

Azo Group Containing Bis Ligand and its Coordination Polymers

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Abstract: Novel bis ligand namely 2,2'-(4,4'-(4,4'-oxybis(4,1-phenylene) bis(diazene-2,1-diyl)) bis(4,1-phenylene))bis(azanediyl) bis (oxomethylene)dibenzoic acid (DDE) has been prepared and characterized. The coordination 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 (\bar{M}_n) and by thermogravimetry. All the novel synthesized compounds were screened for their antibacterial and antifungal activities.

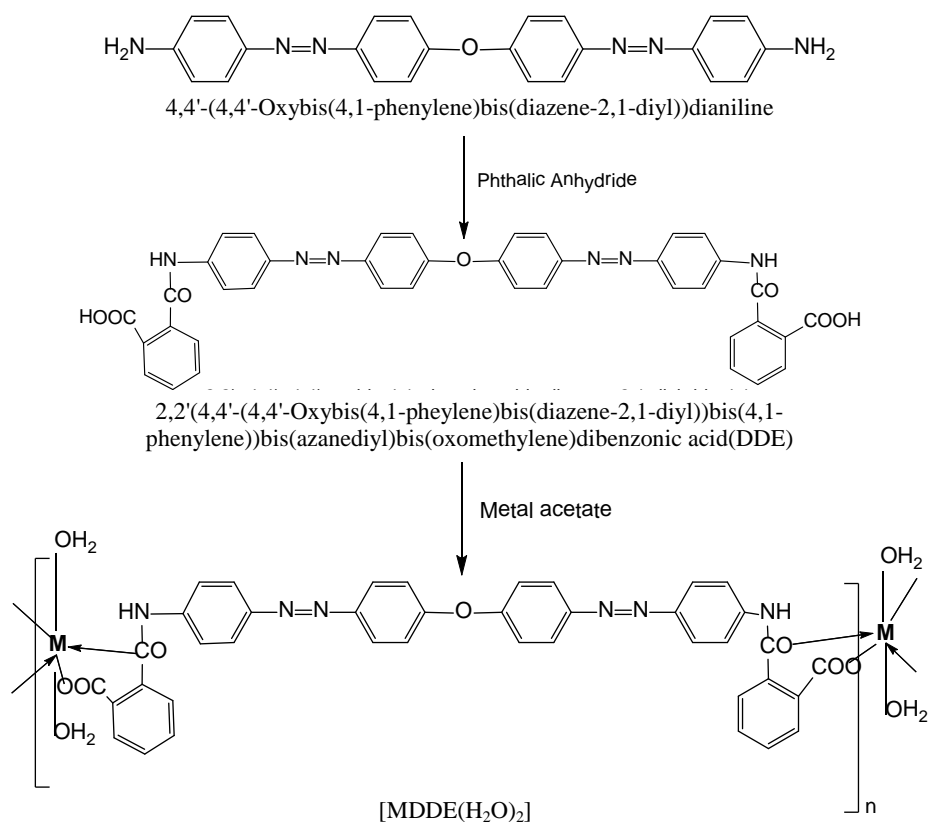
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Introduction

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 generally because of their outstanding thermal and optical properties in purposes such as toner^{3,4}, ink-jet printing^{5,6} and oil-soluble lightfast dyes⁷ optical recording medium⁸⁻¹¹. 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 coordination polymers has been made much progress^{13,14}. These polymers are known for their semi conducting 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 arrayed alternatively. The joining segment of these two similar ligands are mainly -N=N-, SO₂, -CH₂-, -O-¹⁷⁻²³. Coordination polymers mostly derived from

bichelating ligands in which metal ions and chelating agents arrayed alternatively²⁴⁻²⁶. The area in which the coordination polymers having azo dye moiety has been reported²⁷. 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. In the present work, 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 coordination polymers based on amic acid functionalized bis azo dye. The synthetic routes are shown in Scheme 1.



Scheme 1. The synthetic routes, where $\text{M}=\text{Cu}^{+2}$, Co^{+2} , Ni^{+2} , Mn^{+2} and Zn^{+2}

Experimental

4,4'-Diaminodiphenylether was obtained from local dealer. All other chemicals used were of analytical grade.

Synthesis of bis azo dye

4,4'-Diamino diphenyl ether (20 g, 0.1 mole) was dissolved in dilute HCl (30 mL, 1:3v/v). The solution was cooled to 0-2 °C in ice bath and HCl (12 mL) was added with stirring. To the ice cold solution was added drop wise a solution of NaNO_2 (15.8 g, 0.2 mole). To the resulting solution of the tetrazolium salt was rapidly added a solution of aniline (19.6 g, 0.2 mole) in dil. HCl. The mixture was stirred for 10-15 minutes.

In another beaker, sodium acetate (22 g, 0.2 mole) was dissolved in water (30 mL). The sodium acetate solution was added to the reaction mixture and allowed to stand in ice bath for 1 h. with occasional stirring. The reaction mixture was allowed to stand at room temperature and aq.NaOH solution (10 mL, 20%) was added with stirring till a color of aniline was observed. The mixture was left for 1 h. The separated product was filtered, then washed with cold water and dried it over night. Yield-79% and M.P. 173-73 °C (uncorrected). Analysis and calculated for $C_{24}H_{20}N_6O(408)$: %C 70.57, %H 4.94, %N 20.58; Found: %C 70.56, %H 4.92, %N 20.57.

Synthesis of 2,2'-(4,4'-(4,4'-oxybis(4,1-phenylene)bis(diazene-2,1-diyl))bis(4, 1-henylene)) bis(azanediy)bis(oxomethylene)dibenzoic acid(DDE)

The solution of 4,4'-(4,4'-oxybis(4,1-phenylene)bis(diazene-2,1-diyl)dianiline (0.15 mole) in ethanol was cooled to 10 °C. To this solution the phthalic anhydride (0.3 mole) was added with constant stirring. The resulting product was then filtered and air dried. The yield was 82% and M.P. 228-230 °C (uncorrected). Analysis calculated for $C_{40}H_{28}N_6O_7(704)$: C, 68.18; H, 3.98; N, 11.93, Found: C, 68.16; H, 3.97;N,11.91.IR Features (cm^{-1}): 3040, 1530,1650 (Aromatic), 1690 (CO), 3400(Sec.NH),1625(N=N), 1660, 3400(CONH),3200-3600(OH of COOH).¹HNMR(δ ppm/DMSO):7.4-8.5 (24H, m, Aromatic C-H),12.5 (2H,s,COOH), 9.2(2H,s,NH). The predicted structure and formation of polymeric ligand is shown in Scheme 1.

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 DDE (7.04 g, 0.01 mole) in aq.NaOH (200 mL) was added to a solution of copper acetate (1.99 g, 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 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 procedures²⁸. C, H, N analysis of DDE and its coordination polymers were carried out by C, H, N elemental analyzer (Italy) (Table 1).

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{M}_n) of all the coordination polymers were determined by method reported in earlier communications²⁹. Magnetic susceptibility measurements of all coordinate 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.

Table 1. Analytical and spectral data of the coordination polymers of DDE

Compound	Analyses % Found (Calculated)				Absorption band, cm ⁻¹	μ_{eff} (B.M.)	(\bar{M}_n) ± 60	ν_p
	M	C	H	N				
DDE	-	68.16 (68.18)	3.97 (3.98)	11.91 (11.93)	-	-	-	-
[CuDDE (H ₂ O) ₂] _n	7.92 (7.93)	60.21 (60.23)	3.71 (3.74)	10.46 (10.48)	22859 15680	1.96	4075	5
[CoDDE (H ₂ O) ₂] _n	7.38 (7.39)	60.21 (60.23)	3.74 (3.76)	10.52 (10.54)	15746 22203	2.85	4860	6
[NiDDE (H ₂ O) ₂] _n	7.35 (7.37)	60.22 (60.25)	3.75 (3.77)	10.52 (10.54)	14981 22895	4.07	3938	5
[MnDDE (H ₂ O) ₂] _n	6.31 (6.93)	60.52 (60.53)	3.76 (3.78)	10.57 (10.59)	15748 17572 22715	4.78	4826	6
[ZnDDE (H ₂ O) ₂] _n	8.13 (8.14)	59.73 (59.75)	3.72 (3.73)	10.44 (10.46)	-	Dia- magnetic	4084	5

Thermogravimetry of polymer samples were carried out on a Universal DTA-TGA analyzer in air at a heating rate of 10 °C min (Table 2). 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.

Table 2. Thermo gravimetric analysis coordination polymers of DDE

Compounds	% Weight loss at temperature T, °C					
	100	200	400	500	600	700
[CuDDE(H ₂ O) ₂] _n	2.5	4.9	13.2	42.5	47.4	53.3
[CoDDE(H ₂ O) ₂] _n	4.6	8.7	16.6	21.6	43.0	59.2
[NiDDE(H ₂ O) ₂] _n	4.8	8.4	14.5	27.2	45.2	59.7
[MnDDE(H ₂ O) ₂] _n	4.5	6.6	9.7	15.7	24.9	36.4
[ZnDDE(H ₂ O) ₂] _n	2.2	3.1	4.5	15.3	23.5	35.6

Antibacterial activity

Antibacterial activity of DDE 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 µg/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 results revealed that the ligand DDE and its coordination polymers shows weak to good activity are presented in Table 3.

Table 3. Antibacterial activities of coordination polymers

Compounds	Zone of inhibition, mm			
	Gram positive		Gram negative	
	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Salmonella typhi</i>	<i>E.coli</i>
[CuDDE(H ₂ O) ₂] _n	63	73	76	77
[CoDDE(H ₂ O) ₂] _n	66	76	69	75
[NiDDE(H ₂ O) ₂] _n	67	74	78	87
[MnDDE(H ₂ O) ₂] _n	65	75	87	89
[ZnDDE(H ₂ O) ₂] _n	67	70	81	72

Antifungal activity

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 g, dextrose 20 g, agar 20 g 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 15 atm. 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. The antifungal activity results revealed that the ligand DDE and its coordination polymers shows weak to good activity are presented in Table 4.

Table 4. Antifungal activities of coordination polymers

Compounds	<i>Penicillium expansum</i>	<i>Nigrospora Sp.</i>	<i>Trichothesium Sp.</i>	<i>Rhizopus nigricum</i>
[CuDDE(H ₂ O) ₂] _n	81	79	66	62
[CoDDE(H ₂ O) ₂] _n	69	72	69	77
[NiDDE(H ₂ O) ₂] _n	80	83	72	75
[MnDDE(H ₂ O) ₂] _n	78	74	88	79
[ZnDDE(H ₂ O) ₂] _n	61	79	72	75

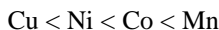
Results and Discussion

The synthesis of the novel bis ligand 2,2'-(4,4'-(4,4'-oxybis(4,1-phenylene))bis(diazene-2,1-diyl)) bis(4,1-phenylene))bis(azanediy)bis(oxomethylene) dibenzoic acid (DDE) has not been reported previously. The ligand DDE was isolated in the form of a 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 due to ν_{CO}. 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 DDE shown in experimental part are also confirming the structure of DDE.

The coordination polymers derived from DDE 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 DDE and those of the coordination polymers reveals certain characteristic differences. The broad band at 3400-3100 cm⁻¹ for DDE has virtually disappeared for the spectra of polymers. However the weak bands around 3200 cm⁻¹ in the spectra of DDE.Co²⁺, DDE.Ni²⁺ and DDE.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 frequency¹⁰. The band at 1430 cm⁻¹ in the IR spectrum of DDE is attributed to the in-plane OH

deformation³⁰. 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 chelates are given in Table 1. The diffusion electronic spectrum of DDE.Cu²⁺ coordination polymers shows two broad bands around 15,680 cm⁻¹ and 22,859 cm⁻¹. The first bands may be due to ${}^2T_{2g} \rightarrow {}^2E_g$ transition, while the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the DDE.Co²⁺ polymers. The higher values of μ_{eff} of the DDE.Cu²⁺ polymer support this view. The DDE.Ni²⁺ and DDE.Co²⁺ polymers give two absorption bands respectively at 14,981 and 22,895 cm⁻¹ and at 15,746 and 22895 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 μ_{eff} indicate an octahedral configuration for the DDE.Ni²⁺ and DDE.Co²⁺ 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 DDE.Co²⁺, DDE.Mn²⁺ and DDE.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 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 oxinates³¹ and for coordination polymers of DDE³². The antimicrobial activity of DDE 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 65 to 87% depending upon the biospecies and coordination polymers. All the polymers have good microbicidal activity.

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