Coordination Polymers of *N, N'*-di-(8-Hydroxyquinolinolyl- 5-methyl)-*N, N*-diethyl-1,3-propane diamine (QEPD)

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Abstract: Coordination polymers containing a novel bis(oxine) bidentate ligand, namely *N, N'*-di(8-hydroxyquinolinolyl-5-methyl)-*N, N'*-diethyl-1,3-propane diamine (QEPD) have been prepared with the metal ions Zn(II), Cu(II), Ni(II), Co(II) and Mn(II). The novel bis-(bidentate) ligand was synthesized by condensation of 5-chloromethyl-8-hydroxyquinoline hydrochloride with *N, N'*-diethyl-1,2- propane diamine in the presence of a base catalyses. All of these coordination polymers and the parent ligand were characterized by elemental analyses, IR spectral and diffuse reflectance spectral studies. The thermal stability and number- average molecular weights ($\overline{M}_n$) of all of the coordination polymers were determined by thermogravimetric analyses and non-aqueous conductometric titrations, respectively. In addition, all of the coordination polymers have been characterized by their magnetic susceptibilities.

Keywords: Coordination polymers, Infrared spectra, Diffuse reflectance spectra, Thermogravimetry, Magnetic susceptibility, Conductometric titrations.

Introduction

The coordination chemistry of bis(oxine), bidentate ligand, has been extensively investigated for their chelating properties¹⁻³. In this context bis(oxine) ligand with two oxine units joined by a bridge of 5,5'- methylene (-CH₂-), 5,5'-sulfonyl (-SO₂-), 5,5'-dimethylene sulfide (-CH₂-S-CH₂-) and -CH-O-CH₂- are reported in literature⁴⁻¹⁰. Recently, we have reported the synthesis and characterization of coordination polymers based on the bis-oxine ligand joined

with a bridge, $-H_2C-O-Ph-O-CH_2$ ($Ph = 1,3$ phenylene) has been replaced¹¹. This work has been further extended with the view of investigation of the chelating ability of a bis-8-quinolinol bis(bidentate) ligand by introducing the bridge of *N,N'*-diethyl-1,3-propane diamine between two 8-hydroxyquinoline moieties. Accordingly, the present work deals with the synthesis and characterization of a bis(oxine) ligand, namely *N,N'*-di(8-hydroxyquinoloyl-5-methyl)-*N,N'*-diethyl-1,3-propane diamine (QEPD) and its coordination polymers with Zn(II), Cu(II), Ni(II), Co(II) and Mn(II) metal ions.

Experimental

All chemicals were of analytical grade. The synthesis of *N,N'*-di(8-hydroxyquinoloyl-5-methyl)-*N,N'*-diethyl-1,3-propane diamine (QEPD) was carried out in two steps. 5-Chloromethyl-8-hydroxyquinolinolyl hydrochloride was prepared according to a literature method¹².

Preparation of polymers of N,N'-di(8-hydroxyquinoloyl-5-methyl)-N,N'-diethyl-1,3-propane diamine (QEPD)

QEPD was prepared as follows; To a suspension of 5-chloromethyl-8-hydroxyquinoline hydrochloride (23 g, 0.02 mol), *N,N'*-diethyl-1,3-propane diamine (17.5 g, 0.1 mol) in an acetone-water mixture was added. K_2CO_3 (5.3 g, 0.03 mol) was added as an acid acceptor. The resulting mixture was refluxed for 3 h with occasional shaking. The resulting suspension, which contained a green precipitate, was poured into ice cold (500 mL) water and then filtered. The solid product was collected and dried to give QEPD (80 % yield). Analysis for $C_{28}H_{34}N_4O_2$; Calculated (%): C, 73.36; H, 7.42; N, 12.23.

Preparation of coordination polymers

A solution of copper acetate (1.9 g, 0.001 mol) in aqueous formic acid (50 mL, 50%) was added drop wise to a solution of QEPD (3.30 g, 0.01 mol) in aqueous formic acid (240 mL, 20%) with stirring. The reaction mixture was heated on a water bath for 0.5 h. The reaction mixture was made alkaline by the addition of dilute aqueous ammonia until the precipitation was completed. The polymer separated out in the form of a suspension and was digested on boiling water bath. Finally, the resultant solid brownish yellow precipitates was collected by filtration and washed with hot water, dimethylformamide (DMF) and then acetone. The polymer (QEPD-Cu[II]) was air dried. A similar procedure was used to prepare the QEPD-Co[II], QEPD-Ni(II), QEPD-Mn(II) and QEPD-Zn(II). The yields of all coordination polymers were almost quantitative.

Measurements

In the co-ordination polymers, metals were analysed by using the EDTA titration and for this process decomposed co-ordination polymers used¹³. The percentage composition. (C, H and N) for the coordination polymers was determined by a C,H,N Elemental analyzer (Table 1). The IR spectra of the bis-ligand QEPD and each of the coordination polymers samples were scanned as KBr pellets using a Perkin Elmer IR spectrophotometer. The solid diffusion, reflectance spectra of all the coordination polymers were recorded on Shimadzu spectrophotometer with a solid reflectance attachment MgO was employed as the reference compound.

The number average molecular weights ($\overline{M}_n$) of all the coordination polymers were estimated by end-group analysis. End-group analysis of the hydroxyl group was carried out by non-aqueous conductometric titration using pyridine as solvent and sodium methoxide as titrant base^{14,15}.

Magnetic susceptibility measurements of all the coordination polymers were carried out at room temperature by the Gouy method. Mercury [tetrathiocynatocobalt] was used for the instrument calibration¹⁸. Molar susceptibilities were corrected for diamagnetism of the component almost using Pascal's constant¹⁸. Thermogravimetry of all these coordination polymers was carried out using a Dupont thermogravimetric analyzer (TGA). The data are reported in Table 3.

Results and Discussion

The synthesis QEPD was performed by chloromethylation of the oxine followed by condensation with *N,N'*-diethyl-1,3-proapne diamine (Scheme 1).

Scheme 1

The important IR spectral features are (i) a broad band from 3550 cm^{-1} to 3200 cm^{-1} that is attributed to the hydrogen-bonded OH group¹⁷. (ii) The weak bands near 1220 cm^{-1} and 1020 cm^{-1} that are due to asymmetric and symmetric stretching vibrations of methylene groups (CH_2) of the $-\text{CH}_2-\text{NH}-\text{CH}_2-$ bridge. (iii) The weak band at 1110 cm^{-1} that confirms the presence of a dialkyl amine function. and (iv) the bands near 1610, 1508, 1470 and 1420 cm^{-1} that are the characteristic frequencies of the 8-hydroxyquinoline nucleus¹². The weak band around 1085 and 1118 cm^{-1} may also be attributed to the amine group bridge. It was also

observed that H₂L has numerous IR spectral features in common with those of 5,5-methylene bis(8-hydroxyquinoline)¹. These features support the proposed structure of H₂L. The coordination polymers derived from H₂L are insoluble in common organic solvents. All these coordination polymers decomposed at approximately 250 °C. The molecular mass was estimated by evaluating the number of terminal OH groups using non-aqueous conductometric titration. Perusal of the literature revealed that there are few reports regarding the determination of the number average molecular weight ($\overline{Mn}$) of coordination polymers.¹⁸⁻²¹ However, efforts are made by the present authors to estimate ($\overline{Mn}$) of the H₂L coordination polymers by utilizing the non-aqueous conductometric titration method under controlled experimental conditions²². For the sake of convenience, the required amount of coordination polymer was suspended in pyridine for 24 h. It was observed that the properties of polymers did not change in the presence of pyridine.

Assuming that the only end-groups in the polymers are OH, the titration was carried out by addition of controlled volume of NaOMe, since more volume of NaOMe may cause de-coordination of polymers. A discernible break was observed in the titration curve and the molecular weights were calculated as shown in Table 1. Examination of the metal content in the polymers (Table 2) reveals a 1:1 metal: ligand (M/L) stoichiometry for all the polymers.

Table 1. Analytical data for coordination polymer of QEPD.

Coordination polymers	Colour	Elemental analysis, %				$\overline{Mn}$
		N		M		
		Cal	Found	Cal	Found	
QEPD-Cu(II)	Green	10.34	10.2	11.73	11.55	5415
QEPD-Ni(II)	Green	10.43	10.3	10.93	10.8	5367
QEPD-Co(II)	Brown	10.42	10.3	10.92	10.85	5369
QEPD-Mn(II)	Light green	10.5	10.3	10.3	10.1	5329
QEPD-Zn(II)	Pale yellow	10.3	10.2	12.03	11.9	5437

Table 2. Thermogravimetry Analysis (TGA) of the coordination polymer of QEPD.

Coordination polymers	% Weight loss at temperature					
	100 °C	200 °C	250 °C	300 °C	400 °C	500 °C
QEPD-Cu(II)	8.05	64.9	68.4	79.53	-	-
QEPD-Ni(II)	7.51	10.22	12.1	14.71	71.44	-
QEPD-Co(II)	7.49	10.22	12.4	14.31	71.44	-
QEPD-Mn(II)	6.0	9.0	15.3	20.5	64.0	85.0
QEPD-Zn(II)	8.0	14.0	45.9	65.25	80.0	82.0

Comparison of the IR spectrum of the ligand H₂L and those of the coordination polymers reveal certain characteristic difference. Thus, the broad band in the region from 3550 to 3200 cm⁻¹ for H₂L is absent in the spectra of the polymers. This is consistent with the involvement of OH groups in a coordinate interacting with the polymers. However, the weak band near 3400 cm⁻¹ for H₂L-Mn^{II} indicates that water molecules might be strongly absorbed by the polymer sample. The band in H₂L due to C = N stretching at 1600 cm⁻¹ is shifted towards lower frequency (ca 1558 cm⁻¹) in the coordination polymers. The red shift suggests coordination of metal ion through the nitrogen of 8-hydroxyquinoline. In addition, a weak band at 1100 cm⁻¹ is attributed to the C-O-M stretching frequency¹⁶. The band at 1430 cm⁻¹ in QEPD is assigned to the in-plane OH deformation¹⁶. This band is shifted toward higher frequency (1468 cm⁻¹) in the spectra of the polymers and supports the formation of a metal-oxygen bond.

The magnetic moments (μ_{eff}) of the polymeric chelates are given in Table 3. The diffuse electronic spectrum of QEPD-Cu(II) coordination polymer shows two broad bands near 15.625 cm^{-1} and 22.222 cm^{-1} . The first band may be due to $2T_g \rightarrow 2E_g$ transition while the second may be due to charge transfer. The first band shows some structural characteristics that suggest a distorted octahedral geometry. The higher theoretical value of μ_{eff} of the QEPD-Cu(II) polymer supports this view. The QEPD-Ni(II) and QEPD-Co(II) polymers exhibit two absorption bands at $16,000$ and $23,809 \text{ cm}^{-1}$ respectively. These bands are assigned to the ${}^4T_{1g} \rightarrow {}^2T_{2g}$, ${}^4T_{1g} \rightarrow {}^2T_{2g}$ (P) transitions, respectively²² both the absorption bands and the values of μ_{eff} lower than required for a spin value only state.

Table 3. Reflectance spectral and magnetic moment data of the QEPD coordination polymers.

Coordination polymers	Absorption band, cm^{-1}	Transitions	Magnetic moment, (μ_{eff})BM
QEPD-Cu(II)	23,470	Charge transfer	1.93
	15,626	${}^2B_{1g} \rightarrow {}^2A_{1g}$	
QEPD-Ni(II)	22,471	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$	3.5
	15,601	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$	
QEPD-Co(II)	22,989	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$	4.4
	16,530	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}$	
	9,051	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{P})$	
	24,051	${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$	
QEPD-Mn(II)	19,651	${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$	5.7
	16,226	${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$	

QEPD-Zn(II) is diamagnetic

The TGA data of all the coordination polymers are summarized in Table 4. The coordination polymers are as thermally stable as bis(8-hydroxy-5-quinolymethylene) sulfide (BHQS) and 5,5'-methylene bis(oxine) (MBQ)²³.

Table 4. Infrared frequencies (cm^{-1}) of QEPD coordination polymers.

Coordination polymers	$\gamma(\text{OH})$	$\gamma \text{C}=\text{N}$	$\delta(\text{C}-\text{N}-\text{C})$	$\delta(\text{C}-\text{O})$	$\delta(\text{M}-\text{N})$	$\delta(\text{M}-\text{O})$
QEPD-Cu(II)	3540	1602	1105	1353	776	500
QEPD-Ni(II)	3600	1602	1100	1367	769	500
QEPD-Co(II)	3520	1595	1105	1353	776	500
QEPD-Mn(II)	3500	1602	1105	1353	762	500
QEPD-Zn(II)	3510	1595	1100	1353	762	500

All the polymers decomposed in a single step. They start their degradation at around 100°C . The rapid degradation after this temperature may be due to catalytic oxidation by metal oxide which forms in situ during decomposition of the polymer. The relative order of thermal stability of the coordination polymers is $\text{Cu} < \text{Co} < \text{Ni} < \text{Mn}$.

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