



Synthesis characterization and biological evaluation of bis-azo dye ligands based coordination polymers

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ABSTRACT

Novel bis ligand namely 2,2'-(4,4'-(1,4-phenylene bis(diazene-2,1-diyl))bis(4,1-phenylene)) bis(azanediyl) bis(oxomethylene)dibenzoic acid(PPDAL) has been prepared and characterized. The co-ordination polymers based on this bis ligand with transition metal ions like Cu^{+2} , Co^{+2} , Ni^{+2} , Mn^{+2} and Zn^{+2} were prepared and studied for their metal: ligand (M/L) ratio, IR and reflectance spectroscopies, magnetic properties, number-average molecular weight and by thermogravimetry. All the novel synthesized compounds were screened for their antibacterial and antifungal activities.

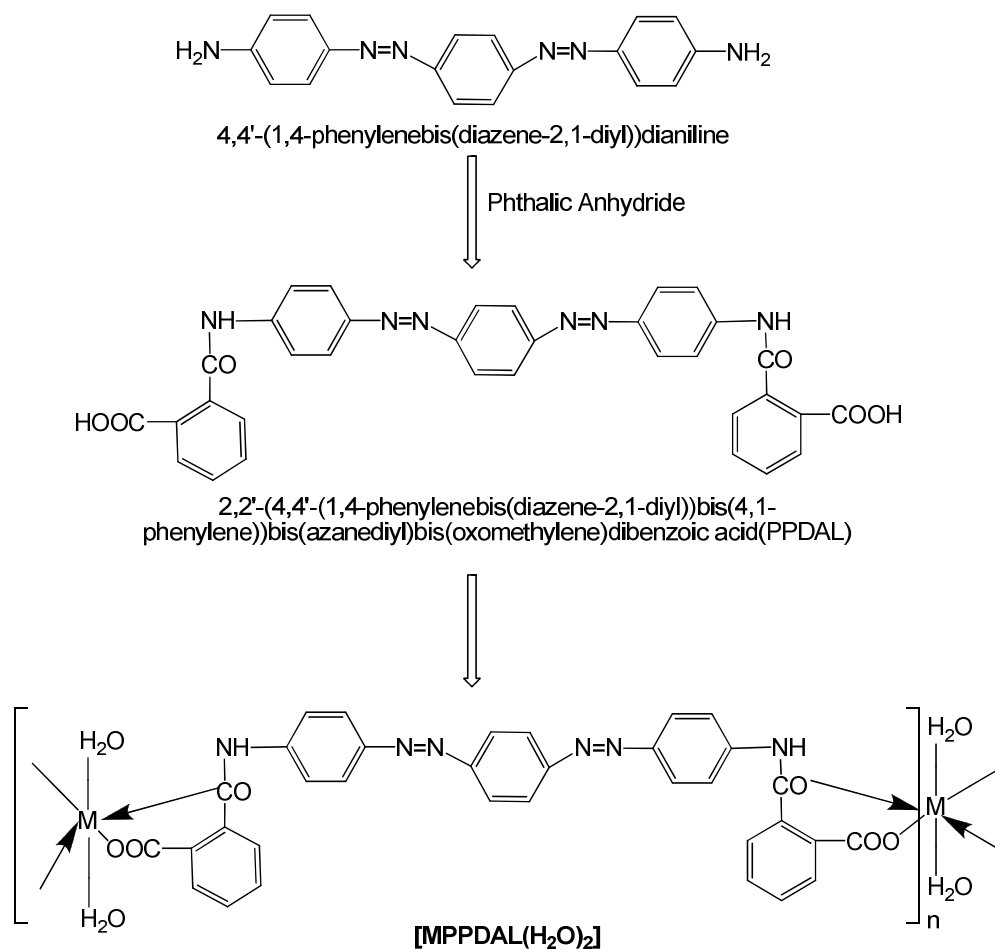
Keywords: Co-ordination polymer, bisazo ligand, magnetic properties, spectral studies and microbicidal activity.

INTRODUCTION

Traditionally, azo dyes are the most fundamental class of commercial dyes. The azo compounds are well colored and have been used as dyes and pigments [1, 2]. In addition, they have been studied usually because of their excellent thermal and optical properties in purposes such as toner [3, 4], ink-jet printing [5, 6] and oil-soluble lightfast dyes [7] optical recording medium [8–11]. In modern times, azo metal chelates have also paying attention due to their interesting electronic and geometrical features in link with their application for molecular memory storage, nonlinear optical elements and printing systems [9,11,12].

Recently, the study of co-ordination polymers has been made much progress [13, 14]. These polymers are known for their semiconducting catalytic properties, waste water treatment for metal recovery, in protective coating, as antifouling paints and anti fungal properties [15, 16]. Such Coordination polymers are mostly derived from bi-chelating ligands in which metal ions and chelating agents are grouped alternatively. The joining segment of these two similar ligands are mainly $-\text{N}=\text{N}-$, SO_2 , $-\text{CH}_2-$, $-\text{O}-$ [17-23]. Co-ordination polymers mostly derived from bichelating ligands in which metal ions and chelating agents arrayed alternatively [24-26]. The area in which the co-ordination polymers having azo dye moiety has been reported by one of author [DSR] [27]. In extension of previous work, the present article comprises the study of co-ordination polymers based on bisazo dye with phthalamic acid segment. Though phthalamic acid also act as good metal chelating agent.

In the present article, we report the synthesis, spectral studies and magnetic properties as well as antibacterial and antifungal activities of all the novel synthesized compounds and its metal chelates. Thus paper connecting with the studies of co-ordination polymers based on amic acid functionalized bisazo dye. The synthetic routes are shown in scheme-1.



Scheme-1

Where $M = Cu^{+2}, Co^{+2}, Ni^{+2}, Mn^{+2}, Zn^{+2}$

MATERIALS AND METHODS

Materials

Benzene-1,4-diamine was obtained from S. D. Fine Chemical Ltd. All other chemicals used were of analytical grade.

Synthesis of 4,4'-(1,4-phenylenebis(diazene-2,1-diyl))dianiline:

A solution of 10.8 g (0.1mole) of Benzene-1,4-diamine in 250 ml 2N HCl was cooled in a round bottom flask, surrounded by ice and stirred with electric motor, when solution was cold, add few pieces of ice and 200 ml 1N nitrite solution was added drop wise from a dropping funnel at below 0°C with stirring. After completing the addition of nitrite mixture was stirred for about 10 mins. Then tested to make sure that it gave strong blue coloration with Congo red paper and weak blue test with starch iodide paper, added distilled water in it dilute the solution & kept it into ice-bath.

A solution of dil. HCl added into aniline 18.6 gm (0.2 mole) till Congo Red Paper gave blue color, now added above diluted diazonium solution into aniline solution gradually in cold situation, stirred it well and add sodium acetate solution till the neutralization of dye. Now wash the dye with cold water. The products were obtained in the form of dark yellow color, collected that dye by vacuum filtration, then wash with cold water & dry it over night, Yield 81%, m.p.192⁰c (uncorrected). Analysis C₁₈H₁₆N₆ (Cal : %C 68.35, % H 5.06, % N 26.58 ; Found: % C 68.26, % H 5.02, % N 26.50).

Synthesis of 2,2'-(4,4'-(1,4-phenylenebis(diazene-2,1-diyl))bis(4,1-phenylene)) bis (azane diy) bis(oxomethylene) dibenzoic acid(PPDAL)

The solution of 4,4'-(1,4-phenylenebis(diazene-2,1-diyl))dianiline (0.1 mole) in acetone is cooled to 10°C. To this solution the phthalic anhydride (0.2 mole) was added with stirring. The resulting product was then filtered and air-

dried. Yield 80%, M.P. 259°C (uncorrected). Analysis: C₃₄H₂₄N₆O₆ (Cal : % C 66.67, % H 3.92, % N 13.73; Found: % C 66.36, % H 3.71, % N 13.42).

¹H-NMR (400 MHz, DMSO-d₆) δ (ppm): 12.6-11.0 (s, 2H, -COOH), 9.3-9.15 (s, 2H, -CONH, D₂O exchangeable), 8.0-7.50 (m, 20H, aromatic, J=0.9, 7.8 Hz).

¹³C-NMR-131.5 (C-1, C-12), 130.1 (C-2, C-11), 128.6 (C-3, C-10), 132.0 (C-4, C-9), 134.0 (C-5, C-8), 123.5 (C-6, C-7), 124.4 (C-13, C-17, C-20, C-24), 119.3 (C-14, C-16, C-21, C-23), 150.9 (C-18, C-19), 140.1 (C-15, C-22), 151.6 (C-25, C-28), 120.3 (C-26, C-27, C-29, C-30), 167.6 (C-31, C-32), 173.0 (C-33, C-34).

The predicted structure and formation of polymeric ligand is shown in Scheme-1.

The brief account of the thermal behaviour of ligand in air is given below:

(I) Examination of the TG curves of ligand sample reveals that it degrades in two steps.

(II) The first of degradation up to 200° to 230°C of the ligand indicate the weight loss in the range at 14% percentages. This is depending up on the molecular weight of sample.

(III) The second stage at degradation of the ligand beyond 200°C is rapid and loss about 75% to 85% at 300°C depending upon the nature of ligand.

(IV) The ligand containing two -COOH groups. Hence the TGA of ligand in air may cause decarboxylation [28]. The calculated value of CO₂ of ligand and % loss of first stage degradation of ligand is presented in Fig-I. Examination of these data reveals that the decarboxylation of ligand consistent with the calculated values. All these facts confirm the structure of ligand.

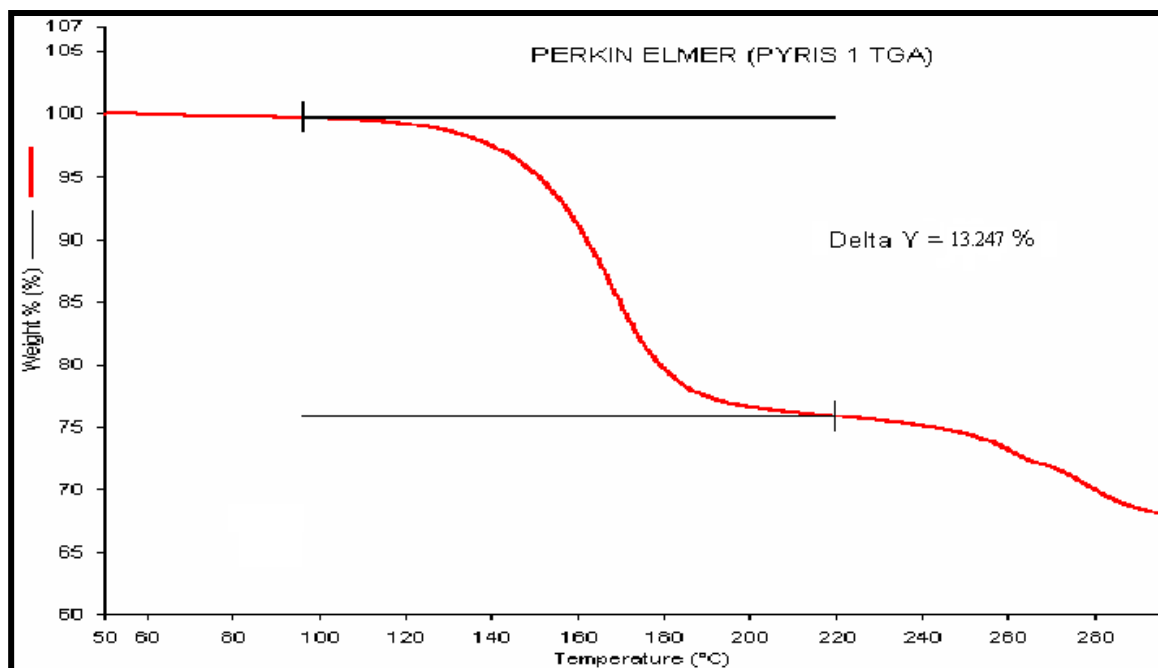


Fig-I TGA Thermogram of Ligand-PPDAL

Estimation of number of carboxylic (-COOH) groups in ligand PPDAL

The structure of ligand was examined by estimation of number of carboxylic -COOH groups per mole of ligand. The non-aqueous conductometric titration was employed for -COOH group estimation following the method reported in the literature [29-32]. The titrant used for this non-aqueous titration was tetra-n-butyl ammonium hydroxide (TBAH) in pyridine. The details procedure followed in titrations described here for PPDAL ligand.

Non-aqueous conductometric titration.

Experimental:

The ligand sample dried at 60°C was finely powdered and used for non-aqueous conductometric titration. A weighed amount of ligand sample (50 mg) was dissolved in 40 ml of anhydrous pyridine.

The solution was allowed to stand overnight for complete dissolution. This ligand solution was transferred into conductance cell and it was then stirred magnetically. The base tetra n-butyl ammonium hydroxide (TBAH) (0.1 N), in pyridine was added to the conductance cell at regular interval of 0.01 ml of titrant beyond the stage of

equivalence. The conductance measurement after addition of each volume of titrant base was carried out by allowing 2-3 minutes to lapse. During the titration the temperature of solution was maintained constant about 25°C, when the point of equivalence was exceeded, there was a continuous increase in conductance on addition of every additional aliquot of tetra-n-butyl ammonium hydroxide (TBAH) indicating the stage of complete neutralization of the –COOH groups in the given amount of ligand sample. The volume of base added is converted into millimoles of tetra-n-butyl ammonium hydroxide (TBAH) required for 100 gm of ligand. A plot of conductance against millimoles of tetra-n-butyl ammonium hydroxide (TBAH) per 100 gm of ligand sample was plotted. Inspection of such plot revealed two breaks. From the plot, the millimole per 100 gm of ligand sample corresponding to the break was noted. From this value, the number of –COOH groups was estimated. Each titration was reported twice as an independent experiments using different amount of the ligand sample. The two values estimated is agreed each other with 5% variation.

(I) Thus millimoles of TBAH required for complete neutralization of –COOH groups present in the sample was found by following formula using break of the titration curve. Finally two no. of COOH group calculated by:

$$\begin{array}{l} \text{No. of carboxylic groups} \\ \text{Per mole of ligand} \\ \text{(X)} \end{array} = \begin{array}{l} \text{Milimoles of TBAH} \\ \text{per 100gm of sample} \\ \text{(Y)} \end{array} \times \begin{array}{l} \text{Mol. weight} \\ \text{of ligand} \\ \text{(M)} \end{array} \times 10^{-5}$$

$$X = Y \times M \times 10^{-5}$$

E.g. For (PPDAL) X = 612 X 331 X 10⁻⁵

RESULTS AND DISCUSSION

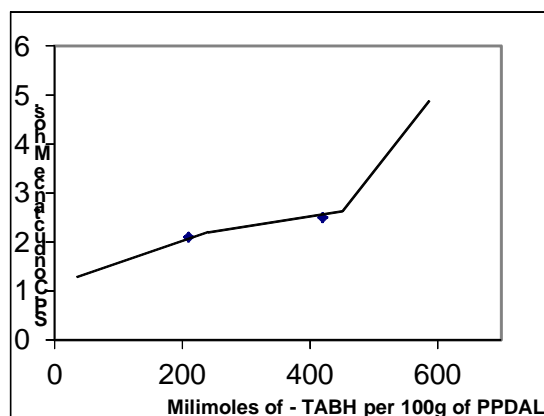
The typical conductometric titration curve of PPDAL Ligand has been shown in Fig II Examination curves of the ligand reveal that, the two breaks observed the all curve. From the value of at second break the number of –COOH group for ligand has been calculated. It was found that the value of carboxylic group is about 2 the ligand.

Table-I Non-aqueous Conductometric titration of Estimation of – COOH groups

Solvent: Anhydrous pyridine.
Reagent: 0.1 N tetra-n-butyl ammonium hydroxide (TBAH) in pyridine

| Ligand | Molecular weight gm | Millimoles of TBAH at break per 100 gm of sample | Estimated No. of –COOH group |
|---------|---------------------|--|------------------------------|
| (PPDAL) | 612 | 331 | 2.02 |

Figure-II



Determination of azo group:

The number of azo group for PPDAL ligand was estimated by method reported [33]. 35 mg. of sample was taken in the titration flask and dissolved in 25 ml. of diluted sulphuric acid (2:5 v/v) and carbon dioxide gas was passed into

it for 5 minutes to displace air. 20 ml. of 0.10 N titanous chloride solutions was added into this air free solution. It was boiled for 5 minutes while maintaining the current of carbon dioxide. Cool the resulting solution and add 10 ml. of ammonium thiocyanate solution. It was titrated with standard 0.10 N ferric ammonium sulphate solutions. Blank set of 20 ml. of titanous chloride solution was also run. Number of azo group for each dye sample was estimated by this method indicates that there are two azo groups (-N=N-) present in the dye molecule. Examination of these data reveals that there are two azo groups (-N=N-) present in the dye molecules.

Preparation of Co-Ordination Polymers

All co-ordination polymers were synthesized by using metal acetate in general method described.

A warm and clear solution (pH~8) of PPDAL (6.12gm, 0.01mole) in aq. NaOH (200 ml) was added to a solution of copper acetate (1.99 gm, 0.01mole) in 50% aq. formic acid (50 ml) with constant stirring. After complete addition of metal salt solution, the pH of reaction mixture was adjusted to about 5 with dilute ammonia solution. The polymer chelate was separated out in the form of suspension, digested on a water bath for on hour and eventually filtered, washed with hot water followed by acetone, dimethyl formamide (DMF) and then dried in air at room temp. The yields of all co-ordination polymers were almost quantitative.

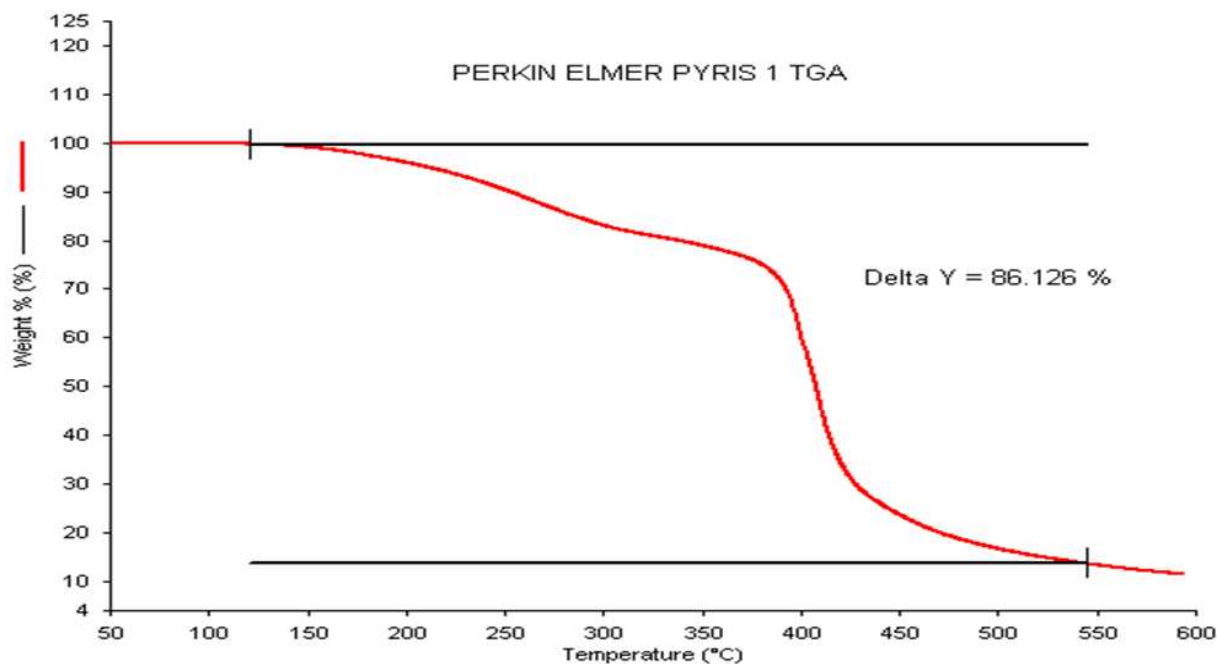


Fig-III TGA of [Cu(PPDAL)(H₂O)₂]_n

Measurements

Elemental Analysis

The metal analysis of co-ordination polymers comprised decomposition of a weighted amount of the polymer followed by EDTA titration following standard procedures [33]. C, H, N analysis of PPDAL and its coordination polymers were carried out by C, H, N elemental analyzer (Italy).

IR spectra of the ligand and of each of the polymer samples were scanned in KBr on a Nicolet 760 D spectrophotometer.

The solid diffusion reflectance spectra of all co-ordination polymer samples were recorded on a Backman DU spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

The number average molecular weight (\overline{M}_n) of all the coordination polymers were determined by method reported in earlier communications [34].

Magnetic Susceptibility measurements of all co-ordinate polymers were carried out at room temperature by the Gouy method, Hg[Co(NCS)] used for calibration. Molar Susceptibilities were corrected for diamagnetism of component atoms using Pascal's constant.

Thermogravimetry of polymer samples were carried out on a "PERKIN ELMER PYRIS 1 TGA in a slow stream of air.

The diffuse reflectance spectra of the solid polymeric chelates were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

Antibacterial Activities

Antibacterial activity of PPDAL ligand and its coordination polymers were studied against gram-positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative bacteria (*E.coli* and *Salmonella typhi*) at a concentration of 50µg/ml by agar cup plate method. Methanol system was used as control in this method. The area of inhibition of zone measured in mm.

Antifungal Activities

The fungicidal activities of all the compounds were studied at 1000 ppm concentration in vitro. Plant pathogenic organisms used were *Penicillium expansum*, *Nigrospora Sp.*, *Trichothesium Sp.* and *Rhizopus nigricum*. The antifungal activity of ligand and its coordination polymers were measured on each of these plant pathogenic strains on a potato dextrose agar (PDA) medium. Such a PDA medium contained potato 200 gm, dextrose 20 gm, agar 20 gm and water one liter. Five days old cultures were employed. 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

The synthesis of the novel 2,2'-(4,4'-(1,4-phenylenebis(diazene-2,1-diyl))bis(4,1-phenylene)) bis(azanediyl)bis(oxomethylene)dibenzoic acid(PPDAL) has not been reported previously. The ligand PPDAL was isolated in the form of a dark yellow crystalline powder. It was soluble in DMF, dioxane, acetone, acetic acid and dilute hydrochloric acid.

The important IR spectral features are a broad band extending from 3200-3600 cm⁻¹ OH of COOH. The band around 1690 cm⁻¹ may be due to carbonyl group. The bands around 1660, 3400 cm⁻¹ may be due to amide group. The strong band at 1625 cm⁻¹ may be due to N=N group. The others bands are at their respective positions.

The NMR data of PPDAL shown in experimental part are also confirming the structure of PPDAL.

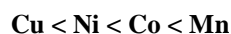
The co-ordination polymers derived from PPDAL were insoluble in common organic solvents. Hence, it is not possible to characterized the co-ordination polymers by molecular mass using conventional methods like osmometry, viscometry etc. These co-ordination polymers did not melt up to 360°C.Examination of the metal content in the polymers (Table-1) revealed that the 1:1 metal: ligand (M: L) stoichiometry for all the polymers.

Comparison of the IR spectrum of the ligand PPDAL and those of the co-ordination polymers reveals certain characteristic differences. The broad band at 3400-3100 cm⁻¹ for PPDAL has virtually disappeared for the spectra of polymers. However the weak bands around 3200 cm⁻¹ in the spectra of PPDAL.Co²⁺, PPDAL.Ni²⁺, PPDAL.Mn²⁺ indicate the presence of water molecules which may have been strongly absorbed by the polymer sample. An indication of this aspect is made later. The weak band around 1110 cm⁻¹ is attributed to the C-O-M stretching frequency. The band at 1430 cm⁻¹ in the IR spectrum of PPDAL is attributed to the in-plane OH deformation [35]. The band is shifted towards higher frequency in the spectra of the polymers indicating formation of metal-oxygen bond. These feature suggest that the structure of the co-ordination polymer.

Magnetic moments (μ_{eff}) of polymeric chelates are given in Table-II. The diffusion electronic spectrum of PPDAL.Cu²⁺ co-ordination polymers shows two broad bands around 15,550 cm⁻¹ and 22,750 cm⁻¹.The first bands may be due to ²T_{2g} → ²E_g transition.While the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the PPDAL.Co²⁺ polymers. The higher value of μ_{eff} of the PPDAL.Cu²⁺ polymer supports this view. The PPDAL.Ni²⁺ and PPDAL.Co²⁺ polymers give two absorption bands respectively at 14,780 and 22,750 cm⁻¹ and at 15,650 and 22,110 cm⁻¹ which can be assigned respectively to ³A_{2g} → ³T_{1g(P)}, ⁴T_{1g} → ⁴T_{1g(P)} transitions. These absorption bands and the values of μ_{eff} indicate an octahedral configuration for the PPDAL.Ni²⁺ and PPDAL.Co²⁺ Polymers.

The TGA data for the polymers are presented in Table-V. The weight loss of the polymer samples at different temperatures indicates that the degradation of the polymers is noticeable beyond 300°C. The rate of degradation becomes a maximum at a temperature lying between 400°C and 500°C depending upon the nature of the polymers. Each polymer lost about 55% of its weight when heated up to 600°C. Inspection of the thermograms of PPDAL.Co²⁺, PPDAL.Mn²⁺ and PPDAL.Ni²⁺ samples revealed that these samples suffered appreciable weight loss in the range 150 to 280°C. This may be due to the presence of water strongly absorbed by the polymers. It has also been indicated earlier that the IR spectra of these three polymer samples have OH bands at around 3200 cm⁻¹ due to associated water.

On the basis of the relative decomposition (% wt. loss) and the nature of thermograms, the co-ordination polymers may be arranged in order in increasing stability as:



This trend also coincides with the stability order already reported for the metal oxinates and for co-ordination polymers of PPDAL [36].

The antimicrobial activity of PPDAL and its coordination polymers are presented in Table-VI and VII. The data suggest that all the samples are toxic to bacteria or fungus. The data also suggest that the percentage of bacteria or fungus is inhibited in the range of 63 to 85% depending upon the biospecies and coordination polymers. All the polymers have good microbicidal activity.

Table-II Analytical and Spectral Data of the Co-Ordination Polymers of PPDAL

| Compound | Empirical Formula | Formula Weight | Analyses | | | | $(\overline{\text{Mn}}) \pm 60$ | % Yield | $\overline{\text{Dp}}$ |
|--|---|----------------|---------------------|-----------------|---------------|-----------------|---------------------------------|---------|------------------------|
| | | | % Found(Calculated) | | | | | | |
| | | | %M | %C | %H | %N | | | |
| PPDAL | C ₃₄ H ₂₄ N ₆ O ₆ | 612 | - | 66.4 (66.67) | 3.7 (3.92) | 13.5 (13.73) | | 78 | - |
| [Cu(PPDAL)(H ₂ O) ₂] _n | Cu.C ₃₄ H ₂₂ N ₆ O ₆ .2H ₂ O | 709.54 | 8.7 (8.95) | 57.4 (57.50) | 3.5 (3.66) | 11.7 (11.84) | 4311 | 81 | 6 |
| [Co(PPDAL)(H ₂ O) ₂] _n | Co.C ₃₄ H ₂₂ N ₆ O ₆ .2H ₂ O | 704.94 | 8.0 (8.36) | 57.6 (57.87) | 3.5 (3.68) | 11.8 (11.91) | 4282 | 80 | 6 |
| [Ni(PPDAL)(H ₂ O) ₂] _n | Ni.C ₃₄ H ₂₂ N ₆ O ₆ .2H ₂ O | 704.71 | 8.1 (8.33) | 57.7 (57.89) | 3.6 (3.68) | 11.8 (11.92) | 4277 | 76 | 6 |
| [Mn(PPDAL)(H ₂ O) ₂] _n | Mn.C ₃₄ H ₂₂ N ₆ O ₆ .2H ₂ O | 700.94 | 7.7 (7.83) | 58.1 (58.20) | 3.8 (3.70) | 11.8 (11.98) | 35520 | 77 | 5 |
| [Zn(PPDAL)(H ₂ O) ₂] _n | Zn.C ₃₄ H ₂₂ N ₆ O ₆ .2H ₂ O | 711.38 | 9.0 (9.19) | 57.1 (57.35) | 3.5 (3.65) | 11.7 (11.80) | 3601 | 80 | 5 |

Table III FT-IR data of ligand PPDAL and its coordination polymers

| Compounds | $\nu(\text{C}=\text{C})$ | $\nu(\text{CONH})$ | $\nu(\text{COOH})$ | $\nu(\text{N}=\text{N})$ | $\nu(\text{M}-\text{O})$ |
|--|--------------------------|--------------------|--------------------|--------------------------|--------------------------|
| PPDAL | 1591 | 1675 | 3430 | 1646 | - |
| [Cu(PPDAL)(H ₂ O) ₂] _n | 1575 | 1669 | 3385 | 1633 | 595 |
| [Co(PPDAL)(H ₂ O) ₂] _n | 1565 | 1641 | 3369 | 1621 | 591 |
| [Ni(PPDAL)(H ₂ O) ₂] _n | 1571 | 1650 | 3375 | 1624 | 592 |
| [Mn(PPDAL)(H ₂ O) ₂] _n | 1561 | 1632 | 3366 | 1608 | 589 |
| [Zn(PPDAL)(H ₂ O) ₂] _n | 1590 | 1671 | 3400 | 1634 | 597 |

Table IV Reflectance spectral and magnetic moment data of the ligand PPDAL containing coordination polymers

| Coordination Polymers | Absorption band(cm ⁻¹) | Transitions | Magnetic moment(μ_{eff}) BM |
|--|------------------------------------|---|--|
| [Cu(PPDAL)(H ₂ O) ₂] _n | 22750 15550 | ² E _g → ² T _{2g} charge transfer | 1.89 |
| [Co(PPDAL)(H ₂ O) ₂] _n | 15650 22110 | ⁴ T _{1g} (F) → ⁴ A _{2g} ⁴ T _{1g} (F) → ⁴ T _{2g} (P) | 2.99 |
| [Ni(PPDAL)(H ₂ O) ₂] _n | 14780 22750 | ³ A _{2g} → ³ T _{1g} (F) ³ A _{2g} → ³ T _{1g} (P) | 4.18 |
| [Mn(PPDAL)(H ₂ O) ₂] _n | 15708 17472 22705 | ⁶ A _{1g} → ⁴ T _{1g} (4G) ⁶ A _{1g} → ⁴ T _{2g} (4G) ⁶ A _{1g} → ⁴ A _{1g} , ⁴ E _g | 4.99 |

*Zn- containing polymers are diamagnetic in nature

Table V TGA data of PPDAL containing coordination polymers

| Co-ordination polymers | % Weight loss at different temperature(°C) | | | | | |
|--|--|-----|------|------|------|------|
| | 100 | 200 | 300 | 400 | 500 | 600 |
| [Cu(PPDAL)(H ₂ O) ₂] _n | 2.7 | 4.9 | 13.2 | 42.5 | 47.4 | 53.3 |
| [Co(PPDAL)(H ₂ O) ₂] _n | 4.1 | 8.6 | 16.8 | 21.8 | 43.2 | 59.4 |
| [Ni(PPDAL)(H ₂ O) ₂] _n | 4.7 | 8.4 | 14.9 | 27.2 | 45.0 | 59.1 |
| [Mn(PPDAL)(H ₂ O) ₂] _n | 4.6 | 6.8 | 9.8 | 15.6 | 25.1 | 36.4 |
| [Zn(PPDAL)(H ₂ O) ₂] _n | 2.1 | 3.4 | 4.8 | 15.4 | 23.3 | 35.5 |

Table: VI Antibacterial Activities of Co-Ordination Polymers

| Compounds | Zone of Inhibition | | | |
|--|--------------------------|------------------------------|-------------------------|---------------|
| | Gram +Ve | | Gram -Ve | |
| | <i>Bacillus subtilis</i> | <i>Staphylococcus aureus</i> | <i>Salmonella typhi</i> | <i>E.coli</i> |
| [Cu(PPDAL)(H ₂ O) ₂] _n | 60 | 67 | 74 | 72 |
| [Co(PPDAL)(H ₂ O) ₂] _n | 63 | 71 | 64 | 70 |
| [Ni(PPDAL)(H ₂ O) ₂] _n | 68 | 69 | 72 | 81 |
| [Mn(PPDAL)(H ₂ O) ₂] _n | 59 | 70 | 83 | 85 |
| [Zn(PPDAL)(H ₂ O) ₂] _n | 62 | 69 | 76 | 70 |

Table: VII Antifungal Activities of Co-Ordination Polymers

| Compounds | <i>Penicillium expansum</i> | <i>Nigrospora Sp.</i> | <i>Trichothesium Sp.</i> | <i>Rhizopus nigricum</i> |
|--|-----------------------------|-----------------------|--------------------------|--------------------------|
| [Cu(PPDAL)(H ₂ O) ₂] _n | 74 | 79 | 61 | 60 |
| [Co(PPDAL)(H ₂ O) ₂] _n | 65 | 64 | 64 | 72 |
| [Ni(PPDAL)(H ₂ O) ₂] _n | 75 | 72 | 66 | 70 |
| [Mn(PPDAL)(H ₂ O) ₂] _n | 72 | 75 | 82 | 77 |
| [Zn(PPDAL)(H ₂ O) ₂] _n | 55 | 71 | 70 | 76 |

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