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## **Studies on synthesis, characterization and antibacterial screening of coordination polymers**

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### **ABSTRACT**

Novel bis ligand namely 2,2'-(4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl) bis (4,1phenylene)) bis(azanediyl) bis (oxomethylene) dibenzoic acid ( $H_2L$ ) has been prepared and characterized. The Coordination polymers based on this bis ligand with transition metal ions viz,  $Cu^{+2}$ ,  $Ni^{+2}$ ,  $Mn^{+2}$ ,  $Zn^{+2}$ ,  $Co^{+2}$  were prepared and studied for their metal:ligand (M/L), stoichiometry, magnetic moment, spectral features, number-average molecular weight ( $\overline{M}_n$ ) and by thermogravimetry. The microbicidal activity of all the samples had also been monitored against plant pathogens.

**Key words:** Coordination polymer, bis azo dye, spectral studies and microbicidal activity.

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### **INTRODUCTION**

Traditionally, azo dyes are the most essential class of commercial dyes. The azo compounds are highly colored and have been used as dyes and pigments.[1,2] In addition, they have been studied broadly because of their outstanding 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 recent times, azo metal chelates have also paying attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storage, nonlinear optical elements and printing systems.[9,11,12]

Recently, the study of Coordination polymers has been made much progress[13, 14].Coordination polymers mostly derived from bichelating ligands in which metal ions and chelating agents arrayed alternatively.[15-17] The area in which the Coordination polymers having azo dye moiety has been reported by one of author [18]. In extension of previous work, the present article comprises the study of Coordination polymers based on bis azo dye with phthalamic acid segment. Though phthalamic acid also act as good metal chelating agent. Thus paper connecting with the studies of Coordination polymers based on amic acid functionalized bis azo dye. The present work is shown in scheme-1.

## EXPERIMENTAL SECTION

### Materials

o-tolidine was obtained from local dealer. All other chemicals used were of analytical grade.

### Synthesis of Bis Azo Dye:

In a R.B.flask 21.2 g. (0.1 mole) of o-tolidine is made into a thin paste with 300 cc. of water and dissolved by the addition of 20 cc. (23.6 g., 0.23 mole) of concentrated hydrochloric acid (sp. gr. 1.18), warming a little if necessary. The solution is cooled to 10° with ice, mechanical agitation is started, and 21 cc. (25 g., 0.24 mole) more of concentrated hydrochloric acid is added (Note 1). This causes partial separation of o-tolidine dihydrochloride. The temperature being kept at 10–15°C, a solution of 14.5 g. (0.2 mole) of 95 per cent sodium nitrite in 40 cc. of water is run in rapidly, the last 10 per cent being held back and added slowly as needed to give a distinct positive test for nitrous acid on starch-iodide paper. This excess is maintained for one-half hour. Throughout the diazotization an excess of hydrochloric acid should be present as shown by a strong test on Congo red paper. When the diazotization is complete, the excess nitrous acid is eliminated by the careful addition of a small amount of o-tolidine hydrochloride solution, using starch-iodide paper to arrive at an exact balance .

A solution of dil.HCl added into aniline 18.6gm(0.2mole) till Congo Red Paper gives blue color,now add above diluted diazonium solution into aniline solution gradually in cold situation , stirr it well & add sodium acetate solution till the neutralization of dye.Now wash the dye with cold water .The ppts were obtained in the form of red color ,collected that dye by vacuum filtration,then wash with cold water & dry it over night,Yeild-86%,.m.p.192-94<sup>0</sup>c (uncorrected).

Analysis C<sub>26</sub>H<sub>24</sub>N<sub>6</sub> ( Cal : %C 74.29 ,% H 5.71,% N 20.00 ; Found: % C 74.05 , % H 5.37, % N 19.63).

### Synthesis of 2,2'-(4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl) bis (4,1phenylene) bis(azanediyl) bis (oxomethylene) dibenzoic acid (H<sub>2</sub>L)

The solution of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)dianiline (0.1mole) in acetone is cooled to 10°C.To this solution the phthalic anhydride (0.2mole) was added with stirring. The resulting product was then filtered and air-dried. The yield of was 83% and M.P. 259-261<sup>0</sup>C(uncorrected).The predicted structure and formation of polymeric ligand is shown in Scheme-1.

### Analysis:

C <sub>42</sub> H <sub>32</sub> N <sub>6</sub> O <sub>6</sub> (716gm/mole)	%C	% H	% N
Cal :	70.38	4.50	11.73
Found:	70.3	4.5	11.7

### Acid Value

**Theoretical:** 184.6 mg KOH/1g. Sample.

**Found:** 185 mg KOH/1g. Sample.

### IR Features

3040, 1530, 1650 cm <sup>-1</sup>	Aromatic
1690 cm <sup>-1</sup>	CO
3400 cm <sup>-1</sup>	Sec.NH
1625 cm <sup>-1</sup>	N=N
1660, 3400 cm <sup>-1</sup>	CONH

NMR (DMSO)	3200-3600 cm <sup>-1</sup>	OH of COOH	
	$\delta$ ppm		
	7.2 – 8.3 (22H)	Multiplet	Aromatic
	12.5 (2H)	Singlet	COOH
	9.2 (2H)	Singlet	NH
	2.44 (6H)	Singlet	CH <sub>3</sub>

### ***Preparation of Coordination Polymers***

All Coordination polymers were synthesized by using metal acetate in general method described.

A warm and clear solution (pH~8) of H<sub>2</sub>L (7.16gm,0.01mole) in aq.NaOH (200ml) was added to a solution of copper acetate (1.99gm,0.01mole) in 50% aq.formic acid (50ml) 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 chelates were 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 Coordination polymers were almost quantitative.

### **MEASUREMENTS**

#### ***Elemental Analysis***

The metal analysis of Coordination polymers comprised decomposition of a weighted amount of the polymer followed by EDTA titration following standard procedures.[19] C,H,N analysis of H<sub>2</sub>L 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.

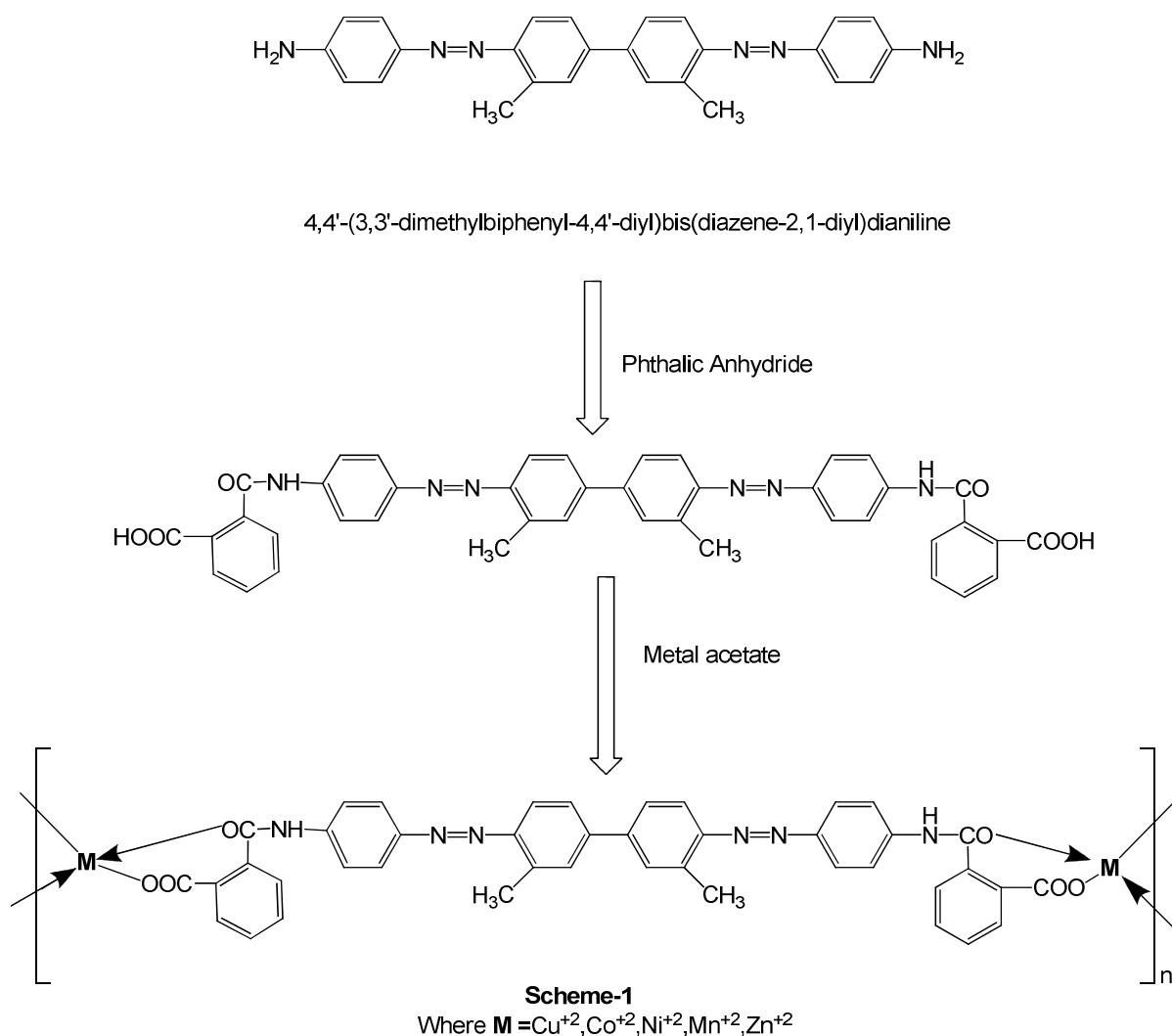
The solid diffuse reflectance spectra of all Coordination polymer samples were recorded on a Beckman DU spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

The number average molecular weight ( $\overline{M}_n$ ) of all the coordination polymers were determined by method reported in earlier communications.[20]

Magnetic Susceptibility measurements of all co-ordinated 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 Universal DTA-TGA analyzer in air at a heating rate of 10°C min.

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  $H_2L$  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  $50\mu\text{g/ml}$  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 200gm, dextrose 20gm, agar 20gm and water one liter. Five days old cultures were employed. The compounds to be tested were suspended (1000ppm) in a PDA medium and autoclaved at  $120^\circ\text{C}$  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:

**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 bis ligand 2,2'-(4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(diazene-2,1-diyl) bis (4,1phenylene)) bis(azanediyl) bis (oxomethylene) dibenzoic acid (H<sub>2</sub>L) has not been reported previously. The ligand H<sub>2</sub>L was isolated in the form of a brown crystalline powder. It was soluble in acetone, DMF, dioxane, acetic acid and dilute hydrochloric acid.

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

The NMR data of H<sub>2</sub>L shown in experimental part are also confirming the structure of H<sub>2</sub>L.

The Coordination polymers derived from H<sub>2</sub>L were insoluble in common organic solvents. Hence, it is not possible to characterized the Coordination polymers by molecular mass using conventional methods like osmometry, viscometry etc. These Coordination 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 H<sub>2</sub>L and those of the Coordination polymers reveals certain characteristic differences. The broad band at 3400-3100 cm<sup>-1</sup> for H<sub>2</sub>L has virtually disappeared for the spectra of polymers. However the weak bands around 3200 cm<sup>-1</sup> in the spectra of H<sub>2</sub>L.Co<sup>2+</sup>, H<sub>2</sub>L.Ni<sup>2+</sup>, H<sub>2</sub>L .Mn<sup>2+</sup> 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<sup>-1</sup> is attributed to the C-O-M stretching frequency.[10]The band at 1430 cm<sup>-1</sup> in the IR spectrum of H<sub>2</sub>L is attributed to the in-plane OH deformation.[21] 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 Coordination polymer.

Magnetic moments (μ<sub>eff</sub>) of polymeric chelates are given in Table-1. The diffusion electronic spectrum of H<sub>2</sub>L.Cu<sup>+2</sup> Coordination polymers show two broad bands around 15,677 cm<sup>-1</sup> and 22,856 cm<sup>-1</sup>.The first bands may be due to <sup>2</sup>T<sub>2g</sub> → <sup>2</sup>E<sub>g</sub> transition. While the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the H<sub>2</sub>L.Co<sup>2+</sup> polymers. The higher value of μ<sub>eff</sub> of the H<sub>2</sub>L.Cu<sup>2+</sup> polymer support this view. The H<sub>2</sub>L.Ni<sup>2+</sup> and H<sub>2</sub>L.Co<sup>2+</sup> polymers give two absorption bands respectively at 14,978 and 22,892 cm<sup>-1</sup> and at 15,743 and 22892 cm<sup>-1</sup> which can be assigned respectively to <sup>4</sup>T<sub>1g</sub> → <sup>2</sup>T<sub>2g</sub>, <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>1g(P)</sub> transitions. These absorption bands and the values of μ<sub>eff</sub> indicate an octahedral configuration for the H<sub>2</sub>L.Ni<sup>2+</sup> and H<sub>2</sub>L.Co<sup>2+</sup> Polymers.

The TGA data for the polymers are presented in Table-2. 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 700°C. Inspection of the thermograms of H<sub>2</sub>L.Co<sup>2+</sup>,

TABLE 1 Analytical and Spectral Data of the Coordination Polymers of H<sub>2</sub>L

Compound	Empirical Formula	Formula Weight	Analyses % Found(Calculated)				Absorption band (cm <sup>-1</sup> )	$\mu_{\text{eff}}$ (B.M.)	$(\overline{Mn}) \pm 60$	$\overline{Dp}$
			%M	%C	%H	%N				
H <sub>2</sub> L	C <sub>42</sub> H <sub>32</sub> N <sub>6</sub> O <sub>6</sub>	716	- -	70.10 (70.39)	4.12 (4.47)	11.36 (11.73)	-	-	-	-
[CuL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Cu.C <sub>42</sub> H <sub>30</sub> N <sub>6</sub> O <sub>6</sub> .2H <sub>2</sub> O	813.54	7.65 (7.81)	61.73 (61.95)	4.01 (4.17)	10.11 (10.33)	22856 15677	1.97	4952	6
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Co.C <sub>42</sub> H <sub>30</sub> N <sub>6</sub> O <sub>6</sub> .2H <sub>2</sub> O	808.93	7.01 (7.28)	62.12 (62.30)	4.02 (4.20)	10.19 (10.38)	15743 22201	2.81	4115	5
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Ni.C <sub>42</sub> H <sub>30</sub> N <sub>6</sub> O <sub>6</sub> .2H <sub>2</sub> O	808.69	7.17 (7.26)	62.04 (62.32)	4.03 (4.20)	10.13 (10.39)	14978 22892	4.02	4918	6
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Mn.C <sub>42</sub> H <sub>30</sub> N <sub>6</sub> O <sub>6</sub> .2H <sub>2</sub> O	804.94	6.72 (6.83)	62.27 (62.61)	3.97 (4.22)	10.17 (10.44)	15745 17569 22712	4.74	4897	6
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Zn.C <sub>42</sub> H <sub>30</sub> N <sub>6</sub> O <sub>6</sub> .2H <sub>2</sub> O	815.38	7.89 (8.01)	61.58 (61.81)	3.92 (4.17)	9.97 (10.30)	-	Diamagnetic	4146	5

H<sub>2</sub>L.Mn<sup>2+</sup> and H<sub>2</sub>L.Ni<sup>2+</sup> 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<sup>-1</sup> due to associated water.

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

**Cu < Ni < Co < Mn**

This trend also coincides with the stability order already reported for the metal oxinates[22] and for Coordination polymers of H<sub>2</sub>L.[23-26]

The antimicrobial activity of H<sub>2</sub>L and its coordination polymers are presented in Table-3 and 4. 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 62 to 84% depending upon the biospecies and coordination polymers. All the polymers have good microbicidal activity.

**Table 2 Thermo gravimetric Analysis Co-ordination Polymers of H<sub>2</sub>L**

Compounds	% weight loss at temperature T(°C)					
	100	200	400	500	600	700
[CuL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	2.2	4.5	12.8	42.2	47.2	52.9
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	4.3	8.3	16.4	21.4	42.7	59.1
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	4.4	8.1	14.5	26.8	45.1	59.3
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	4.1	6.5	9.6	15.3	25.0	36.2
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	2.0	3.2	4.5	15.0	23.4	35.4

**Table 3 Antibacterial Activities of Coordination 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>
[CuL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	60	68	69	72
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	62	72	62	70
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	64	69	71	82
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	63	70	83	81
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	65	63	75	67

**Table 4 Antifungal Activities of Coordination Polymers**

Compounds	<i>Penicillium expansum</i>	<i>Nigrospora Sp.</i>	<i>Trichothesium Sp.</i>	<i>Rhizopus nigricum</i>
[CuL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	74	72	59	55
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	63	66	62	71
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	73	77	65	68
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	71	65	82	71
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	54	72	66	70

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