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Studies on some coordination polymers

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ABSTRACT

Novel bis ligand namely $2,2'-(4,4'-(4,4'-methylenebis(4,1-phenylene)bis (diazene-2,1-diyl))bis(4,1-phenylene))bis(azanediyl)bis(oxomethylene)dibenzoic acid (ADM) has been prepared and characterized. The coordination polymers based on this bis ligand with transition metal ions like <math>Cu^{+2}, Co^{+2}, Ni^{+2}, Mn^{+2}$ and Zn^{+2} were prepared and characterized on the basis of elemental analyses, infrared spectra, electronic spectra, magnetic measurements and thermogravimetric analyses. All the coordination polymers are insoluble in acetone, ethanol, chloroform, methanol, benzene, DMF and DMSO. All the novel synthesized compounds were screened for their antibacterial and antifungal activities.

Keywords: bisazo ligand; spectral studies; microbicidal activity.

INTRODUCTION

Recently, the study of coordination polymers has been made much progress [1,2]. 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 [3,4]. Such coordination polymers are mostly derived from bi-chelating ligands in which metal ions and chelating agents are arrayed alternatively. The joining segment of these two similar ligands are mainly -N=N-, SO₂, $-CH_2$ -, -O-[5-11]. Coordination polymers mostly derived from bichelating ligands in which metal ions and chelating agents arrayed alternatively [12-14]. The area in which the coordination polymers having azo dye moiety has been reported by one of author [DSR][15]. Most fundamental class of commercial dyes are azo group containing dyes. The azo group containing compounds are well attractive colored and have been used as dyes and pigments [16,17]. In addition, they have been studied generally because of their outstanding thermal and optical properties in purposes such as toner [18,19], ink-jet printing[20,21] and oil-soluble lightfast dyes [22] optical recording medium [23-26]. In modern times, azo metal complexes 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 [24- 27].

In continuation of prior 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.

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 complexes. The synthetic steps are shown in scheme-1.



Where **M** =Cu⁺²,Co⁺²,Ni⁺²,Mn⁺²,Zn⁺² Scheme-1: Synthesis of novel coordination polymers

MATERIALS AND METHODS

4,4'-methylenedianiline (DDM) was obtained from local dealer. All other chemicals used were of analytical grade.

Synthesis of Bis Azo Dye 4,4'-(4,4'-methylenebis(4,1-phenylene)bis(diazene-2,1-diyl)) dianiline:

In round bottom flask take 245 ml of water and 19 ml of con. HCl. This solution was heated to boiling, the flame was removed and 19.8gm (0.1mole) of 4,4'-methylenedianiline was added, the hot mixture was 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 had fallen to 10-13°C, a solution of 13.8 gm (0.2 mole) of sodium nitrite in 32ml of water was added from a dropping funnel in the course of 10-15 minutes. The contents of the beaker were stirred for 15-20 minutes at 5-10°C, add distilled water in it dilute the solution and keep it into ice-bath.

A solution of dil. HCl added into aniline 18.6 gm (0.2mole) till Congo red paper gives blue color. Now add above prepared diazonium salt solution into aniline solution gradually in cold situation, stir 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 brown color, collected that dye by vacuum filtration, then washed with cold water and dry it over night,Yeild-82%,.m.p.190-92⁰c (uncorrected).Analysis $C_{25}H_{22}N_6$ (Cal : %C 73.87 ,% H 5.46, % N 20.67 ; Found: % C 73.8 , % H 5.4, % N 20.5).

IR (KBr) vcm⁻¹: 3420-3328(NH₂ stretching of amine), 1592, 1500, 1446 (C=C stretching of aromatic ring), 1635(-N=N-stretching of azo group). ¹H-NMR (400 MHz, DMSO-d₆) δ (ppm): 8.4-6.6 (m, 16H, aromatic, *J* = 0.9, 7.8 Hz), 4.2- 4.1(*s*, 2H, -CH₂), 6.6-5.8(*s*, 4H, NH₂). ¹³C NMR: 125.0(C-1&C-5&C-8&C-12), 113.8(C-2&C-4&C-9&C-11), 150.6(C-3 &C-10), 113.8 (C-4&C-9), 125.0(C-5&C-8), 145.3(C-6&C-7), 129.8 (C-13&C-24), 123.5(C-14&C-23), 150.2(C-15&C-22), 123.5(C-16&C-21), 129.8(C-17&C-20), 143.7(C-18&C-19), 41.3(C-25).

Synthesis of 2,2'-(4,4'-(4,4'-methylenebis(4,1-phenylene)bis(diazene-2,1-diyl))bis(4,1-phenylene)) bis(azanediyl)bis(oxomethylene)dibenzoic acid (ADM):

The solution of 4,4'-(4,4'-methylenebis(4,1-phenylene)bis(diazene-2,1-diyl))dianiline (40.6 gm, 0.1mole) in acetone was cool to 10°C.To this solution the phthalic anhydride (29.6 gm,0.2 mole) was added with stirring. The resulting product was then filtered and air-dried. Yield: 76 %; m.p. 256-58°C (uncorrected); Anal. For C₄₁H₃₀N₆O₆ (702 gm/mole): Calcd: %C, 70.08; %H 4.30; %N, 11.96. Found: %C, 69.92, %H, 4.22, %N, 11.89. IR (KBr) vcm⁻¹: 3328(-NH stretching of secondary amine), 1595, 1513, 1452(C=C stretching of aromatic ring), 3410(OH stretching of –COOH group), 1670(C=O stretching of–CONH group), 1635(N=N-stretching of azo group). ¹H-NMR: (400 MHz, DMSO-d₆) δ (ppm):12.6-12.5(s, 2H,-COOH), 9.3-9.2 (*s*, 2H,CONH, D₂O exchangeable), 8.5-6.3 (m, 24H, aromatic, *J* = 0.9, 7.8 Hz), 4.10-3.60(d, 2H,CH₂). 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-32&C-36), 119.3(C-14&C-16&C-33&C-35), 140.1(C-15&C-34), 150.9 (C-18&C-31), 150.2(C-19&C-28), 123.5(C-20&C-24 &C-27&C-29),129.8(C-21&C-23&C-26&C-30), 143.7(C-37),173.0(C-38&C-40),167.6(C-39&C-41).

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 23% 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.

(IV) The ligand containing two –COOH groups. Hence the TGA of ligand in air may cause decarboxylation [28]. The calculated value of CO_2 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.

Estimation of number of carboxylic (-COOH) groups in ligand ADM:

The structure of ligand was examined by estimation of number of carboxylic –COOH groups per mole of ligand. The non-aqueous conductometric nitration 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 ADM ligand.

Non-aqueous conductometric titration.

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) (0.1N), 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) per 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:

No. of carboxylic groups = Milimoles of TBAH X Mol. weight X 10^{-5}

Per mole of ligand	per 100gm of sample	of ligand
(X)	(Y)	(M)

RESULTS AND DISCUSSION

The typical conductometric titration curve of ADM Ligand has been shown in Fig. I 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. o -COOH group
ADM	702	296	2.07



Fig. I conductometric titration curve of ADM Ligand

Determination of azo group:

The number of azo group for ADM 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 titaneous 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 titaneous 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 Coordination Polymers

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

A warm and clear solution (pH~8) of ADM (7.02gm, 0.01mole) in aq.NaOH (200 ml) was added to a solution of copper acetate (1.99gm, 0.01mole) in50% 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 metal complexes were separated out in the form of suspension, digested on a water bath for an 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 [33]. C, H, N analysis of ADM and its coordination polymers were carried out by C, H, N elemental analyzer (Italy).

Compound	Empirical Formula	Formula		Found (Calcd.) %			Absorption	$\mu_{\rm eff.}$		
Compound	Empirical Formula	Weight	М	С	Н	Ν	$/\text{cm}^{-1}$	/B.M.	$(1VIII) \pm 60$	Dp
ADM	$C_{41}H_{30}N_6O_6\\$	702	-	69.99 (70.08)	4.21 (4.30)	11.80 (11.96)	-	-	-	-
[CuADM(H ₂ O) ₂] _n	$Cu.C_{41}H_{28}N_6O_6.2H_2O$	799.54	7.83 (7.94)	61.45 (61.53)	3.85 (4.00)	10.35 (10.50)	22857 15678	1.98	4856	6
[CoADM(H ₂ O) ₂] _n	$Co.C_{41}H_{28}N_6O_6.2H_2O$	794.94	7.30 (7.41)	61.78 (61.89)	3.85 (4.02)	10.41 (10.56)	15744 22201	2.82	4038	5
[NiADM(H ₂ O) ₂] _n	Ni.C ₄₁ H ₂₈ N ₆ O ₆ .2H ₂ O	794.71	7.23 (7.38)	61.78 (61.90)	3.89 (4.02)	10.45 (10.56)	14979 22893	4.03	4832	6
[MnADM(H ₂ O) ₂] _n	$Mn.C_{41}H_{28}N_6O_6.2H_2O$	790.94	6.75 (6.94)	61.01 (62.20)	4.00 (4.04)	10.56 (10.62)	15746 17570 22713	4.75	4810	6
$[ZnADM(H_2O)_2]_n$	Zn.C41H28N6O6.2H2O	801.38	8.01 (8.15)	61.23 (61.39)	3.79 (3.99)	10.24 (10.48)	-	Diamagnetic	4069	5

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 coordination 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{Mn}) of all the coordination polymers were determined by method reported in earlier communications [34].

Magnetic Susceptibility measurements of all coordination polymers and its metal complexs 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.

Compounds	% weight loss at temperature $T/{}^{0}C$						
Compounds	100	200	300	400	500	600	700
ADM	-	8.8	9.2	23.5	28.9	32.3	34.2
[CuADM(H ₂ O) ₂] _n	1.2	8.6	11.7	26.4	30.5	33.5	37.1
[CoADM(H ₂ O) ₂] _n	4.9	8.9	23.9	16.8	21.9	43.3	59.5
[NiADM(H ₂ O) ₂] _n	5.0	8.6	19.2	14.8	27.4	45.5	59.8
$[MnADM(H_2O)_2]_n$	4.7	6.8	13.61	9.9	15.8	25.2	36.6
$[ZnADM(H_2O)_2]_n$	2.4	3.3	10.2	4.7	15.6	23.7	35.8

The diffuse reflectance spectra of the solid coordination polymers and its metal 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 ADM 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 50μ 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. The antibacterial activity displayed by various compounds are shown in Tables-IV (Fig.II)

TABLE IV. Antibacterial Activities of coordination Polymers

Zone of Inhibition							
Compounds	Gram	+Ve	Gram –Ve				
	B. subtilis	S.aureus	S.typhi	E.coli			
$[CuADM(H_2O)_2]_n$	60	69	73	74			
$[\text{CoADM}(\text{H}_2\text{O})_2]_n$	63	73	66	72			
[NiADM(H ₂ O) ₂] _n	64	70	75	84			
[MnADM(H ₂ O) ₂] _n	62	73	85	86			
[ZnADM(H ₂ O) ₂] _n	64	67	78	69			



Fig.II. Antibacterial Activities of coordination Polymers

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,agar20gm 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 inhibition level, % for fungi was calculated after five days using the formula given below:

Inhibition level, % = 100(X-Y)

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

The fungicidal activity displayed by various compounds are shown in Table-V(Fig.III).

Compounds [CuADM(H₂O)₂]_n Rhizopus nig.

59



TABLE V. Antifungal Activities of coordination Polymers

Trichothesium Sp.

63

Nigrospora Sp

76

Penicillium exp.

78

Fig. Fig.III. Antifungal Activities of coordination Polymers

RESULTS AND DISCUSSION

The synthesis of the novel bis ligand 2,2'-(4,4'- (4,4'-methylenebis (4,1-phenylene) bis (diazene-2,1-diyl)) bis (4,1-phenylene))bis (azanediyl) bis (oxomethylene) dibenzoic acid (ADM) has not been reported previously. The ligand ADM was isolated in the form of a Dark red 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 3410 cm⁻¹ OH of -COOH. The band around 1670 cm⁻¹ may due to v_{CO} . The bands around 1670cm⁻¹ may be due to amide group. The strong band at 1635 cm⁻¹ may be due to N=N group. The others bands are at their respective positions.

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

The coordination polymers derived from ADM 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-II) revealed that the 1:1 metal: ligand (M: L) stoichiometry for all the polymers.

Comparison of the IR spectrum of the ligand ADM and those of the coordination polymers reveals certain characteristic differences. The broad band at $3400-3100 \text{ cm}^{-1}$ for ADM has virtually disappeared for the spectra of polymers. However the weak bands around 3200 cm^{-1} in the spectra of ADM.Co²⁺, ADM.Ni²⁺, ADM.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 ADM 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 coordination polymer.

Magnetic moments (μ_{eff}) of polymeric complexes are given in Table-VII. The diffusion electronic spectrum of ADM.Cu⁺² coordination polymers shows two broad bands around 15,677 cm⁻¹ and 22,856 cm⁻¹.The first bands may

be due to ${}^{2}T_{2g} \rightarrow {}^{2}E_{g}$ transition. While the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the ADM.Co²⁺ polymers. The higher value of μ_{eff} of the ADM.Cu²⁺ polymer support this view. The ADM.Ni²⁺ and ADM.Co²⁺ polymers give two absorption bands respectively at 14,978 and 22,892cm⁻¹ and at 15,743 and 22201 cm⁻¹ which can be assigned respectively to ${}^{4}T_{1g} \rightarrow {}^{4}T_{2g(P)}$ transitions. These absorption bands and the values of μ_{eff} indicate an octahedral configuration for the ADM.Ni²⁺ and ADM.Co²⁺ Polymers.

The TGA data for the polymers are presented in Table-II. 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 ADM.Co²⁺, ADM.Mn²⁺ and ADM.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.

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:

This trend also coincides with the stability order already reported for the metal oxinates and for coordination polymers of ADM [36].

The antimicrobial activity of ADM and its coordination polymers are presented in Table-IV and V. 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 VI FT-IR data of ligand	ADM and its coordination po	olymers
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Compounds	v(C=C)	v(CONH)	v(COOH)	v(N=N)	υ(M-O)
ADM	1592	1670	3410	1635	-
$[Cu(ADM)(H_2O)_2]_n$	1580	1625	3388	1611	592
$[Co(ADM)(H_2O)_2]_n$	1577	1598	3379	1590	589
[Ni(ADM)(H ₂ O) ₂] _n	1579	1600	3381	1599	590
$[Mn(ADM)(H_2O)_2]_n$	1565	1586	3374	1585	586
$[Zn(ADM)(H_2O)_2]_n$	1587	1655	3400	1623	596

Table V	/II Reflectance spectral a	ind magnetic moment	data of the ligand ADM	containing coordination po	lymers
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Coordination polymers	Absorption band(cm ⁻¹)	Transitions	Magnetic moment(µeff) BM
$[Cu(ADM)(H_2O)_2]_n$	22856 15677	$^{2}\text{Eg} \rightarrow ^{2}\text{T}_{2g}$ charge transfer	1.97
$[Co(ADM)(H_2O)_2]_n$	15743 22201	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}$ ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(P)$	2.81
[Ni(ADM)(H ₂ O) ₂] _n	14978 22892	${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$ ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$	4.02
[Mn(ADM)(H ₂ O) ₂] _n	15745 17569 22712	${}^{^{6}}A_{^{1}g} \rightarrow {}^{^{4}}T_{^{1}g}(4G)$ ${}^{^{6}}A_{^{1}g} \rightarrow {}^{^{4}}T_{^{2}g}(4G)$ ${}^{^{6}}A_{^{1}g} \rightarrow {}^{^{4}}A_{^{1}g}, {}^{^{4}}Eg$	4.74

• Zn- containing polymers are diamagnetic in nature

CONCLUSION

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

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