



## CO-ORDINATION POLYMERS OF AZO GROUP CONTAINING BIS LIGAND

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### ABSTRACT

Novel bis ligand namely 2,2'-(4,4'-(3,3'-dimethoxybiphenyl-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 co-ordination 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 ( $\bar{M}_n$ ) and by thermogravimetry. The microbicidal activity of all the samples had also been monitored against plant pathogens.

**Keywords:** co-ordination polymer, bis azo dye, spectral studies and microbicidal activity.

### 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.<sup>1,2</sup> In addition, they have been studied broadly because of their outstanding thermal and optical properties in purposes such as toner,<sup>3,4</sup> ink-jet printing<sup>5,6</sup> and oil-soluble lightfast dyes<sup>7</sup> optical recording medium.<sup>8-11</sup> 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.<sup>9,11,12</sup> Recently, the study of co-ordination polymers has been made much progress<sup>13,14</sup>. co-ordination polymers mostly derived from bichelating ligands in which metal ions and chelating agents arrayed alternatively<sup>15-17</sup>. The area in which the co-ordination polymers having azo dye moiety has been reported by one of author [DSR]<sup>18</sup>. In extension of previous work, the present article comprises the study of co-ordination 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 co-ordination polymers based on amic acid functionalized bis azo dye. The present work is shown in Scheme-1.

### EXPERIMENTAL

#### Materials

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

#### Synthesis of Bis Azo Dye

In round bottom flask take 245ml of water and 19ml of Con.HCl (Sp.gra-1.19). This solution is heated to boiling, the flame is removed and 24.43(0.1mole) of o-dianisidine is added, the hot mixture is stirred for 3 minutes, until only a small amount of solid remains, put beaker in an ice-salt mixture, stir it till temp dropped to about 15°C. Now add 22ml of more Con.HCl, when Temp of Mixture has fallen to 10-13°C, a solution of 13.8gm(0.2mole) of 97% sodium nitrite in 32ml of water is added from a dropping funnel in the course of 10-15 minutes. The Contents of the beaker are stirred for 15-20 minutes at 5-10°C, add distilled water in it dilute the solution & keep at into ice-bath.

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, stir 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 brown color, collected that dye by vacuum filtration, then wash with cold water & dry it over night, Yield-82%, m.p. 185-86<sup>o</sup>c (uncorrected).

Analysis C<sub>26</sub>H<sub>24</sub>N<sub>6</sub>O<sub>2</sub> (Cal : %C 69.03, %H 5.31, %N 18.58 ; Found: %C 68.9, %H 5.3, %N 18.5).

**Synthesis of 2,2'-(4,4'-(3,3'-dimethoxybiphenyl-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'-dimethoxybiphenyl-4,4'-diyl)bis(diazene-2,1-diyl)dianiline (0.1mole) in acetone is cooled to 10<sup>o</sup>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 80% and M.P. 252<sup>o</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>8</sub> (748gm/mole)	%C	%H	%N
	Cal : 67.38 Found:67.15	4.28 4.15	11.23 11.10
Acid Value	Theoretical: 184 mg KOH/1g. Sample. Found: 186 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
	3200-3600 cm <sup>-1</sup>		OH of COOH
	1250,1055cm <sup>-1</sup>		OCH <sub>3</sub>
NMR (DMSO)	7.2 – 8.3 (22H)	Multiplet	Aromatic
	12.5 (2H)	Singlet	COOH
	9.2 (2H)	Singlet	NH
	3.9 (6H)	Singlet	OCH <sub>3</sub>

**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 H<sub>2</sub>L (7.48gm, 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 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.

**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<sup>19</sup>. 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 diffusion reflectance spectra of all co-ordination 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.<sup>20</sup>

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<sub>2</sub>L 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 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°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 DISCUSSIONS**

The synthesis of the novel bis ligand 2,2'-(4,4'-(3,3'-dimethoxybiphenyl-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 DMF, dioxane, acetone, 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 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.

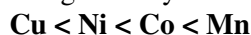
Comparison of the IR spectrum of the ligand H<sub>2</sub>L and those of the co-ordination polymers reveals certain characteristic differences. The broad band at 3400-3100 cm<sup>-1</sup> for H<sub>2</sub>L has virtually disappeared for the spectra of polymers. However the weak bands around 3200 cm<sup>-1</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<sup>10</sup>. 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.<sup>21</sup> 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<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> co-ordination polymers shows two broad bands around 15,675 cm<sup>-1</sup> and 22,854 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 14,976 and 22,890  $\text{cm}^{-1}$  and at 15,741 and 22890  $\text{cm}^{-1}$  which can be assigned respectively to  ${}^4T_{1g} \rightarrow {}^2T_{2g}$ ,  ${}^4T_{1g} \rightarrow {}^4T_{1g(P)}$  transitions. These absorption bands and the values of  $\mu_{\text{eff}}$  indicate an octahedral configuration for the  $\text{H}_2\text{L.Ni}^{2+}$  and  $\text{H}_2\text{L.Co}^{2+}$  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  $\text{H}_2\text{L.Co}^{2+}$ ,  $\text{H}_2\text{L.Mn}^{2+}$  and  $\text{H}_2\text{L.Ni}^{2+}$  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  $\text{cm}^{-1}$  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<sup>22</sup> and for co-ordination polymers of  $\text{H}_2\text{L}$ <sup>23</sup>.

The antimicrobial activity of  $\text{H}_2\text{L}$  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.

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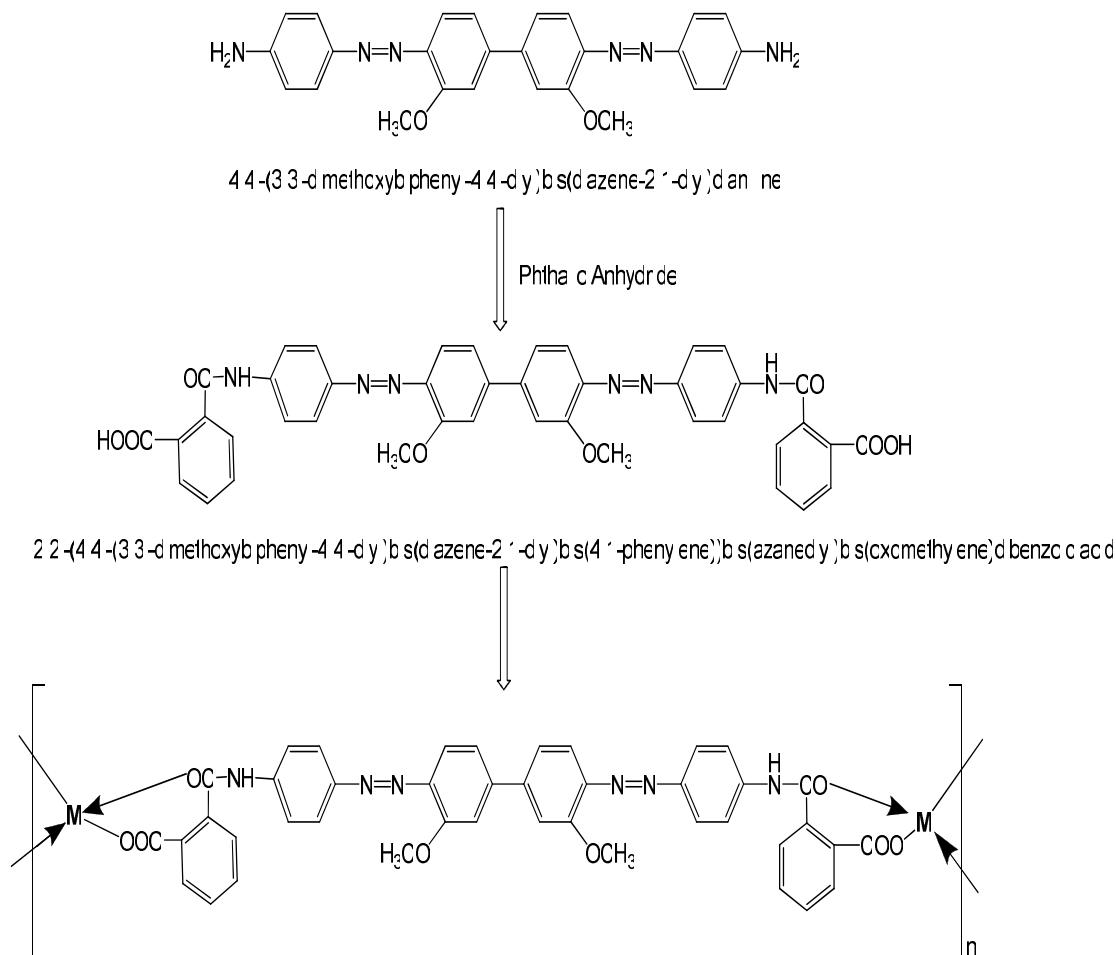
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Table-1: Analytical and Spectral Data of the Co-Ordination Polymers of H<sub>2</sub>L

Compound	Empirical Formula	Formula Weight	Analyses % Found(Calculated)				Absorption band (cm <sup>-1</sup> )	μ <sub>eff.</sub> (B.M.)	$\overline{M}_n$ ± 60	$\overline{D}_p$
			%M	%C	%H	%N				
H <sub>2</sub> L	C <sub>42</sub> H <sub>32</sub> N <sub>6</sub> O <sub>8</sub>	748	-	67.15 (67.38)	4.15 (4.28)	11.10 (11.23)	-	-	-	-
[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>8</sub> .2H <sub>2</sub> O	845.54	7.40 (7.51)	59.32 (59.61)	3.91 (4.02)	9.78 (9.93)	22854 15675	1.99	5134	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>8</sub> .2H <sub>2</sub> O	840.93	6.90 (7.01)	58.73 (59.03)	3.81 (4.04)	9.70 (9.99)	15741 22198	2.83	4206	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>8</sub> .2H <sub>2</sub> O	840.69	6.71 (6.98)	59.72 (59.95)	3.85 (4.04)	9.73 (9.99)	14976 22890	4.04	5047	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>8</sub> .2H <sub>2</sub> O	836.94	6.40 (6.56)	60.01 (60.22)	3.91 (4.06)	9.80 (10.04)	15743 17567 22710	4.76	5023	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>8</sub> .2H <sub>2</sub> O	847.38	7.50 (7.72)	59.13 (59.48)	3.81 (4.01)	9.69 (9.91)	-	Diamagnetic	4238	5

Table-2: Thermo gravimetric Analysis Co-ordinations 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>	2.6	4.9	13.2	42.5	47.5	53.3
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	4.7	8.7	16.8	21.8	43.1	59.4
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	4.8	8.4	14.9	27.2	45.3	59.6
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	4.5	6.8	9.8	15.6	25.0	36.4
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	2.2	3.4	4.8	15.4	23.6	35.5



Scheme-1

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

Table-3: 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>
[CuL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	62	70	71	71
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	64	74	64	70
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	66	71	73	83
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	64	72	84	84
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	66	65	77	68

Table-4: Antifungal Activities of Co-Ordination 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>	76	74	61	57
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	65	68	64	73
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	75	79	67	70
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	73	68	84	74
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	57	74	68	72

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