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COORDINATION POLYMERS OF N,N'-DI-(8-HYDROXYQUINOLINOLYL-5-METHYL)-N,N'DIETHYL-1,4-BUT-2-ENEDIAMINE (QEBD)

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ABSTRACT

A novel bis-(bidentate) ligand, namely N,N'-di(8-hydroxyquinolinolyl-5-methyl)-N,N'-diethyl-1,4-but-2-enediamine (QEBD) was synthesized by condensation of 5-chloromethyl-8-hydroxyquinoline hydrochloride with N,N'-diethyl-1,4-but-2-ene-diamine in the presence of a base catalyst. The coordination polymers of this bis-ligand QEBD have been prepared with the metal ions Zn (II), Cu (II), Ni (II), Co (II) and Mn (II). All of these coordination polymers and the parent ligand QEBD were characterized by elemental analyses, IR spectral and diffuse reflectance spectral studies. The number-average molecular weights ($\overline{M}_n$) of all the coordination polymers were determined by non-aqueous conductometric titrations. The thermal properties of all the four coordination polymers were determined by thermogravimetry. In addition, all the coordination polymers have also been characterized by their magnetic susceptibilities.

Key words: Coordination polymers, Infrared spectra, Diffuse reflectance spectra, Thermogravimetry, Magnetic susceptibility, Number average molecular weight.

INTRODUCTION

The coordination chemistry of 8-hydroxyquinoline (HQ), a bidentate ligand, has been extensively investigated for its metal gripping properties[1-3]. In this context, bis- (8-hydroxyquinoline) ligands with two 8-hydroxyquinoline (HQ) units joined by a bridge of 5,5'-methylene (-CH_2-); 5,5'-sulfonyl (-SO_2-); 5,5'-dimethylene sulfide (-CH_2-S-CH_2-) and –CH-O-CH_2- are reported in literature[4-10]. Recently, Patel and Pachani[11] reported the synthesis and characterization of coordination polymers based on the bis-HQ ligand joined

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with a bridge, -H_2C-O-Ph-O-CH_2 (Ph = 1,3 phenylene)has been replaced. This work has been further carried out with a view of investigating the chelating ability of a bis-8-quinolinol bis(bidentate) ligand by introducing the bridge of aliphatic diamine between two 8-hydroxyquinoline moieties. Accordingly, the present work deals with the synthesis and characterization of a bis-HQ ligand, namely N,N'-di(8-hydroxyquinolinolyl)-5-methyl)-N,N'-diethyl-1,4-but-2-ene diamine (QEBD) and its coordination polymers with Zn (II), Cu (II) Ni (II), Co (II) and Mn (II) metal ions. The whole process is summarised in **Scheme 1**.

EXPERIMENTAL

Preparation of bis-ligands; N,N'-di(8-hydroxyquinolinolyl-5-methyl)-N,N'-diethyl-1,4-but-2-ene diamine (QEBD)

First of all, QEBD was prepared. To a suspension of 5-chloromethyl-8-hydroxyquinoline hydrochloride prepared by reported method[12] (46.2 g, 0.2 mol), N, N'-diethyl-1,4-but-2-ene diamine (14.2 g, 0.1 mol) in an acetone-water mixture was added. K_2CO_3 (14.0 g, 0.1 mole) 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 QEBD (80% yield). Analysis for $C_{28}H_{34}N_4O_2$; Calculated (%): C= 73.33; H=7.47; N=12.22; O=6.98; Found (%) : C = 75.30; H = 7.67; N = 12.22; O = 6.80

Preparation of coordination polymers

For example, Cu (II) complex : A solution of copper acetate (1.9 g, 0.001) in aqueous formic acid (50 mL, 50%) was added dropwise to a solution of QEBD (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 half an hour. The reaction mixture was made alkaline by the addition of diltute aqueous ammonia until the precipitation was complete. The polymer was separated in the form of a suspension and it was digested on a boiling water bath. Finally, the resultant solid brown precipitates were collected by filtration and washed with hot water, N,N-dimethylformamide (DMF) and then acetone. The polymer {QEBD-Cu (II)} was air dried. A similar procedure was used to prepare the QEBD-Co (II), QEBD-Ni (II), QEBD-Mn (II) and QEBD-Zn (II). The yields of all coordination polymers were almost quantitative.

Measurements

The metal content determination of all coordination polymers comprised the decomposition of a weighed amount of the polymer followed by EDTA titration using a standard procedure[13]. The percentage composition. (C, H and N) for the coordination polymers was determined by C,H,N Elemental analyzer (Table 1). The IR spectra of the bis-ligand QEBD and for 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 employed as the reference compound.

Table 1: Analytical data for the coordination polymers of QEBD

Coordination polymers	Colour	Elemental analysis (%)				$\overline{M}n$
		N		M		
		Calc.	Found	Calc.	Found	
QEBD-Cu (II)	Light green	10.20	10.1	11.5	11.4	5575
QEBD-Ni (II)	Light green	10.25	10.15	10.7	10.5	5510
QEBD-Co (II)	Brown	10.18	10.15	10.65	10.45	5520
QEBD-Mn (II)	Light green	10.30	10.20	10.15	10.15	5489
QEBD-Zn (II)	Pale yellow	10.10	10.0	11.80	11.5	5560

Table 2: Infrared frequencies (cm^{-1}) of QEBD coordination polymers

Coordination polymer	γ(OH)	γ C=N)	δ(C-N-C)	δ (C-O)	δ (M-N)	δ (M-O)
QEBD-Cu (II)	3545	1605	1110	1353	775	505
QEBD-Ni (II)	3590	1605	1105	1367	770	505
QEBD-Co (II)	3510	1590	1110	1353	773	505
QEBD-Mn (II)	3500	1602	1110	1353	765	505
QEBD-Zn (II)	3520	1590	1105	1353	760	505

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]; Hg $[Co(NCS)_4]$) was used for the calibration of instrument[16-18]. Molar susceptibilities were corrected for diamagnetism of the component using Pascal's constants. The data are reported in Table 3.

Thermogravimetry of all these coordination polymers was carried out using a Dupont thermogravimetric analyzer (TGA).

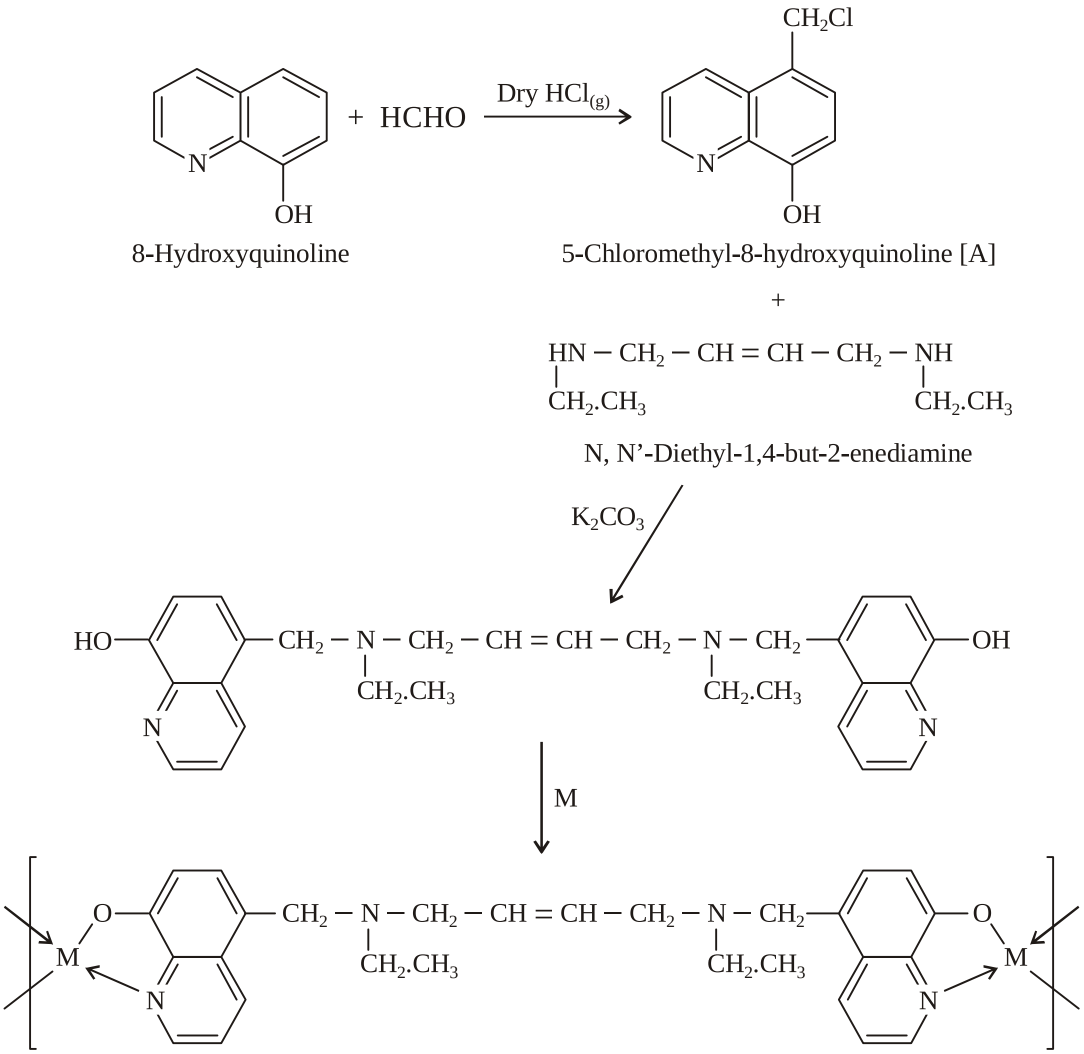
Table 3: Reflectance spectral and magnetic moment data of QEBD coordination polymers

Coordination polymers	Absorption band (cm^{-1})	Transitions	Magnetic moment (μeff) BM
QEBD-Cu (II)	23,481	Charge transfer	1.95
	15,630	$^2B_{1g} \rightarrow {}^2A_{1g}$	
QEBD-Ni (II)	22,475	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	3.30
	15,605	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	
QEBD-Co (II)	22,992	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	4.70
	16,535	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$	
	9,055	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$	
QEBD-Mn (II)	24,056	$^6A_{1g} \rightarrow {}^4A_{1g}.{}^4E_g$	5.82
	19,655	$^6A_{1g} \rightarrow {}^4T_{2g}(4G)$	
	16,230	$^6A_{1g} \rightarrow {}^4T_{1g}(4G)$	

QEBD-Zn (II) is diamagnetic

RESULTS AND DISCUSSION

The synthesis of the bis- (bidentate) ligand namely N,N'-di(8-hydroxyquinolinolyl-5-methyl)-N,N'-diethyl-1,4-but-2-ene diamine (QEBD), has not been previously reported. the synthesis QEBD was performed by chloromethylation of the 8-hydroxyquinoline followed by condensation with N,N'-diethyl-1,4-but-2-ene diamine (**Scheme 1**).



Coordination polymers, QEBD - M
Where M = Cu, Ni, Co, Mn, Zn

The IR spectrum (not shown) of QEBD show the prominent characteristic features. The broad band appearing from 3500 to 3200 cm^{-1} was attributed to phenolic -OH group[17]. The bands at 2980 and 1370 cm^{-1} due to $–CH_{2.}CH_3$ group and the bands at 2950 and 2850 cm^{-1} arised from symmetric and asymmetric vibrations of CH_2 group. Both these groups are present in bridge between two HQ units. The band due to aliphatic double bond did not appear properly, but determination of unsaturation by iodometry confirms the presence of this double bond. The other bands appeared due to HQ units at their respective positions and are almost identical to those of methylene bis- HQ[1]. All these features support the proposed structure of QEBD. The coordination polymers derived from QEBD are insoluble in common organic solvents. All these coordination polymers decomposed at approximately 250^0C. The molecular mass was estimated by evaluating the number of terminal OH groups using non-aqueous conductometrie titrations. Perusal of the literature revealed that there are few reports regarding the determination of the number average molecular weight ($\overline{M}_n$) of coordination polymers[18-21]. However, efforts are made by the present authors to estimate ($\overline{M}_n$) of the QEBD coordination polymers by utilizing the non-aqueous conductometrie titration method under controlled experimental conditions[22]. 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 (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.

Comparison of the IR spectra (not shown) of coordination polmers and QEBD reveal certain characteristic differences. The broad band in the region from 3550 to 3200 cm^{-1} for QEBD is absent in the spectra of the polymers. This is consistent with the involvement of OH groups in a coordinate interaction in the polymers. The band in QEBD due to C=N stretching at 1600 cm^{-1} is shifted towards lower frequency (ca 1558 cm^{-1}) in the spectra of 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 frequency[17]. The band at 1430 cm^{-1} in QEBD is assigned to in-plane OH deformation[17]. This band is shifted toward higher frequency (1468 cm^{-1}) in the spectra of the polymers supporting the formation of a metal-oxygen bond.

The magnetic moments ($\mu_{\mathbf{eff}}$) of the polymeric chelates are given in Table 1. The diffuse electronic spectrum of QEBD-Cu (II) coordination polymer shows two broad bands near 15630 cm^{-1} and 23481 cm^{-1}. The first band may be due to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition while the second may be due to charge transfer. The first band shows some structural charactersitcs that suggest a distorted octahedral geometry. The higher theroretical value of μ_{eff} of the QEBD-Cu (II) polymer also supports this view. The QEBD-Co (II) polymers exhibit three absorption bands at 9050; 16,535 and 22,992 cm^{-1}, respectively. These bands are assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}$, $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (P) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions, respectively[23]; two absorption bands and the values of μ_{eff} lower then required for a spin value only state.

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-quinolylmethylene) sulfide (BHQS) and 5,5'-methylene bis(8-hydroxyquinoline) (MBQ)[1,3].

Table 4: Thermogravimetiric analysis (TGA) of the coordination polymer of QEBD

Coordination polymers	% Weight loss at temperature T (°C)					
	100	200	250	300	400	500
QEBD-Cu (II)	2.43	67.17	69.1	88.0	-	-
QEBD-Ni (II)	3.46	6.89	235	36.72	84.72	-
QEBD-Co (II)	8.2	17.1	49.0	77.9	80.1	-
QEBD-Mn (II)	7.1	9.15	13.1	18.1	31.25	87.1
QEBD-Zn (II)	9.6	11.45	12.5	14.12	65.95	83.60

All the polmers start their degradation in a single step. They start their degradation at around 100°C. The rapid degradation after this transition may be due to the 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 –

Cu < Co < Ni < Mn.

REFERENCES

1. E. Horowitz and T. P. Perros, J. Inorg. Nucl. Chem., **26**, 139 (1964).
2. J. C. Bailer Jr, M. L. Judd and M. J. Mclean, WADC. Technical Reports, **58- 61** Part-II, 116 (1969).
3. R. D. Patel, H. S. Patel and S. R. Patel, Eur. Polym. J., **23**, 229 (1987).
4. T. B. Shah, H. S. Patel and R. B. Dixit, Orien. J. Chem, **15**, 107 (1999).
5. N. Manolova, M. Ignatova and I. Rashkov, Eur. Polym. J., **34**, 1133 (1938).
6. L. M. Raj, M. M. Raj, H. S. Patel and T. B. Shah, Eur. Polym. J., **35**, 1537 (1999).
7. M. Garaleh, M. Lahcini, H. R. Kricheldorf and S. M. Weidner, J. Polym. Sci. Part A: Polym. Chem., **47**, 170 (2009).
8. Y. H. Tsai, C. H. Lin, C. C. Lin and B. T. Ko, J. Polym. Sci. Part A: Polym. Chem., **47**, 4927 (2009).

9. J. M. Pandya and D. C. Patel, Bull. Chem. Sci., **29**, 33 (2002).
10. T. B. Shah, H. S. Patel and R. B. Dixit, Synthc. React. Inor. Mrt. Org. Chem, **31**, 649 (2001).
11. K. D. Patel and S. C. Pachani, Ultra Sci. Phys. Sci., **15(2)**, 195 (2003).
12. J. H. Burkhalter and R. I. Laib, J. Org. Chem., **26**, 4078 (1961).
13. A. I. Vogel, Inorganic Quantitative Analysis, ELBS, London (1978).
14. S. K. Chatterjee and N. D. Gupta, J. Poly. Sci. Part A– I, **11**, 1261 (1973).
15. R. P. Mitra and S. K. Chatterjee, Indian. J. Chem., **1**, 62 (1963).
16. K. D. Patel and S. C. Panchani, E-J. Chem., **1(3)**, 158 (2004).
17. B. N. Figgis and J. Lewis, Modern Coordination Chemistry, Wiley Interscience, NJ (1964).
18. R. G. Figgis, H. F. Freiser, R. Priedel, L. E. Hilliand and R. D. Johnston, Spectrochem. Acta, 8, **1** (1958).
19. H. Nierengarten, J. Rojo, E. Leize, J-M. Lehn and A. V. Dorsselaer, Euro. J. Inorg. Chem., **3**, 573 (2002).
20. Paulusse, Chem. Comm., 1313, 1494 (2003).
21. Y. S. Cho, H. K. Lee and J. S. Lee, Macromol. Chem. Phys., **203(17),** 2495 (2002).
22. R. N. Patel and S. R. Patel, Angew. Makro mol. Chem., **96**, 85 (1981).
23. A. B. P. Lever, Inorganic Electronic Spectroscopy 2nd Ed., Elsevier, Amsterdam (1984).

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