



Coordination Polymers of N,N'-Di-(8-hydroxyquinolinolyl-5-methyl)-N,N'-dimethyl-1,3-propane diamine (QMPD)

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ABSTRACT

Coordination polymers containing a novel bis(oxine) bidentate ligand, namely N,N'-di(8-hydroxyquinolinolyl-5-methyl)-N,N'-dimethyl-1,3-propanediamine (QMPD) 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'-dimethyl-1,3-propanediamine in the presence of a base catalyses. All of these coordination polymers and the parent ligand were characterized by elemental analyses and IR spectral and diffuse reflectance spectral studies. The thermal stability and number- average molecular weights (Mn) 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: bis(oxine) bidentate ligand, N,N'-di(8-hydroxyquinolinolyl-5-methyl)-N,N'-dimethyl-1,3-propanediamine(QMPD),infrared spectra, degradation, thermogravimetry,

INTRODUCTION

The coordination chemistry of bis (oxine), bidentate ligand, has been extensively investigated for their metal gripping properties¹⁻³ In this context bis(oxine) legends 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 the synthesis and characterization of coordination polymers based on the is-oxine ligand joined with a bridge, -H₂C-O-Ph-O-CH₂ (Ph = 1,3 phenylene) has been replaced¹¹. This work has been further thought with the view of investigation the chelating ability of a bis-8-quinolinol bis(bidentate) ligand by introducing the bridge aof 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'-dimethyl-1,3-propanediamine (QMPD) and its coordination polymers with Zn(II), Cu(II) Ni(II), Co(II) and Mn(II) metal ions.

MATERIALS AND METHODS

Materials

All chemicals were of analytical grade. The synthesis of N,N'-di(8-hydroxyquinolinolyl-5-methyl)-N,N'-dimethyl-1,3-propanediamine (QMPD) was carried out in two steps. The preparation of 5-chloromethyl-8-hydroxyquinolinolyl hydrochloride according to a literature method¹².

Preparation of polymers of N, N'-di(8-hydroxyquinoloyl-5-methyl)-N,N'-dimethyl-1,3-propanediamine (QMPD)

QMPD was prepared as follows. For example to a suspension of 5-chloromethyl-8-hydroxyquinoline hydrochloride (23g, 0.02 mol), N,N'-dimethyl-1,3-propane diamine (17.5g, 0.1mol) in an acetone-water mixture was added. K₂CO₃ (5.3gm,0.03mole) was added as an acid acceptor. The resulting mixture was refluxed for 3 h with occasional shaking the resulting suspension, which contained for a green precipitate, was poured into ice cold (500ml) water and then filtered. The solid product was collected and dried to give QMPD (80% yield).

Analysis for C₂₅H₃₀N₄O₂; Calculated (%): C=71.74; H=7.22; N=13.39.

Found (%): C=72.56; H=6.98; N=13.02 .

Preparation of coordination polymers

For example, Cu(II); a solution of copper acetate (1.9g, 0.001) in aqueous formic acid (50ml, 50%) was added drop wise to a solution of QMPD (3.30g, 0.01 mol) in aqueous formic acid (240ml, 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 of 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 {QMPD-Cu(II)} was air dried. A similar procedure was used to prepare the QMPD-Co(II), QMPD-Ni(II), QMPD-Mn(II)and QMPD-Zn(II). The yields of all coordination polymers were almost quantitative.

Measurements.

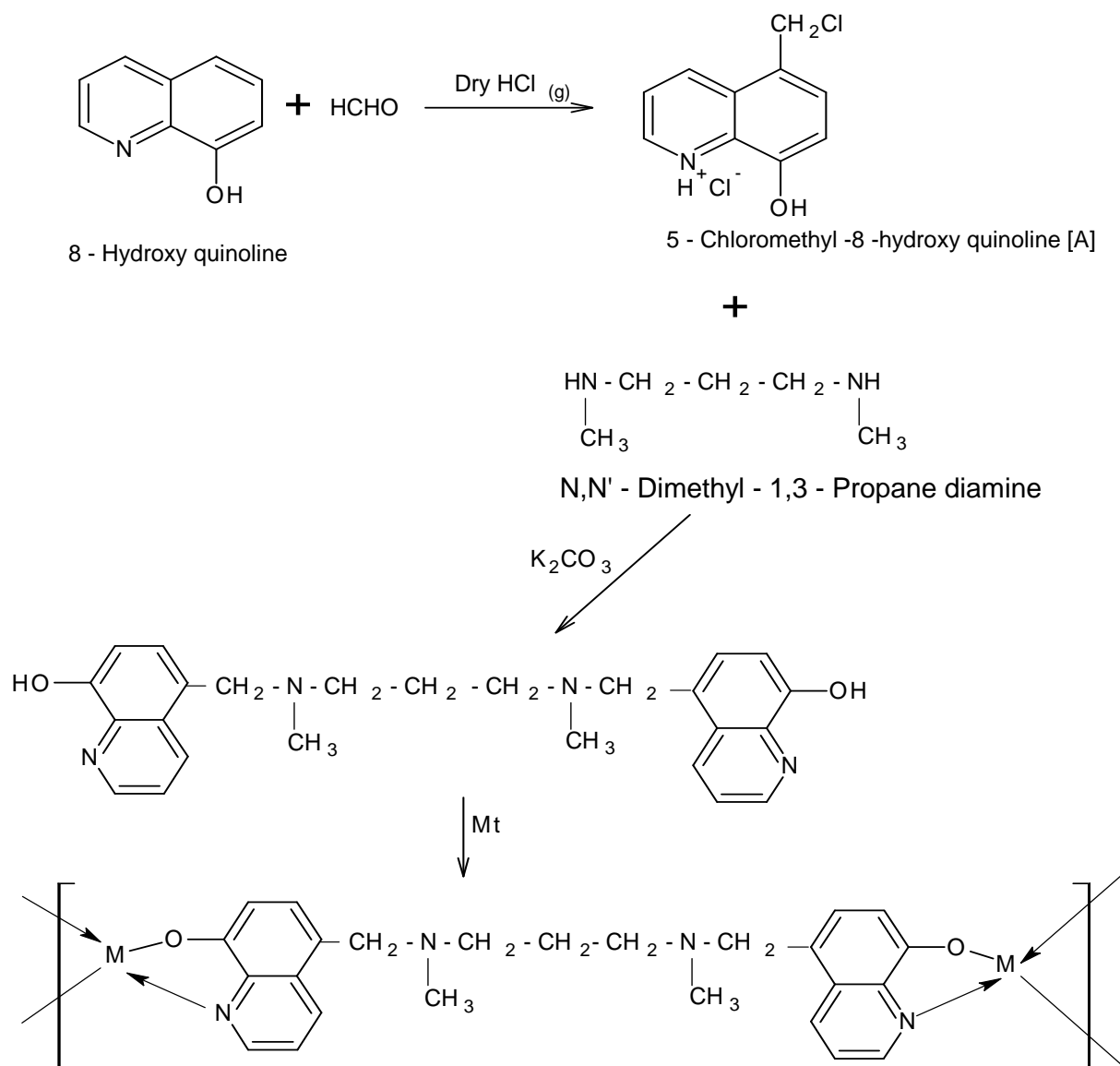
The metal analysis of co-ordination polymers comprised decomposition of a weighed amount of the polymer followed by EDTA titration using a standard procedure¹³. The percentage composition. (C, H and N) for the coordination polymers was determined with a C,H,N Elemental analyzer (Table-1). The IR spectra of the bis-ligand QMPD and of 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 (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 [tetrathiocyanatocobalt] Hg [Co(NCS)₄] 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.

SCHEME - 1



Co - ordination polymers, QMPD - Mt
Where Mt = Cu, Ni, Co, Mn, Zn.

RESULT AND DISCUSSION

The synthesis of the bis (bidentate) legend N,N'-di(8-hydroxyquinolinolyl-5-methyl)-N,N'-dimethyl-1,3-propanediamine (QMPD), has not been previously reported. The synthesis QMPD

was performed by chloromethylation of the oxine followed by condensation with N,N'-dimethyl-1,3-propane diamine. (Scheme 1).

The IR spectrum of H₂L is shown fig. 1. The important IR spectral features (figures not shown) are

(i) a broad band from 3550 cm⁻¹ to 3200cm⁻¹ that is attributed to the hydrogen-bonded OH group¹⁷.
(ii) The weak bands near 2950 cm⁻¹ and 2800 cm⁻¹ that are due to asymmetric and symmetric stretching vibrations of methylene groups (-CH₂) of the -CH₂-O-CH₃ - bridge.
(iii) The weak band at 1110cm⁻¹ that confirms the presence of a dialkyl ether function. And (iv) the bands near 1610, 1508, 1470 and 1420 cm⁻¹ that are the characteristic frequencies of the 8-hydroxyquinolinolyl nucleus¹². The weak band around 1085 and 1118 cm⁻¹ may also be attributed to the ether 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 250⁰C. 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 (Mn) of coordination polymers¹⁸⁻²¹ However, efforts are made by the present authors to estimate 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-1) reveals a 1:1 metal: ligand (M/L) stoichiometry for all the polymers.

The IR spectra of all the coordination polymers of H₂L are not shown. Comparison of the IR spectrum of the legend H₂L (see above) 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. This point will be discussed later. 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 QMPD is assigned to the in-plane OH deformation¹⁶. This band is shifted toward higher frequency (1468cm⁻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 QMPD-Cu(II) coordination polymer shows two broad bands near 15625 cm⁻¹ and 22222 cm⁻¹. The first band may be due to ²B_{1g} → ²A_{1g} transition while the second may be due to charge transfer. The first band shows some structural charactersitics that suggest a distorted octahedral geometry. The higher theoretical value of μ_{eff} of the QMPD-Cu(II)

polymer supports this view. The QMPD-Ni(II) and QMPD-Co(II) polymers exhibit three absorption bands at 22989, 16,530 and 9051 cm^{-1} , respectively. These bands are assigned to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively²³ both the absorption bands and the values of μ_{eff} lower than required for a spin value only state.

The TGA data of all the co-ordination 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)^{1,3}.

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 the metal oxide which forms in situ during the decomposition of the polymer. The relative order of thermal stability of the coordination polymers is $\text{Cu} < \text{Co} < \text{Ni} < \text{Mn}$.

Table-1 Analytical data for the coordination polymers of QMPD

Co-ordination polymers	Colour	Elemental analysis				\bar{M}_n
		N%		M%		
		Cal	Found	Cal	Found	
QMPD-Cu(II)	Green	10.9	10.7	12.37	12.1	5134
QMPD-Ni(II)	Green	11.0	10.8	11.54	11.4	5087
QMPD-Co(II)	Brown	10.98	10.8	11.53	11.35	5089
QMPD-Mn(II)	Light green	11.09	11.8	10.88	10.7	5049
QMPD-Zn(II)	Pale yellow	10.86	10.7	12.68	12.5	5157

Table-2. Infrared frequencies (cm^{-1}) of QMPD coordination polymers

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

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

Coordination polymers	Absorption band (cm^{-1})	Transitions	Magnetic moment (\square_{eff})BM
QMPD-Cu(II)	23,470 15,626	Charge transfer ${}^2B_{1g} \rightarrow {}^2A_{1g}$	2.1
QMPD-Ni(II)	22,471 15,601	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	4.02
QMPD-Co(II)	22,989 16,530 9,051	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.66
QMPD-Mn(II)	24,051 19,651 16,226	${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$ ${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$	5.92

QMPD-Zn(II) is diamagnetic

Table - 4 Thermogravimetric analysis (tga) of the co-ordination polymer of QMPD.

Co-ordination polymers	% Weight loss at temperature T(°C)					
	100	200	250	300	400	500
QMPD-Cu(II)	6.58	7.5	56.7	81.5	-	-
QMPD-Ni(II)	8.0	14.1	35.1	47.6	87.5	-
QMPD-Co(II)	7.5	8.9	9.3	13.61	76.2	-
QMPD-Mn(II)	7.0	11.5	35.6	50.0	86.0	-
QMPD-Zn(II)	12.0	14.0	37.9	50.0	73.0	88.6

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