



Synthesis, Characterization and Antimicrobial Studies of Coordination Polymers

Shukla Hemang M.¹, Solanki Yogesh K.¹, Shah Ashish R.¹, Shah Purvesh J.², Shah Amish I.² and Raj Dilipsinh S.¹

¹Chemistry Department, M.B. Patel Science College, Managed by C. E. Society, Anand -388001, Gujrat, INDIA

²Chemistry Department, Shri A.N. Patel P.G. Institute, Managed by C. E. Society, Anand-388001, Gujrat, INDIA

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Abstract

Novel bis ligand namely 2,2'-(4,4'-(1,2-phenylenebis(diazene-2,1-diyl))bis(4,1-phenylene))bis(azanediyl) bis(oxomethylene) dibenzoic acid(OPDAL) 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, bis azo 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 pigments¹. In addition, they have been studied usually because of their excellent thermal and optical properties in purposes such as toner², ink-jet printing³ and oil-soluble lightfast dyes⁴ optical recording medium⁵⁻⁶. 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^{6,7}.

Recently, the study of co-ordination polymers has been made much progress^{8,9}. These polymers are known for their semiconducting catalytic properties, waste water treatment for metal recovery, in protective coating, as antifouling paints and anti fungal properties¹⁰. 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 -N=N-, SO₂, -CH₂-, -O⁻¹¹⁻¹⁵. Co-ordination polymers mostly derived from bichelating ligands in which metal ions and chelating agents arrayed alternatively¹⁶⁻¹⁷. The area in which the co-ordination polymers having azo dye moiety has been reported¹⁸. 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 figure-1.

Material and Methods

Benzene-1, 2-diamine was obtained from S. D. Fine Chemical Ltd. All other chemicals used were of analytical grade.

Synthesis of 4,4'-(1,2-phenylenebis(diazene-2,1-diyl))dianiline (A): A solution of 10.8 g (0.1 mole) of Benzene-1,2-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 and 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 washed 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 78%, M.P.196⁰c (uncorrected). Analysis C₁₈H₁₆N₆ (Cal : %C 68.34, % H 5.10, % N 26.56; Found: % C 68.26, % H 5.02, % N 26.50).

Synthesis of 2,2'-(4,4'-(1,2-phenylenebis(diazene-2,1-diyl))bis(4,1-phenylene))bis(azanediyl) bis(oxo methylene) dibenzoic acid(OPDAL): The solution of 4,4'-(1,2-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 79%, M.P. 260⁰C (uncorrected). Analysis: C₃₄H₂₄N₆O₆ (Cal : %C 66.66, % H 3.95, % N

13.72; 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). ¹³CNMR-131.5 (C-1, C-13), 130.1 (C-2, C-12), 128.6 (C-3, C-11), 132.0 (C-4, C-10), 134.0 (C-5, C-9), 123.5 (C-6, C-8), 124.4 (C-17, C-21, C-24, C-28), 119.3 (C-18, C-20, C-25, C-27), 150.9 (C-22, C-23), 140.1 (C-19, C-26), 167.6 (C-7, C-16), 173.0 (C-14, C-15), 146.7 (C-30, C-31), 123.3 (C-29, C-32), 131.2 (C-33, C-34). The predicted structure and formation of polymeric ligand is shown in figure-1.

Estimation of number of carboxylic (-COOH) groups in ligand OPDAL: 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 literature¹⁹⁻²⁰. The titrant used for this non-

aqueous titration was tetra-n-butyl ammonium hydroxide (TBAH) in pyridine.

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 OPDAL (6.12 gm, 0.01 mole) in aq. NaOH (200 ml) was added to a solution of copper acetate (1.99 gm, 0.01 mole) 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 one 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.

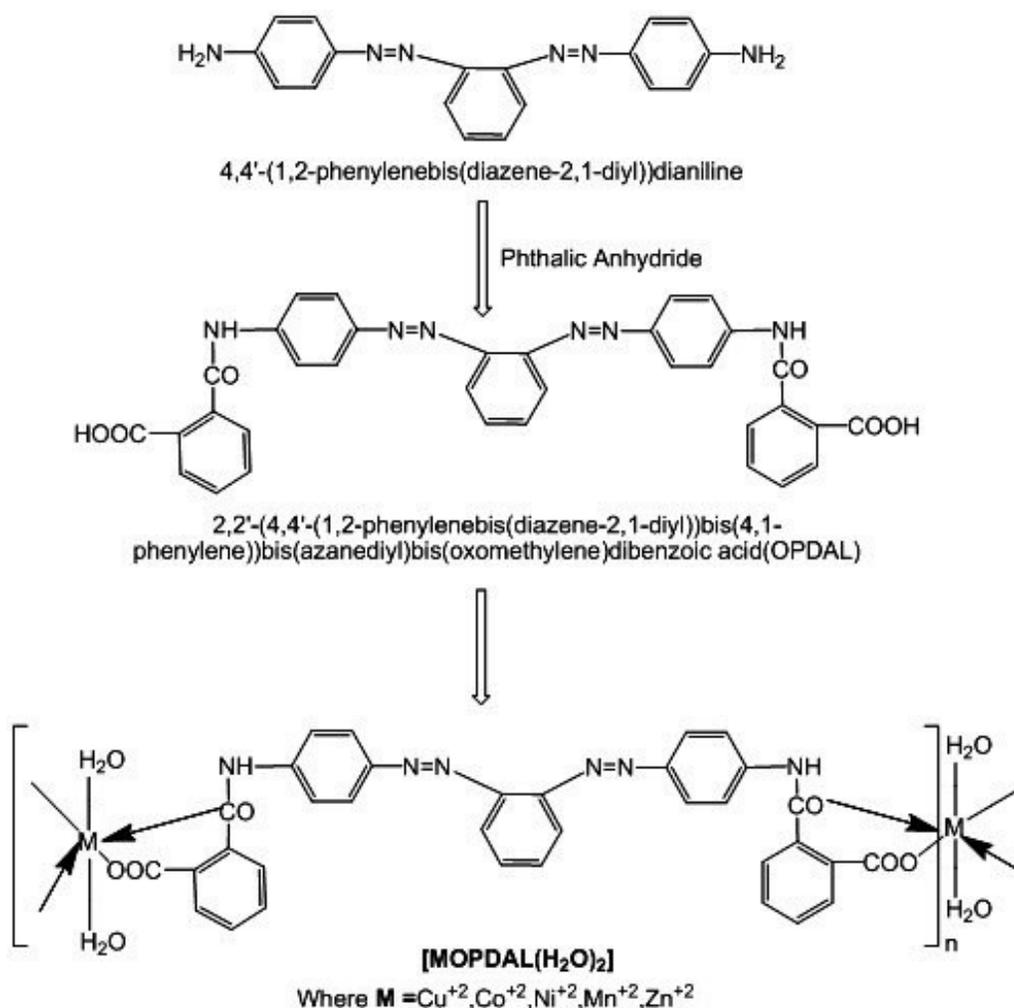


Figure-1
Synthetic route for Preparation of Co-Ordination Polymers

Measurements: The metal analysis of co-ordination polymers comprised decomposition of a weighted amount of the polymer followed by EDTA titration following standard procedures²¹. C, H, N analysis of OPDAL 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 communications²². 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 OPDAL 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 and Y = Area of colony in test plate

Results and Discussion

The synthesis of the novel 2,2'-(4,4'-(1,2-phenylenebis(diazene-2,1-diyl))bis(4,1-phenylene))bis(azanediyl) bis(oxomethylene)dibenzoic acid(OPDAL) has not been reported previously. The ligand OPDAL was isolated in the form of a dark brown 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 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 OPDAL shown in experimental part are also confirming the structure of OPDAL.

The co-ordination polymers derived from OPDAL 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 OPDAL and those of the co-ordination polymers reveals certain characteristic differences. The broad band at 3400-3100 cm⁻¹ for OPDAL has virtually disappeared for the spectra of polymers. However the weak bands around 3200 cm⁻¹ in the spectra of OPDAL.Co²⁺, OPDAL.Ni²⁺, OPDAL.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 OPDAL is attributed to the in-plane OH deformation²³. 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 (table-3).

Table-1
Non-aqueous Conductometric titration of Estimation of – COOH groups

Ligand	Molecular weight gm	Millimoles of TBAH at break per 100 gm of sample	Estimated No. of –COOH group
OPDAL	612	331	2.02

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

Table-2
Analytical and Spectral Data of the Co-Ordination Polymers of OPDAL

Compound (Empirical Formula)	Formula Weight	Analyses % Found (Calculated)				$\overline{M}_n \pm 60$	% Yield	\overline{D}_p
		%M	%C	%H	%N			
OPDAL (C ₃₄ H ₂₄ N ₆ O ₆)	612	-	66.4 (66.67)	3.7 (3.92)	13.5 (13.73)	-	76	-
[Cu(OPDAL)(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)	4310	78	6
[Co(OPDAL)(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)	4287	79	6
[Ni(OPDAL)(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)	4273	75	6
[Mn(OPDAL)(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)	3550	73	5
[Zn(OPDAL)(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)	3599	77	5

Table-3
FT-IR data of ligand OPDAL and its coordination polymers

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

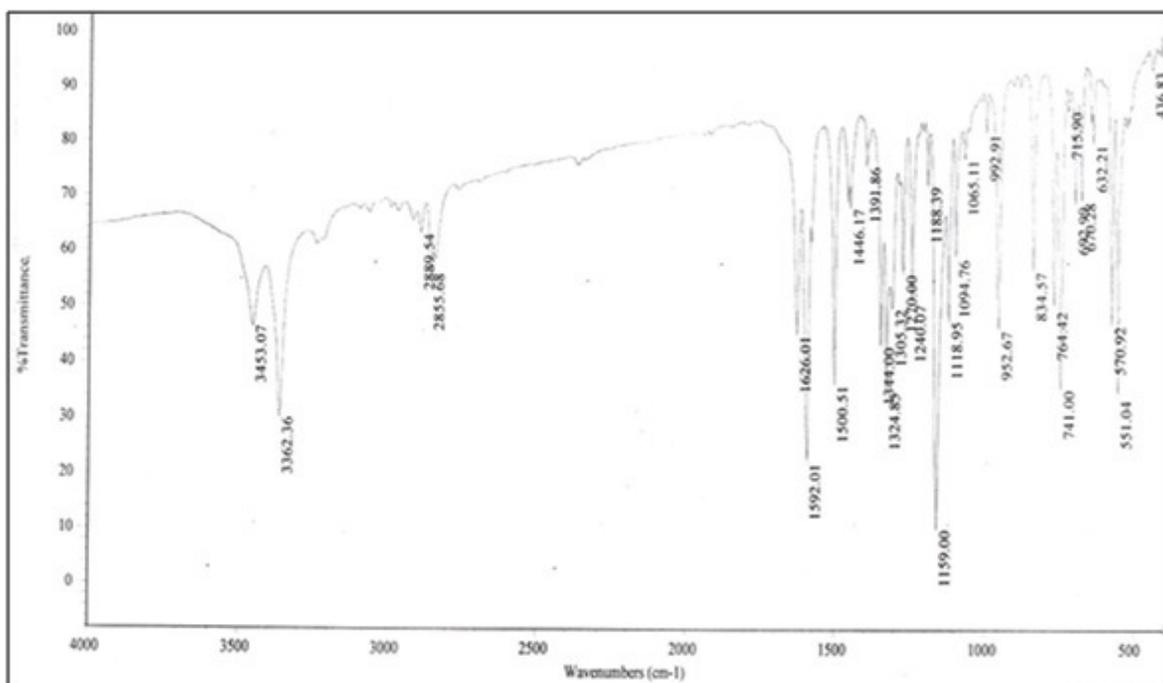


Figure-2
IR spectrum of compound A

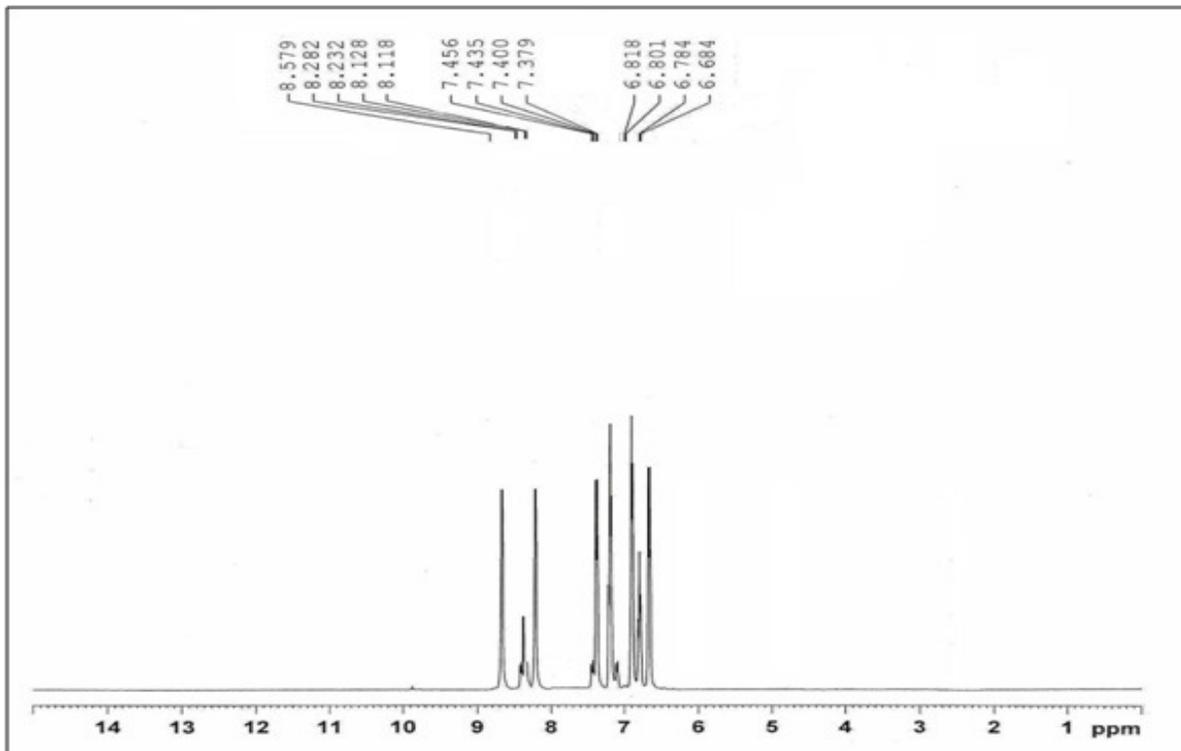


Figure-3
The ¹H NMR spectrum of Compound A

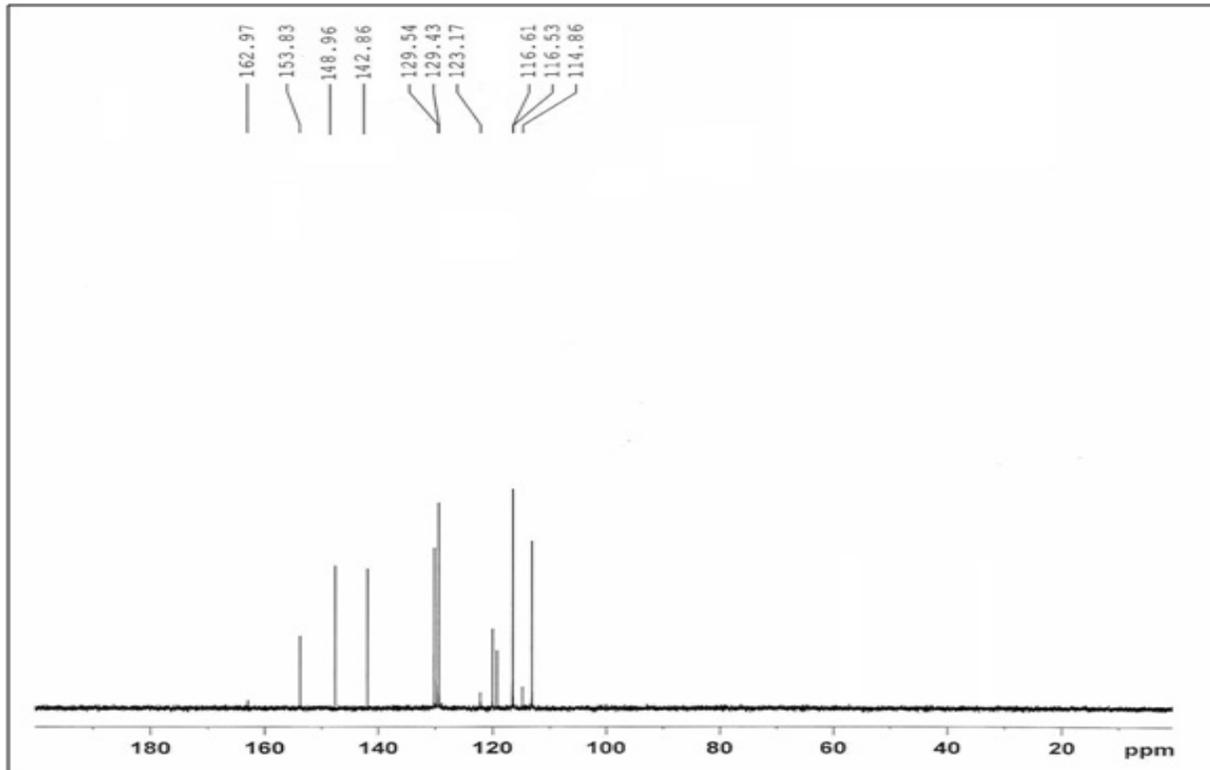


Figure-4
The ¹³C NMR spectrum of Compound A

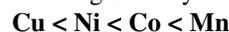
Magnetic moments (μ_{eff}) of polymeric chelates are given in table-2. The diffusion electronic spectrum of OPDAL.Cu²⁺ co-ordination polymers shows two broad bands around 15,552 cm⁻¹ and 22,753 cm⁻¹. The first bands may be due to ²T_{2g} → ²E_g transition. While the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the OPDAL.Co²⁺ polymers. The higher value of μ_{eff} of the OPDAL.Cu²⁺ polymer supports this view. The OPDAL.Ni²⁺ and OPDAL.Co²⁺ polymers give two absorption bands respectively at 14,779 and 22,752 cm⁻¹ and at 15,655 and 22,111 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 OPDAL.Ni²⁺ and OPDAL.Co²⁺ Polymers (table-4).

The typical conductometric titration curve of OPDAL 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.

The TGA data for the polymers are presented in Table-5. 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 OPDAL.Co²⁺, OPDAL.Mn²⁺ and OPDAL.Ni²⁺ samples revealed that these samples suffered appreciable weight loss in the range 150 to 280°C. This may 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. The ligand containing two -COOH groups. Hence the TGA of ligand in air may cause decarboxylation²⁴. Examination of these data reveals that the decarboxylation of ligand consistent with the calculated values. All these facts confirm the structure of ligand.

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 OPDAL²⁵.

The antimicrobial activity of OPDAL and its coordination polymers are presented in Table-6 and 7. 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.

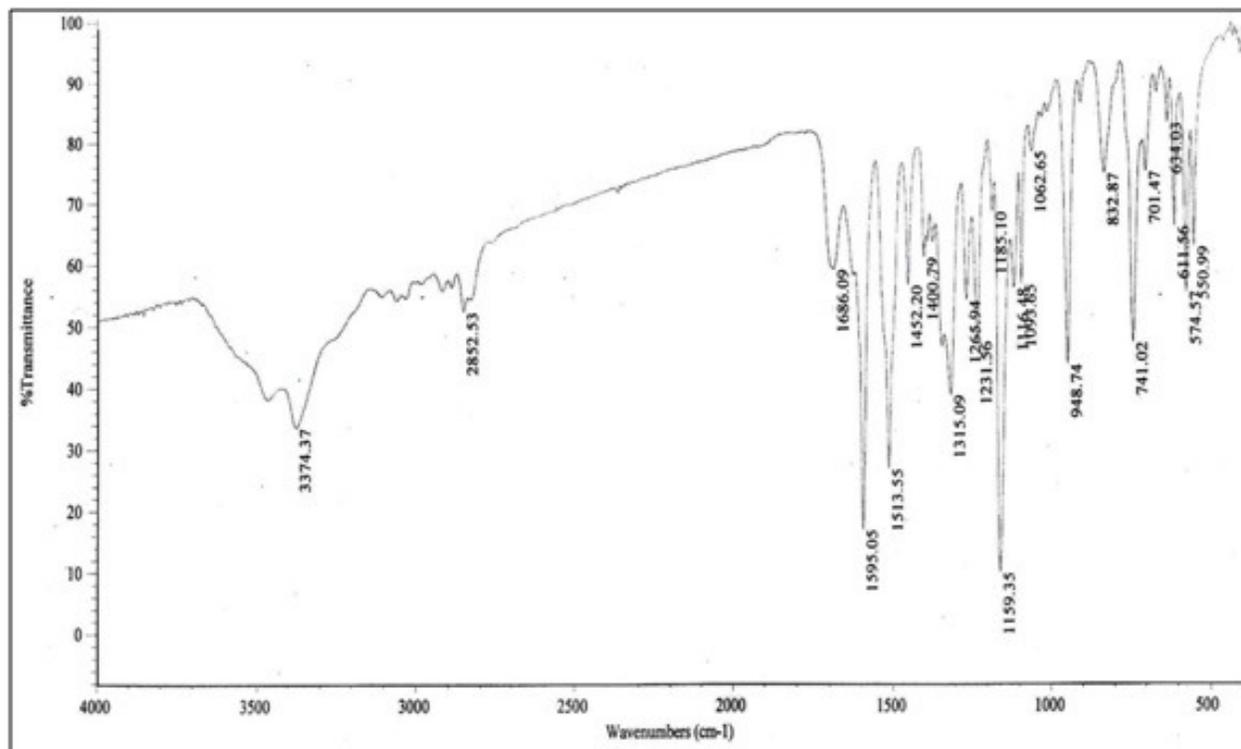


Figure-5
 IR spectrum of compound (OPDAL)

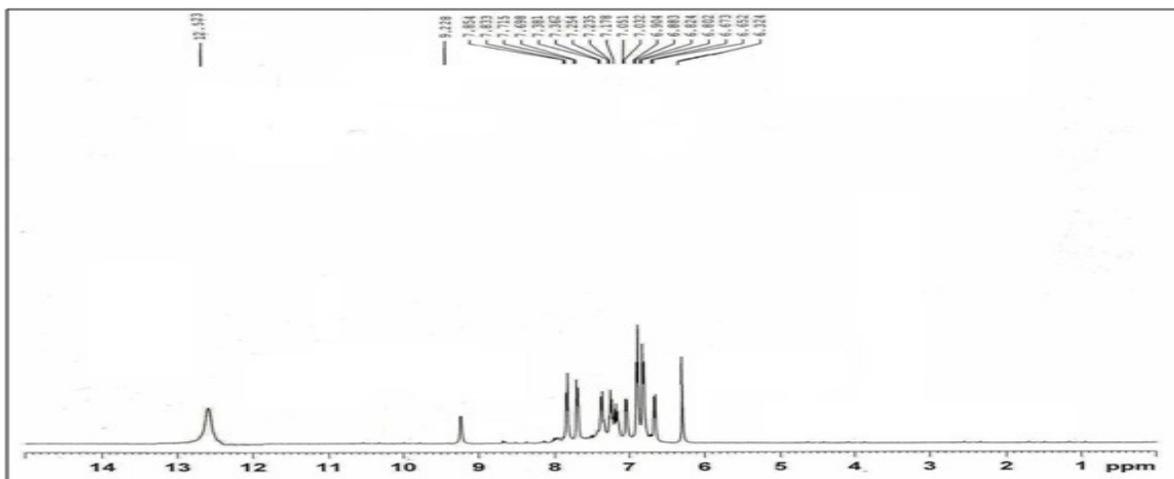


Figure-6
The ^1H NMR spectrum of Compound (OPDAL)

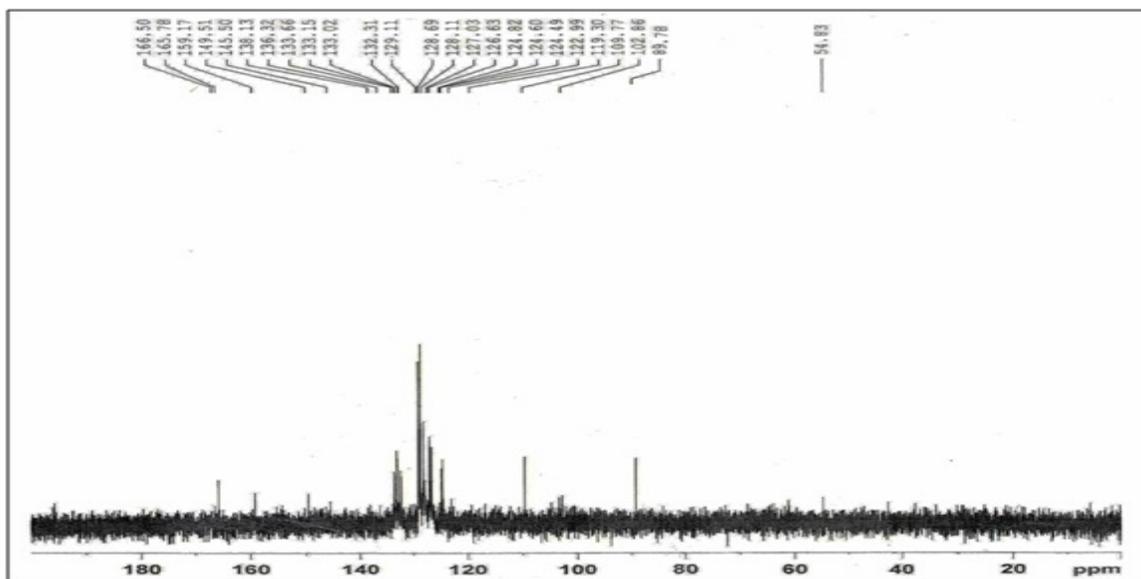


Figure-7
The ^{13}C NMR spectrum of Compound (OPDAL)

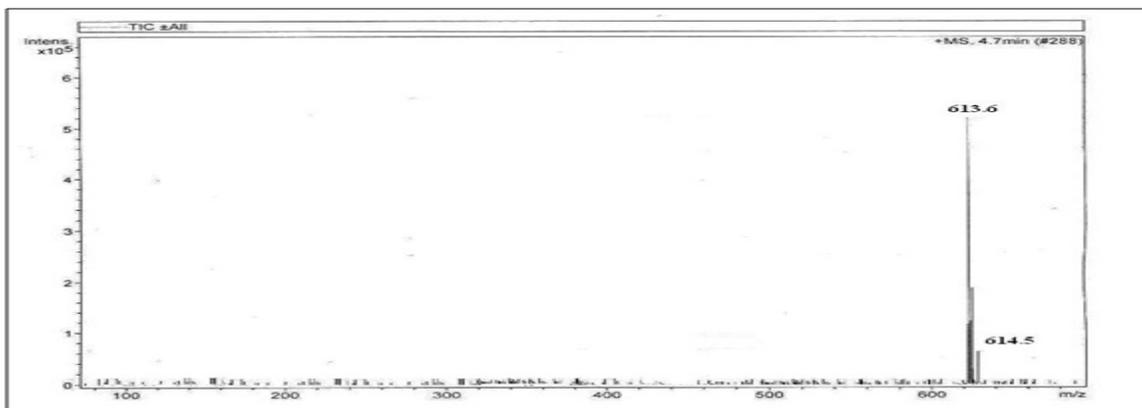


Figure-8
The Mass spectrum of Compound (OPDAL)

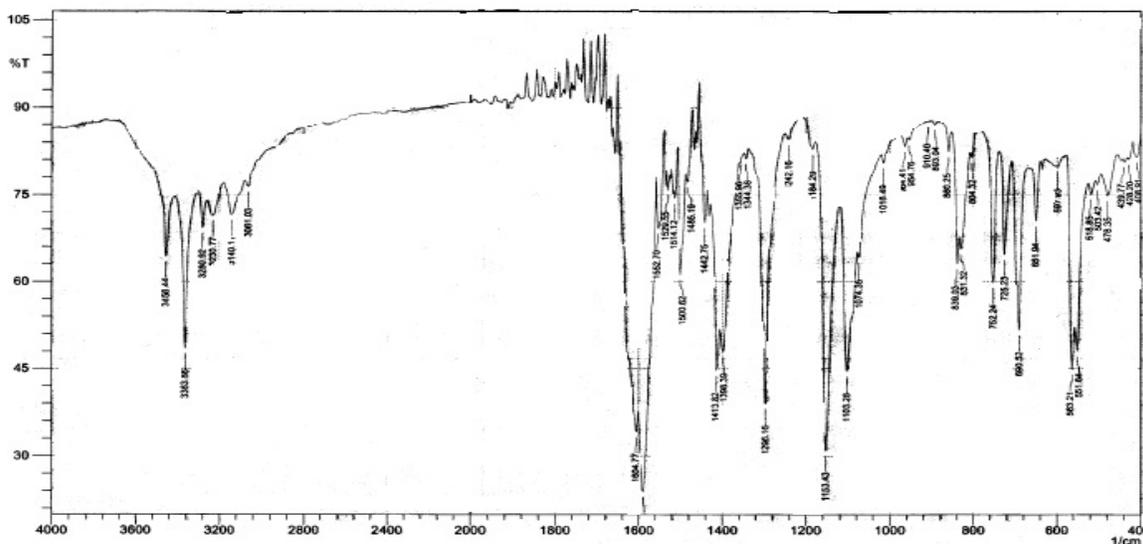


Figure-9
IR Spectrum of $[Cu(OPDAL)(H_2O)_2]_n$

Table-4
Reflectance spectral and magnetic moment data of the ligand OPDAL containing coordination polymers

Coordination Polymers	Absorption band(cm^{-1})	Transitions	Magnetic moment(μ_{eff}) BM
$[Cu(OPDAL)(H_2O)_2]_n$	22753 15552	${}^2E_g \rightarrow {}^2T_{2g}$ charge transfer	1.89
$[Co(OPDAL)(H_2O)_2]_n$	15655 22111	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$	2.98
$[Ni(OPDAL)(H_2O)_2]_n$	14779 22752	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	4.17
$[Mn(OPDAL)(H_2O)_2]_n$	15709 17473 22708	${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$ ${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ ${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$	4.98

*Zn- containing polymers are diamagnetic in nature

Table-5
TGA data of OPDAL containing coordination polymers

Co-ordination polymers	% Weight loss at different temperature($^{\circ}C$)					
	100	200	300	400	500	600
$[Cu(OPDAL)(H_2O)_2]_n$	2.6	4.8	13.3	42.6	47.5	53.5
$[Co(OPDAL)(H_2O)_2]_n$	3.9	8.7	16.7	21.7	43.3	59.6
$[Ni(OPDAL)(H_2O)_2]_n$	4.6	8.5	14.6	27.4	45.1	59.2
$[Mn(OPDAL)(H_2O)_2]_n$	4.4	6.7	9.9	15.7	25.2	36.5
$[Zn(OPDAL)(H_2O)_2]_n$	2.2	3.6	4.8	15.2	23.4	35.6

Table-6
Antibacterial Activities of Co-Ordination Polymers

Compounds	Zone of Inhibition			
	Gram +Ve		Gram -Ve	
	Bacillus subtilis	Staphylococcus aureus	Salmonella typhi	E.coli
$[Cu(OPDAL)(H_2O)_2]_n$	61	65	72	73
$[Co(OPDAL)(H_2O)_2]_n$	62	70	63	71
$[Ni(OPDAL)(H_2O)_2]_n$	67	68	70	79
$[Mn(OPDAL)(H_2O)_2]_n$	60	72	81	84
$[Zn(OPDAL)(H_2O)_2]_n$	61	68	77	72

Table-7
Antifungal Activities of Co-Ordination Polymers

Compounds	Penicillium expansum	Nigrospora Sp.	Trichothesium Sp.	Rhizopus nigricum
[Cu(OPDAL)(H ₂ O) ₂] _n	72	78	60	63
[Co(OPDAL)(H ₂ O) ₂] _n	61	62	62	70
[Ni(OPDAL)(H ₂ O) ₂] _n	72	71	65	73
[Mn(OPDAL)(H ₂ O) ₂] _n	70	73	79	75
[Zn(OPDAL)(H ₂ O) ₂] _n	54	69	72	74

Conclusions

The 4,4'-(1,2-phenylenebis(diazeno-2,1-diyl)dianiline and phthalic anhydride was react and afforded novel bisazo ligand namely, 2,2'-(4,4'-(1,2-phenylenebis(diazeno-2,1-diyl))bis(4,1-phenylene)bis(azanediyl)bis(oxo methylene) dibenzoic acid(OPDAL).The novel bis azo ligand made complexes with different transition metal. The ligand coordinating through the carboxylic oxygen and the amide carbonyl group. The ligand and its metal complexes show good thermal stability. The Ligand and its metal complexes also show good microbicidal activity.

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