form of a suspension was digested on a water bath for 1 h and eventually filtered, washed and then dried in air at room temperature. Empirical formula $C_{22}H_{19}N_2O_8Cu$ (yield 70%, Empirical wt. 502.94, green), Elemental analysis calculated: C, 52.54; H, 3.81; N, 5.57; Cu, 12.63. Found C, 52.48; H, 3.78; N, 5.50; Cu, 12.56%. IR (KBr, cm^{-1}): 3248, 2980, 1682, 1662, 1603, 1463, 1397, 1239, 1175, 1021, 632, 532. Magnetic moment μ_{eff}: 2.1 B.M. Number average molecular weight ($\overline{Mn}$): 3020. Degree of polymerization (Dp): 6.

$[Co(bpctpa)(H_2O_2)]_n$ was prepared in an analogous manner except the reaction was carried out at about 6 pH in presence of cobalt salt. Empirical formula $C_{22}H_{19}N_2O_8Co$ (yield 52%, Empirical wt. 498.33, pink), Elemental analysis calculated: C, 53.02; H, 3.84; N, 5.62; Co, 11.83. Found C, 52.92; H, 3.80; N, 5.56; Co, 11.78%. IR (KBr, cm^{-1}): 3249, 2983, 1686, 1668, 1607, 1465, 1399, 1237, 1171, 1024, 635, 536. Magnetic moment μ_{eff}: 3.3 B.M. Number average molecular weight ($\overline{Mn}$): 2511. Degree of polymerization (Dp): 5.
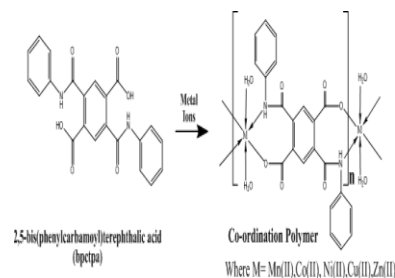
$[Ni(bpctpa)(H_2O_2)]_n$ was prepared in an analogous manner by using nickel salt. Empirical formula $C_{22}H_{19}N_2O_8Ni$ (yield 57%, Empirical wt. 498.09, light green), Elemental analysis calculated: C, 53.05; H, 3.84; N, 5.62; Ni, 11.78. Found C, 53.00; H, 3.78; N, 5.56; Ni, 11.72%. IR (KBr, cm^{-1}): 3245, 2984, 1685, 1663, 1605, 1467, 1397, 1240, 1177, 1026, 638, 533. Magnetic moment μ_{eff}: 3.1 B.M. Number average molecular weight ($\overline{Mn}$): 2534. Degree of polymerization (Dp): 5.

$[Mn(bpctpa)(H_2O_2)]_n$ was prepared in an analogous manner by using manganese salt. Empirical formula $C_{22}H_{19}N_2O_8Mn$ (yield 45%, Empirical wt. 494.33, light pink), Elemental analysis calculated: C, 53.45; H, 3.87; N, 5.67; Mn, 11.11. Found C, 53.40; H, 3.82; N, 5.61; Mn, 11.05%. IR (KBr, cm^{-1}): 3234, 2978, 1680, 1663, 1609, 1464, 1395, 1239, 1174, 1021, 630, 535. Magnetic moment μ_{eff}: 4.9 B.M. Number average molecular weight ($\overline{Mn}$): 3010. Degree of polymerization (Dp): 6.

$[Zn(bpctpa)(H_2O_2)]_n$ was prepared in an analogous manner by using zinc salt. Empirical formula $C_{22}H_{19}N_2O_8Zn$ (yield 40%, Empirical wt. 504.80, white), Elemental analysis calculated: C, 52.34; H, 3.79; N, 5.55; Zn, 12.96. Found C, 52.29; H, 3.72; N, 5.50; Zn, 12.90%. IR (KBr, cm^{-1}): 3244, 2981, 1684, 1662, 1603, 1465, 1397, 1234, 1179, 1025, 638, 531. Magnetic moment μ_{eff} : Diamagnetic. Number average molecular weight ($\overline{Mn}$): 2520. Degree of polymerization (Dp): 5.

Scheme 1: The synthetic route for the co-ordination polymers.

2,5-bis(phenylcarbamoyl)terephthalic acid (bpctpa)   Co-ordination Polymer

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

Results And Discussion

Elemental analysis and Polymeric analysis

The elemental analysis of ligand and its co-ordination polymers are in agreement with proposed structures. All the co-ordination polymers exhibited 1:1 metal to ligand stoichiometry. The value of the Degree of polymerization (Dp) of all the co-ordination polymers are in the range of 5 to 6.

IR Spectra

Ligand exhibit a broad band at 3530 cm^{-1} attributed to carboxylic –OH group and at 3254 cm^{-1} and 1658 cm^{-1} are due to O=C-NH group. Comparison of the IR spectrum of ligand with the co-ordination polymers revels that, a broad band at about 3530 cm^{-1} for ligand is virtually disappeared from the spectra of polymers. In the case of metal complexes, vibrational bands appeared for O=C-NH (amide carbonyl linkage) shifted to the lower frequencies and indicating the co-ordination of amide nitrogen to metal ion, and this can be explained by the donation of electrons from nitrogen to metal atom. The v C-O also registered a significant shift to lower frequency indicating the participation of metal through the carboxylate oxygen. In all the polymer metal complexes, some additional bands also appeared in the regions of 525-550 cm^{-1} and 620-640 cm^{-1}, which support the co-ordination of metal through nitrogen and oxygen respectively.[16,17] These features confirm the proposed structure of ligand 2,5-bis(phenylcarbamoyl)terephthalic acid (bpctpa) with metals.

#### Electronic spectra and Magnetic measurements

The information regarding geometry of the co-ordination polymers were obtained from their electronic spectral data and magnetic moment values. The diffuse electronic spectrum of the [Cu-bpctpa-(H$_2$O)$_2$] shows two broad bands around 15,966 cm^{-1} and 22,780 cm^{-1} due to the $2_{T2g} \rightarrow 2_{Eg}$ transition while the second may be due to charge transfer, respectively, This suggest a distorted octahedral structure for the [Cu-bpctpa-(H$_2$O)$_2$] polymer. The higher value of μ_{eff} of the [Cu-bpctpa-(H$_2$O)$_2$] polymer support this view. The [Ni-bpctpa-(H$_2$O)$_2$] co-ordination polymer shows two absorption bands, at 15,590 cm^{-1} and 22,981 cm^{-1} due to $3_{A2g} \rightarrow 3_{T1g}$ (F) and $3_{A2g} \rightarrow 3_{T1g}$ (P) respectively. The [Co-bpctpa-(H$_2$O)$_2$] polymer shows two absorption bands, at 19,611 and 22,923 cm^{-1} corresponding to $4_{T1g}(F) \rightarrow 4_{T2g}$ and $4_{T1g}(F) \rightarrow 4_{T2g}(F)$ transitions, respectively. Thus, the absorption bands of the diffuse reflectance spectra and the values of the magnetic moments (μ_{eff}) indicate an octahedral configuration for the [Ni-bpctpa-(H$_2$O)$_2$]and [Co-bpctpa-(H$_2$O)$_2$] polymers. The spectrum of [Mn-bpctpa-(H$_2$O)$_2$] show weak bands at 16,478, 17,690, and 23,150 cm^{-1} assigned to the transitions $6_{A1g} \rightarrow 4_{T1g}(4G)$, $6_{A1g} \rightarrow 4_{T2g}(4G)$ and $6_{A1g} \rightarrow 4_{A1g}, 4_{Eg}$ respectively, suggesting an octahedral structure for the [Mn-bpctpa-(H$_2$O)$_2$] polymer[21]. As the spectrum of the [Zn-bpctpa-(H$_2$O)$_2$] polymer is not well interpreted, but its μ_{eff} value shows that it is diamagnetic as expected.

Magnetic Moments μ_eff of co-ordination polymers revels that all the polymers except Zn(II) metal ion polymer are paramagnetic while Zn(II) metal ion polymer is diamagnetic.

Thermogravimetric analysis

The TGA results of all the samples are presented in Table 1. Thermogram of ligand bpctpa is given in figure-1. The thermogram of ligand degrade in to two steps. The first step of degradation starts from 125^oC to 240^oC may be attributed to decarboxylation of bis ligand. The value of wt. loss 21.37% is consistent with theoretical value 21.76%. The weight loss of the co-ordination polymer samples at different temperature indicates that the degradation of the polymers is noticeable beyond 300^oC. Thermograms of all coordinated polymers revealed that all samples suffered appreciable weight loss in the range 170 to 340^oC. This may be due to the presence of coordinated water molecule. The rate of degradation becomes a maximum at a temperature lying between 350^oC and 500^oC. This may be due to accelerating by metal oxide which forms in situ. Each polymer lost about 50% of its weight when heated up to 700^oC. On the basis of the relative decomposition (% wt. loss) and the nature of thermogram, the co-ordination polymers may be arranged in order in increasing stability as: Cu < Ni < Co < Zn < Mn.

Figure-1: Thermogram of Ligand bpctpa
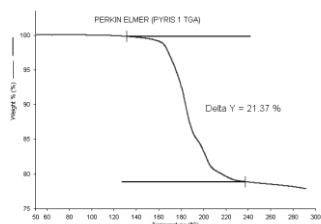
Biological Activity

The antimicrobial activity of ligand and its co-ordination polymers was studied against standard gram positive and gram negative bacteria. (Table 2) The compounds were tested at different concentration ranging from 50 to 1,000 ppm to find out the minimum concentration of the ligand and polychelates, which inhibits the microbial growth. The inhibition of growth from ditch was measured in millimeter.

The fungicidal activity of all the compounds was studied at 1000 ppm concentration against Plant pathogenic organisms. (Table 2) The ligand was found biologically active, and their polychelates showed significantly enhanced biological activity compared to the uncomplexed ligand.

BS : *Bacillus subtilis*, SA : *Staphylococcus aureus*, ST: *Salmonella typhi*,

EC : *Escherichia coli*, PE : *Penicillium Expansum*, BT : *Botrydepladia Thiobromine*, NS : *Nigrospora Sp.*, TS : *Trichothe-sium Sp.*

Conclusion

The present paper describes the novel ligand having dianhydride and aromatic amine moieties. The ligand offers the co-ordination polymers with metal ions. The polymers have moderate thermal stability. All the polymers have good microbicidal activity.

References

[1] Khyati D Patel and Hasmukh S Patel. Studies of the Co-ordination Polymers Based on Divalent Transition Metal Ion with Bis ligands. Der Pharmacia Lettre. 2011; 3(1):356-363.

[2] Arun Singh and Jayesh Bhanderi. Poly(ester-amide) having pendent 8-quinolinol moiety as a novel polymeric ligand. Rasayan J. Chem. 2009; 2:846-852.

[3] Khyati D Patel and Hasmukh S Patel. Antimicrobial, spectral and thermal aspects of some novel co-ordination polymers-based on 8-hydroxy quinoline. Elixir Appl. Chem. 2011; 41:5693-5698.

[4] Wen-Kui Dong, Jun-Feng Tong, Yin-Xia Sun, Jian-Chao Wu, Jian Yao, Shang Sheng Gong, Studies on mono-and dinuclear bisoxime copper complexes with different co-ordination geometries. Transition Met. Chem. 2010, 35:419–426.

[5] Arjun K Rana, , Navnit R Shah, Manak S Patil, Asger M Karampurwala, Jayant R Shah. Polychelates derived from 4,4′-(4,4′-biphenylylenebisazo) di (salicyla ldehyde oxime). DieMakromolekulareChemie. 1981; 182:3387-3395.

[6] Hasmukh S Patel, Darshana J Patel. Co-ordination polymers based on Bis-ligand containing Indole and 8-hydroxy quinoline moieties. International Journal of Polymeric Material. 2010; 59:307–317.

[7] H S Patel, K K Panchal. Novel Unsaturated Polyester Resins Containing Epoxy Residues. International Journal of Polymeric Materials. 2005; 54:1-7.

[8] Hasmukh S Patel, Kumar K Panchal. Flame Retardant Unsaturated Poly(Ester Amide) Resins Based on Epoxy Resins. International Journal of Polymeric Materials. 2005; 54:795–803.

[9] Pragnesh N Dave, Nikul N Patel. Studies on Interacting Blends of Acrylated Epoxy Resin Based Poly(Ester-Amide)s and Vinyl Ester Resin. Materials Sciences and Application. 2011; 2:771-776.

[10] Ryo Tamaki, Jiwon Choi and Richard M Laine. A Polyimide Nano composite from Octa(aminophenyl)silsesquioxane. Chem. Mater. 2003; 15:793-797.

[11] Seung Koo Park, Richard J. Farris and Simon W. Kantor. Polyhydroxyamic Acid from 3,3'-Dihydroxybenzidine and Pyromellitic Dianhydride as a Fire-safe Polymer. Fibers and Polymers. 2004; 5:83-88.

[12] Mitsuru Ueda and Tomonari Nakayama. A New Negative-Type Photo sensitive Polyimide Based on Poly(hydroxyimide), a Cross-Linker, and a Photoacid Generator. Macromolecules. 1996; 29:6427-6431.

[13] Li Yan , Cheol Park, Zoubeida Ounaies, Eugene A Irene. An ellipsometric study of polymer film curing: 2,6-Bis(3-aminophenoxy)benzonitrile/4,4 oxidi phthalic anhydride poly(amic acid). Polymer. 2006; 47:2822–2829.

[14] Yogesh S Patel, Hasmukh S Patel. Studies on Novel Co-ordination Polymers Based on 2,5-bis(4-chlorophenylcarbamoyl)terephthalic acid and Divalent Transition Metal Ions. Der Chemica Sinica, 2011; 2(6):58-67.

[15] A.I.Vogel, A textbook of Quantitative Inorganic Analysis, 3rd ed., Longman, London, p.433 1961.

[16] T B Shah, H S Patel, R B Dixit, B C Dixit. Co-ordination Polymers of 1,8-Bis(8-Hydroxyquinolin-5-yl)-2,7-Dioxaoctane. International Journal of polymeric Analysis and Characterization. 2003; 8:369.

[17] J Lewis and R S Wilkins, Modern Co-ordination Chemistry. Interscience, NY, p. 290. 1960.

[18] Awad, William I, Ali, Imad T, Dehydration of Pyromellitamic acids. Journal of the Iraqi Chemical Society. 1977; 2(2):39-51.

[19] R M Silverstein, and F X Webste. Spectrometric Identification of Organic Compounds. 6th Ed.; John Wiley &

[20] Sons, Inc: New York, 2004.

[21] Lever ABP Electronic spectra of d^n Inorganic Electronic Spectroscopy; 2nd Ed.; Elsevier: Amsterdam, 1984

[22] R Papplardo. Note on the Optical Absorption of $MnCl_2$ and $MnBr_2$. J. Chem. Phys. 1960; 33:613.

Table 1 Thermogravimetric analysis of Co-ordination polymers

Compound	% Weight loss at different temperature(^{O}C)							Activation energy Ea Kcal/mol
	100	200	300	400	500	600	700	
[Cu-bpctpa-$(H_2O)_2$]n	1.3	10.1	22.8	31.5	36.2	43.2	57.4	6.5
[Co-bpctpa-$(H_2O)_2$]n	1.9	12.5	21.6	33.1	38.1	44.1	58.9	7.9
[Ni-bpctpa-$(H_2O)_2$]n	2.4	14.0	21.9	32.7	37.5	46.5	59.9	7.5
[Mn-bpctpa-$(H_2O)_2$]n	2.9	10.5	23.0	33.4	37.6	45.9	59.8	8.3
[Zn-bpctpa-$(H_2O)_2$]n	3.9	13.6	25.2	35.1	38.9	49.9	63.8	8.1

Table 2 Antibacterial and Antifungal activity of ligand and its polymers

Compound	Antibacterial Activity				Antifungal Activity			
	Zone of Inhibition				Zone of Inhibition			
	Gram +Ve		Gram −Ve		*PE*	*BT*	*NS*	*TS*
	BS	*SA*	*ST*	*EC*				
bpctpa	19	18	21	21	26	20	23	20
[Cu-bpctpa-$(H_2O)_2$]$_n$	30	33	30	18	38	29	26	33
[Co-bpctpa-$(H_2O)_2$]$_n$	28	29	22	22	32	27	28	25
[Ni-bpctpa-$(H_2O)_2$]$_n$	26	26	24	24	28	22	29	24
[Mn-bpctpa-$(H_2O)_2$]$_n$	27	30	24	20	30	26	31	23
[Zn-bpctpa-$(H_2O)_2$]$_n$	28	31	25	21	31	25	28	24