Studies on Novel Co-ordination Polymers Based on 2,5-bis(4-chloro phenylcarbamoyl)terephthalic acid and Divalent Transition Metal Ions

Yogesh S. Patel and Hasmukh S. Patel*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat (India)
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ABSTRACT

Novel bis-ligand namely, 2,5-bis(4-chlorophenylcarbamoyl)terephthalic acid (BCPCTPA) was synthesized by condensation of anhydride of 1,2,4,5-benzene tetracarboxylic (pyromellitic dianhydride –abbreviated PMDA) with 4-chloro aniline. Co-ordination polymers of this bis-ligand were prepared with Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) metal salts. All these co-ordination polymers and the parent ligand were characterized by elemental analysis, infrared spectra, number-average molecular weights, magnetic susceptibilities and by thermogravimetry. The antimicrobicidal activity of all the samples has also been monitored against plant pathogens.

Keywords: Number average molecular weight ($\overline{Mn}$); Thermogravimetric analysis (TGA), Magnetic susceptibilities, Antimicrobicidal activity.

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INTRODUCTION

In recent years, the study on coordination polymer has made much progress [1-4]. Pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic dianhydride-PMDA) has been used extensively as an important monomer in the preparation of a variety of thermoplastics such as polyesters, polycarbonates, polyethers, plasticizers, expoxy resins, etc. Moreover, it is also useful in the preparation of high performance coatings that have been widely used in many fields in our daily life because of its excellent thermal, oxidative stability and excellent mechanical properties [5-9].

Our Indian scientists have explored the co-ordination study of phthalamic, maleimic and bisamic acid [10-15]. A great deal of work has been done on the polyimide based pyromellitic dianhydride. The most well-known is based on PMDA and 4-oxydianiline [16-18]. Though the PMDA is a versatile monomer for high performance polymers i.e. Polyimides[19-21], it is worthwhile to divert the utility of PMDA. Some of the polyimide based on mallophanic dianhydride, an isomer of PMDA is also known[22]. In context to this, the literature survey reviewed that the co-ordination polymers (polyamide) based on pyromellitic dianhydride (PMDA) has not been attracted much attention.

The novel polyamide-acids can be prepared by dianhydride with amine. This invention can be used immediately or stored for subsequent use. They are useful as coating composition which can be applied to a variety of substrates, for example, metals, like copper, brass, aluminum, steel etc., the metals in the form of sheets, fibers, foams, fabrics, etc.; cellulosic materials such as cellophane, wood, paper, etc., polyolefin such as polyethylene, polypropylene. These coating can than be converted to polyimide coating by any convenient method [23].

This may offer the compound, not only the metal gripping potentiality but may also have good biological efficacy due to anhydride moiety. Hence the present article describes the synthesis and characterization of a Novel bis-ligand namely, 2,5-bis(4-chlorophenylcarbamoyl)terephthalic acid (BCPCTPA) and its co-ordination polymers with Cu(II), Co(II), Ni(II), Mn(II) and Zn(II) metal ions. The synthetic route is shown in scheme 1.

2,5-bis(4-chlorophenylcarbamoyl)terephthalic acid (BCPCTPA)
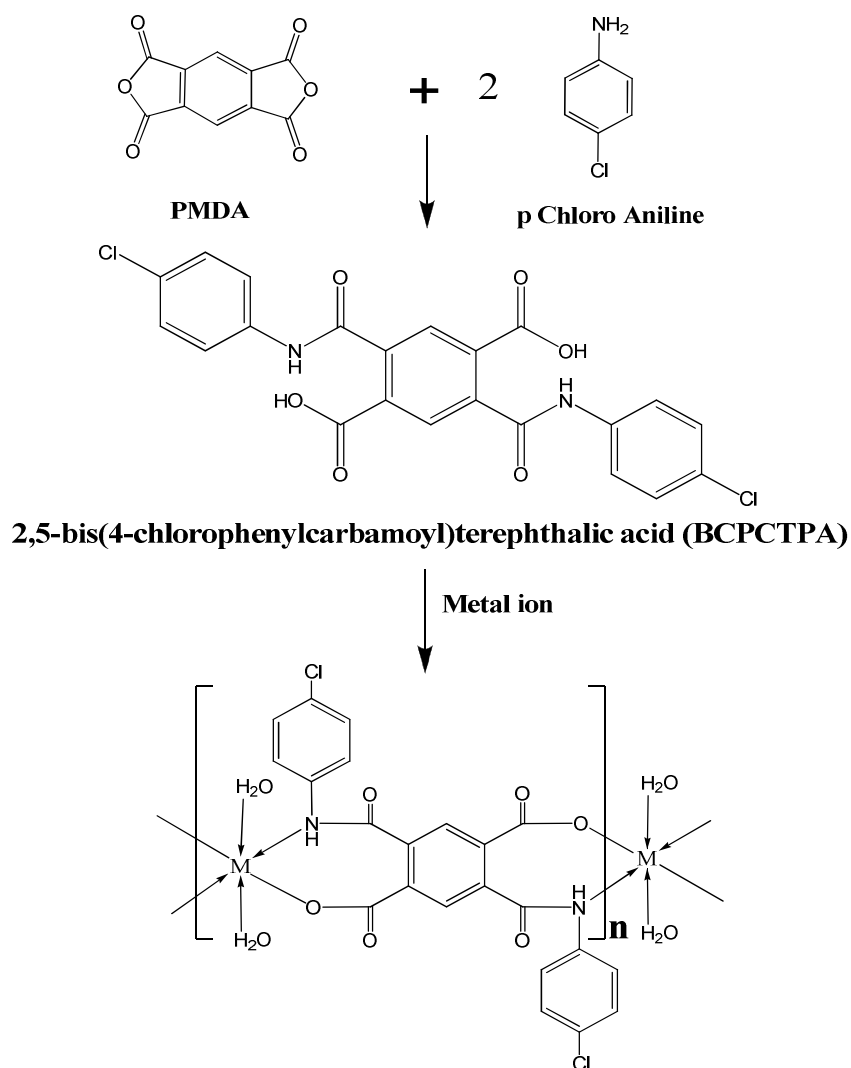
Where M= Mn(II),Co(II), Ni(II),Cu(II),Zn(II)

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

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MATERIALS AND METHODS

Experimental
All chemicals used are of analar or chemically pure grade.

Preparation of 2,5-bis(4-chlorophenylcarbamoyl)terephthalic acid (BCPCTPA)
The BCPCTPA was prepared by method reported [24]. According to this method, a mixture of 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride-PMDA) (m.p. 397-400˚C) of Fluka Analytical-Japan (21.81 g, 0.1 mole) and 4-chloroaniline (25.514 g, 0.2 mole) was refluxed at 60-70 ˚C for one hour with occasional stirring. Thus obtained precipitate was then filtered and washed. Lastly it was air dried. The yield was of approx 65% and it decomposed at 252-280˚C

Preparation of co-ordination polymers
All co-ordination polymers were synthesized by using equimolar amount of ligand BCPCTPA and metal acetate. A warm clear solution of bis-ligand (4.733g, 0.01 mol) in Dimethyl sulphoxide - DMSO (50 ml) was neutralized with 0.1 M Sodium hydroxide solution and pH about 7-8 was maintained. A pasty mass was observed. Minimum amount of water was added to dissolve the precipitates and make the solution clear. To the resulting solution, add drop wise solution of copper acetate (1.99g, 0.01 mol) in water (50 ml) with constant stirring. After complete addition of the metal salt solution, the 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 hour and eventually filtered, washed and then dried in air at room temperature. The yields of all co-ordination polymers were almost quantitative. According to the same process, other metal like Ni(II), Co(II), Mn(II) and Zn(II) can also be used to prepare various coordination polymers by maintaining pH.

Measurements
Elemental analysis of bis-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 aminetetraacetate)[25].

Infrared (IR) spectra of all the samples were scanned on a Nicolet-760 FTIR spectrophotometer. The number average molecular weight of all the co-ordination polymers were determined by method reported [26].

Magnetic susceptibility measurements of all the co-ordination polymers were carried out at room temperature by the Gouy method. Mercury tetrathiocynato cobaltate(II) -Hg[Co(NCS)$_4$], was used as a calibrant. Molar susceptibilies were corrected for diamagnetism of component atoms using Pascal's Constant [27].

The solid diffuse reflectance spectra of all the co-ordination polymers and bis-ligand samples were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was used as the reference compound. Thermo gravimetric analysis of co-ordination polymers were carried on Perkin Elmer (PYRIS 1 TGA) analyzer in air at a heating rate of 20°C/min

Antibacterial activity of BCPCTPA ligand and its co-ordination polymers were studied against gram-positive bacteria (*Bacillus subtilis and staphylococcus aureus*) and gram-negative bacteria

(*E.coli, salmonella typhi and klebsiella promioe*) at a concentration of 50 µg/ml by agar cup plate method. Methanol system was used as control in this method. The area of inhibition zone was measured in mm.

The fungicidal activity of all the compounds was studied at 1000 ppm concentration in vitro. Plant pathogenic organisms used were *penicillium expansum, Botrydepladia thiobromine, Nigrospora Sp., Trichothesium Sp., and Rhizopus nigricum*. The antifungal activity of bis-ligand and its co-ordination polymers (1a-e) was measured on each of these plant pathogenic strains on a potato dextrose agar (PDA) medium. Such a PDA medium contains potato 200gm, dextrose 20gm, agar 20gm and water one liter. Five days old cultures were used. The compounds to be tested were suspended (1000 ppm) in a PDA medium and autoclaved at 120° C for 15 min. at 15atm. pressure. These medium were poured into sterile Petri plates and the organisms were inoculated after cooling the Petri plates. The percentage inhibition for fungi was calculated after five days using the formula given below:

$$\text{Percentage of inhibition} = 100(X-Y) / X$$

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

RESULTS AND DISCUSSION

Elemental analysis is summarized in Table 1. 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 structure of ligand and its co-ordination polymers are consistent with the FTIR, Elemental analysis, ^{1}H NMR, Reflectance spectra and TGA. The geometry of the central metal ion was confirmed by reflectance spectra (UV-Visible) and magnetic susceptibility measurements. All the data provides good evidence that the chelate are polymeric in nature. The suggested structure of the co-ordination polymers is shown in Scheme 1.

IR Spectra

The IR spectra of the co-ordination polymers were carried out by KBr pellets. All the polymers exhibit a broad band in the 3400-3000 cm^{-1} region attributed to –OH group, which supports the presence of co-ordinated water molecules [28,29]. In addition, the rocking and wagging modes of υ(O-H) are observed at 850 and 710 cm^{-1} respectively [30-32]. The presence of sharp band in the region 525-535 cm^{-1}, for all the co-ordination polymers can be assigned to υ (M-N)[33], which supports the involvement of nitrogen in co-ordination. The asymmetric and symmetric stretching frequencies of the carboxylate ions in the polymers are observed at 1595 cm^{-1} and 1400 cm^{-1} respectively, and are shifted to lower frequencies (~1582 cm^{-1} and ~1387 cm^{-1})[34-35]. The medium intensity bands for υ(M-O)[36] have been observed at 415-420 cm^{-1}, thereby confirming M-O co-ordination. Sharp bands at 768-772 and 1525-1535 cm^{-1} are due to aromatic υ(C-H) [37] and υ (C=C)[38], respectively and bands in the region 1160-1170 cm^{-1}, are attributed to υ (C-N).

The co-ordination polymers derived from BCPCTPA and metal ions Cu(II), Co(II), Ni(II), Mn(II) and Zn(II) are vary in color from bluish green to pinkish brown. These polymers do not melt upto 300^oC. On the basis of the proposed structure shown in Scheme1, the molecular formula of the BCPCTPA ligand is $C_{22}H_{14}Cl_2N_2O_6$, which coordinates with one central metal atom at four co-ordination sites and two water molecules on chelation. Therefore, the general

molecular formula of the resulting co-ordination polymer is given by [M(BCPCTPA)(H$_2$O)$_2$] as shown in scheme 1. This has been confirmed by the results of elemental analysis of all of the five co-ordination polymers and their bis ligand. The data of elemental analysis reported in Table 1 are in good agreement with the calculated values of C, H and N based on the above mentioned molecular formula of the bis ligand as well as co-ordination polymers.

Table 1 Analytical data of Ligand and its co-ordination polymers

Empirical Formula for Monomer	Mol. Wt.	Yield (%)	Elemental analysis Calc. / (Found)			
			C	**H**	**N**	**M**
C$_{22}$H$_{14}$Cl$_2$N$_2$O$_6$	473.26	70	55.83(55.30)	2.98(2.95)	5.92(5.89)	-
Cu.C$_{22}$H$_{17}$Cl$_2$N$_2$O$_8$	571.83	82	46.21 (45.60)	3.00 (2.87)	4.90 (4.50)	11.11 (10.94)
Co.C$_{22}$H$_{17}$Cl$_2$N$_2$O$_8$	567.22	70	46.58 (46.10)	3.02 (2.88)	4.94 (4.68)	10.39 (10.00)
Ni.C$_{22}$H$_{17}$Cl$_2$N$_2$O$_8$	566.98	65	46.60 (46.12)	3.02 (2.90)	4.94 (4.60)	10.35 (10.96)
Mn.C$_{22}$H$_{17}$Cl$_2$N$_2$O$_8$	563.22	71	46.91 (46.50)	3.04 (2.92)	4.97 (4.68)	9.75 (9.60)
Zn.C$_{22}$H$_{17}$Cl$_2$N$_2$O$_8$	573.69	74	46.06 (45.80)	2.99 (2.86)	4.88 (4.58)	11.40 (11.12)

Examination of data of the metal content in each polymer (Table 1) revealed a 1:1 ratio of metal:ligand (M/L) stoichiometry in all of the co-ordination polymers. The IR spectra of all of the co-ordination polymers of BCPCTPA resemble to each other in their general shape. Comparison of the IR spectrum of the parent ligand BCPCTPA with those of the co-ordination polymers reveals certain characteristic differences. The broad band at 3400-3100 cm^{-1} for BCPCTPA has virtually disappeared from spectra of the polymers. However, the weak band around 3200 cm^{-1} in the spectra of polymers indicates the presence of coordinated water molecule.

^{1}H NMR and ^{13}C NMR Spectral data of the Ligand

The ^{1}H-NMR spectrum of the synthesized ligand show a signal at δ = 6.8 to 8.2 ppm (m, 10H) corresponding to aromatic proton. The peak at δ = 10.5 ppm (brs., 2H) analogous to amide group and a shark peak at δ = 11.1 ppm is indicate the presence of –COOH group. The structure of the synthesized was also confirmed by ^{13}C-NMR spectrum.

These features confirm the proposed structure of bis-ligand ***2,5-bis(4-chlorophenylcarbamoyl)terephthalicacid(BCPCTPA)***and its co-ordination polymers. The value of the degree of polymerization of all the co-ordination polymers listed in Table2 suggest that the average Dp for all the polymers is in a range of 5 to 6

Table 2   Polymeric data of Ligand and its co-ordination polymers
^{a}Magnetic moment; D is diamagnetic

Ligand/ Co-ordination polymers	Empirical Formula for Monomer	Mol. Wt.	μeff^a (B.M)	($\overline{Mn}$) $\pm$ 60	$\overline{Dp}$
BCPCTPA	C$_{22}$H$_{14}$Cl$_2$N$_2$O$_6$	473.26	-	-	-
[Cu(BCPCTPA)(H$_2$O)$_2$]n	Cu.C$_{22}$H$_{17}$Cl$_2$N$_2$O$_8$	571.83	2.0	3056	6
[Co(BCPCTPA)(H$_2$O)$_2$]n	Co.C$_{22}$H$_{17}$Cl$_2$N$_2$O$_8$	567.22	3.6	2824	5
[Ni(BCPCTPA) (H$_2$O)$_2$]n	Ni.C$_{22}$H$_{17}$Cl$_2$N$_2$O$_8$	566.98	3.1	3010	5
[Mn(BCPCTPA)(H$_2$O)$_2$]n	Mn.C$_{22}$H$_{17}$Cl$_2$N$_2$O$_8$	563.22	5.2	3008	6
[Zn(BCPCTPA)(H$_2$O)$_2$]n	Zn.C$_{22}$H$_{17}$Cl$_2$N$_2$O$_8$	573.69	D	3149	5

Magnetic moments (μ_{eff}) of co-ordination polymers are given in Table 2. Examination of these data reveals that all co-ordination polymers except Zn (II) metal ion polymer are paramagnetic while that of Zn (II) metal ion polymer is diamagnetic nature.

Electronic Spectra and Magnetic Measurements
The information regarding geometry of the co-ordination polymers were obtained from their diffused reflectance spectra and magnetic moment values.

The diffuse electronic spectrum of the [Cu(BCPCTPA)(H_2O)_2] co-ordination polymers shows two broad bands around 15,973 cm^{-1} and 22,791 cm^{-1} due to the $^2T_{2g} \rightarrow {}^2E_g$ transition while the second may be due to charge transfer, respectively. This suggest a distorted octahedral structure for the [Cu(BCPCTPA)(H_2O)_2] polymer. The higher value of μ_{eff} of the [Cu(BCPCTPA)(H_2O)_2] polymer support this view [39-40]. The [Ni(BCPCTPA)(H_2O)_2] co-ordination polymer shows two absorption bands, at 15,603 cm^{-1} and 22,990cm^{-1} due to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P)transitions, respectively**.** The [Co(BCPCTPA)(H_2O)_2] polymer shows two absorption bands, at 19,618 and 22,927 cm^{-1} corresponding to $^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ and $^4T_{1g}$(F) $\rightarrow {}^4T_{2g}$(F) transitions, respectively[41]. 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(BCPCTPA)(H_2O)_2] and [Co(BCPCTPA)(H_2O)_2] polymers [42,43]. The spectrum of [Mn(BCPCTPA)(H_2O)_2] show weak bands at 16,484, 17,695, and 23,155 cm^{-1} assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}$(4G), $^6A_{1g} \rightarrow {}^4T_{2g}$(4G) and $^6A_{1g} \rightarrow 4A_{1g}, {}^4E_g$ respectively, suggesting an octahedral structure for the [Mn(BCPCTPA)(H_2O)_2] polymer[41]. As the spectrum of the [Zn(BCPCTPA) (H_2O)_2] polymer is not well resolved, it is not interpreted, but its μ_{eff} value shows that it is diamagnetic as expected.

Thermogravimetric Analysis
The thermal behaviour of co-ordination polymers and parent bis-ligand was investigated by TGA. The TGA results of all the samples are presented in Table 3. TGA Thermogram of Bis Ligand BCPCTPA and its co-ordination polymer [Cu(BCPCTPA)(H_2O)_2]_n is given in figure 1 and figure 2 respectively.

Table 3 Thermo gravimetric analysis of co-ordination polymers.

Ligand/ Co-ordination polymers	% Weight loss at different temperature(^{O}C)							Activation energy (Ea) Kcal / mol
	100	200	300	400	500	600	700	
[Cu(BCPCTPA)(H_2O)_2]n	1.1	8.2	10.2	28.3	34.4	41.9	54.2	5.9
[Co(BCPCTPA)(H_2O)_2]n	1.7	12.0	23.9	35.1	44.4	58.3	61.9	7.4
[Ni(BCPCTPA)(H_2O)_2]n	2.6	14.3	17.5	30.8	49.3	54.5	65.1	7.2
[Mn(BCPCTPA)H_2O)_2]n	2.3	9.0	12.2	33.0	45.2	56.1	61.8	8.1
[Zn(BCPCTPA)(H_2O)_2]n	6.0	14.2	28.8	36.0	46.2	58.6	65.4	7.9

The thermogram of bis ligand degrade in to two steps. The first step of degradation starts from 130°C to 260°C. may be attributed to decarboxylation of bis ligand. The value of wt. loss 18.53 % is consistent with theoretical value (18.59 %). The weight loss of the co-ordination polymer samples at different temperature indicates that the degradation of the polymers is noticeable beyond 300°C. Inspection of the thermograms of all coordinated polymer samples revealed that all samples suffered appreciable weight loss in the range 150 to 280°C. This may be due to the presence of coordinated water molecule. The rate of degradation becomes a maximum at a temperature lying between 400°C and 500°C. This may be due to accelerating by metal oxide which forms in situ. Each polymer lost about 55% of its weight when heated up to 700°C. 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.
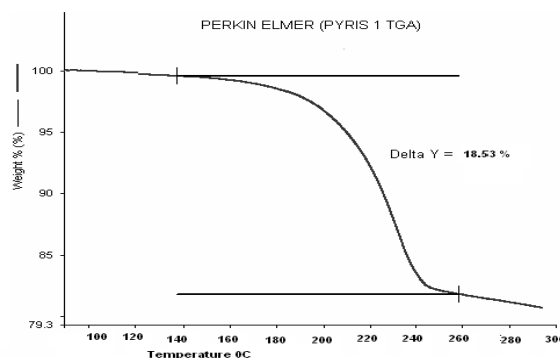

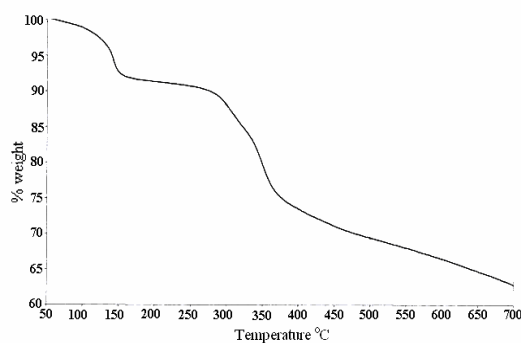**Figure 1   TGA Thermogram of Ligand BCPCTPA**

Figure 2   TGA Thermogram of [Cu(BCPCTPA)(H$_2$O)$_2$]$_n$

Antimicrobial Activity of Ligand and its co-ordination polymers

The antimicrobial activity of ligand and its coordination polymers was studied against standard bacterial strains of Escherichia coli, Bacillus subtillis, Staphylo coccus aureus and yeast strain of Saccharomyces cerevisiae.

The compounds were tested at different concentration ranging from 50 to 1,000 ppm to find out the minimum concentration of the bis-ligand and polychelates, which inhibits the microbial growth. The minimum concentration was to be found. The inhibition of growth from ditch was measured in millimeter (mm) and the results shows that all metal complexes exhibit antimicrobial activity against one or more strain (Table 4).

The ligand was found biologically active, and their polychelates showed significantly enhanced antibacterial activity against one or more bacterial species compared to the uncomplexed ligand. It is known that chelation tends to make the ligand a more potent bactericidal agent. The antimicrobial activity of the compounds increases after chelation. Chelation reduces the polarity of the metal ion by partial sharing of its positive charge with the donor groups, increasing lipophilic nature of the central metal ion, which in turn favours its permeation to the lipid layer of the bacterial membrane. Generally it is suggested that the chelated complexes deactivate various cellular enzymes, which play a vital role in various metabolic pathways of these micro organism. Other factors, viz., stability constant, molar conductivity, solubility and magnetic moment, are also responsible for the increase in the anti-microbial activity of the complexes. On

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the basis of Overtone's concept, Tweedy's chelation theory and the partial sharing of the positive charge of metal ions with donor groups. This may support the argument that some type of biomolecular binding to the metal ions or interchelation or electrostatic interactions causes the inhibition of biological synthesis and thus preventing the reproduction of organisms. The enhanced biological activity and lower toxicity of the transition metal polymers compared to the biological active bis-ligand make them useful in medicine and other biological applications. So it can be concluded that complex exhibit higher antimicrobial activity than the free ligand.

Table 4 Antibacterial Activity of co-ordination polymers

Compounds	Zone of Inhibition				
	Gram +Ve		Gram –Ve		
	Bacillus subtilis	*Staphylococcus aureus*	*Klebsiella promioe*	*Salmonella typhi*	*E. coli*
BCPCTPA	20	19	22	22	23
[Cu(BCPCTPA)(H$_2$O)$_2$]n	32	36	31	32	20
[Co(BCPCTPA)(H$_2$O)$_2$]n	32	30	24	23	23
[Ni(BCPCTPA) (H$_2$O)$_2$]n	30	26	26	25	26
[Mn(BCPCTPA)(H$_2$O)$_2$]n	31	33	24	24	22
[Zn(BCPCTPA) (H$_2$O)$_2$]n	30	32	29	32	23

Table 5 Antifungal Activity of co-ordination polymers

Compounds	Zone of Inhibition at 1000 ppm (%)				
	Penicillium Expansum	*Botrydep-ladia Thio bromine*	*Nigro-spora Sp.*	*Trichothesium Sp.*	*Rhizopus Nigricum*
BCPCTPA	28	22	24	20	21
[Cu(BCPCTPA)(H$_2$O)$_2$]n	40	30	28	34	30
[Co(BCPCTPA)(H$_2$O)$_2$]n	32	28	30	28	30
[Ni(BCPCTPA)(H$_2$O)$_2$]n	30	26	32	25	26
[Mn(BCPCTPA)(H$_2$O)$_2$]n	31	28	32	25	32
[Zn(BCPCTPA)(H$_2$O)$_2$]n	34	27	30	24	28

CONCLUSION

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

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