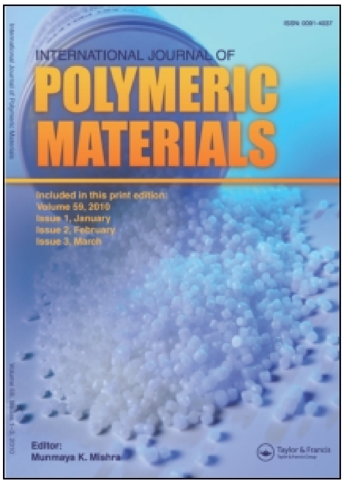

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Coordination Polymers of 1,9-Bis(8-Hydroxyquinolin-5-yl)-2,5,8-Trioxanonane

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Coordination polymers of a novel bis(oxine) bidentate ligand, namely 1,9-bis(8-hydroxyquinolin-5-yl)-2,5,8-trioxanonane (BHQTN) (H_2L) have been prepared with the metal ions Zn^{+2}, Cu^{+2}, Ni^{+2}, Co^{+2}, and Mn^{+2}. The novel bis(bidentate) ligand BHQTN was synthesized by condensation of 5-chloromethyl-8-hydroxyquinoline hydrochloride with diethylene glycol in the presence of a base catalyst. All of these coordination polymers and the parent ligand were characterized by elemental analyses and IR spectral studies. The diffuse reflectance spectral studies and magnetic susceptibilities of all of the coordination polymers have also been performed. Thermogravimetric parameters such as T_o, T_{10}, $T_{max.}$, IPDT, and the activation energy of the thermo-degradation process were calculated.

Keywords: bis(oxine) bidentate ligand BHQTN (H_2L), co-ordination polymer

INTRODUCTION

Several literature reports are directed towards chelating polymers of 8-hydroxyquinoline and its derivatives, because they found applications in various areas such as in wastewater treatment for metal recovery, in protective coatings, as antifouling paints, as antimicrobial surgical materials, and as disinfectants in solutions, gels, and ointment for medicinal uses [1–3]. Furthermore, literature survey has revealed a

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promising method for the formation of coordination polymers with enhanced chelating ability by using a bidentate 8-hydroxyquinoline moiety in which two 8-hydroxyquinolinyl end groups are joined by a linear aliphatic bridge of 5,5′-methylene ($-CH_2-$), 5,5′-sulfonyl ($-SO_2-$), or 5,5′-dimethylene sulfide ($-CH_2-S-CH_2$) usually at the 5,5′-positions [4–6]. In this context, the authors have also reported the synthesis and characterization of coordination polymers based on a novel 8-hydroxyquinoline bis(bidentate) ligand containing a dimethylene oxide ($-CH_2-O-CH_2-$) aliphatic bridge [7]. This work has been further extended with a view to explore the chelating ability of a 8-hydroxyquinoline bis(bidentate) ligand by increasing the chain length of the aliphatic bridge between two 8-hydroxyquinoline moieties.

Thus, the present work comprises the synthesis and characterization of a novel bis(oxine) ligand, namely 1,9-bis(8-hydroxyquinolin-5-yl)-2,5,8-trioxanonane (BHQTN), and its coordination polymers with Zn^{+2}, Cu^{+2}, Ni^{+2}, Co^{+2}, and Mn^{+2} metal ions.

EXPERIMENTAL

Materials

All the chemicals used were of AR grade.

Procedure

Synthesis of 1,9-bis(8-hydroxyquinolin-5-yl)-2,5,8-trioxanonane BHQTN (H_2L)

The ligand BHQTN was prepared in two steps. (1) The precursor 5-chloromethyl-8-hydroxyquinoline hydrochloride was prepared by reported method [8]. It is a yellow colored product and has a melting point of 280°C. (2) Synthesis of parent ligand BHQTN (H_2L). BHQTN was prepared by following a method reported for 5-alkoxymethylene-8-quinolinol [8]. According to this method, a mixture of 5-chloromethyl-8-hydroxyquinoline hydrochloride (23 g, 0.1 mole), diethylene glycol (4.75 ml, 0.05 mole) in THF (30 ml) and sodium bicarbonate (8.4 g, 0.1 mole) was refluxed at 80 ± 2°C for 2.5 h with occasional shaking. The resulting solution was then made alkaline with dilute ammonia to precipitate out the ligand; it was then filtered and air-dried. The yield of BHQTN was 75%, and its melting point was 178°C.

Preparation of Coordination Polymers

All coordination polymers were synthesized by using metal acetates in a general method described in what follows:

A warm and clear solution of BHQTN (4.20 g, 0.01 mole) in 20% aqueous formic acid (200 ml) was added to a solution of copper acetate (1.99 g, 0.01 mole) in 50% aqueous formic acid (50 ml) with constant stirring. After complete addition of the metal salt solution, the pH of the reaction mixture was adjusted to about 5 with dilute ammonia solution. The polymer chelate, thus separated out in the form of suspension, was digested on a water bath for one hour and eventually filtered, washed with hot water followed by acetone and DMF, and then dried in air at room temperature. The yields of all coordination polymers were almost quantitative.

Measurements

Elemental analyses for C, H, and N of BHQTN and its coordination polymers were carried out on a Carlo Erba elemental analyzer (Italy). IR spectra of BHQTN and the coordination polymers in KBr were scanned on a Nicolet-400D FTIR spectrophotometer-meter. The metal content analyses of the coordination polymers were performed by decomposing a weighed amount of each coordination polymer followed by complexometric titration with EDTA as reported in the literature [9].

Magnetic susceptibility measurements of all the coordination polymers were carried out at room temperature by the Gouy method. $Hg[Co(NCS)_4]$ was used as a calibrant and molar susceptibilities were corrected for diamagnetism of the component atom using Pascal's constant [10]. The diffuse reflectance spectra of the solid coordination polymers were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

Thermograms of the coordination polymers were recorded on a DuPont 950 thermogravimetric analyzer at a heating rate of 10°C/min in air atmosphere. In order to determine thermal stability trend, thermogravimetric parameters such as T_o (initial decomposition temperature), T_{10} (temperature for 10% weight loss), T_{max} (temperature of maximum rate of degradation), IPDT (integral procedural decomposition temperature) [11–12] and the activation energy E_a [13], of the degradation process were calculated by following the method reported in the literature. T_0 and T_{10} are the main criteria used to indicate the heat stability of polymers. Higher values of T_0 and T_{10}, suggest higher thermal stability of polymers. To obtain the quantitative picture of the relative thermal stability, IPDT values can be regarded of significant importance; because they represent the over all nature of TGA curves. The IPDT values can be calculated using the following equation,

$$IDPT = T_0 + \frac{Area\ under\ the\ thermogram}{Total\ area\ of\ thermogram}(T_f - T_0)$$

Where T_0 and T_f are, respectively, the initial and final temperatures of thermal degradation process.

RESULTS AND DISCUSSION

The parent ligand BHQTN (H_2L) is a light green powder, soluble in organic solvents such as dioxane, DMSO, and DMF. The results of elemental analyses of the ligand reported in Table 1 are consistent with the predicted structure as shown in Scheme 1.

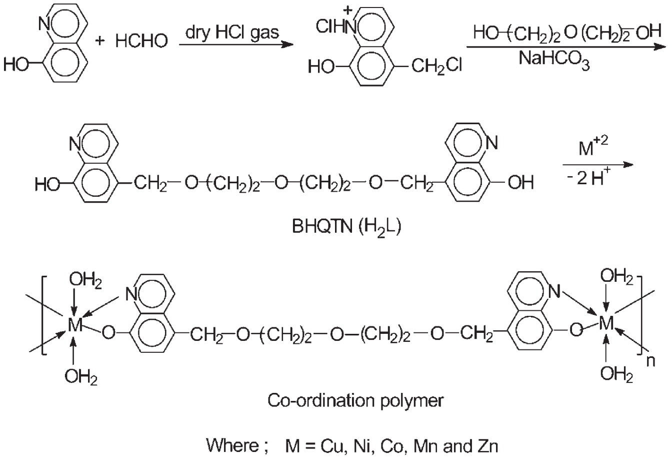
The IR spectrum of BHQTN has shown a broad band at $3335-3550\,cm^{-1}$ due to phenolic hydroxyl group, whereas the characteristic IR frequencies of 8-hydroxyquinoline moiety appear at 1420, 1460, 1590, and $1600\,cm^{-1}$ as expected [14]. The weak bands at $2930\,cm^{-1}$ are attributed to aliphatic stretching vibrations of methylene bridge ($-CH_2-$) and bands at 1086 and $1160\,cm^{-1}$ indicate C−O stretching of the ether groups of the 2,5,8-trioxanonane bridges.

The coordination polymers of BHQTN with the metal ions Zn^{+2}, Cu^{+2}, Ni^{+2}, Co^{+2}, and Mn^{+2} vary in color from light green to dark green. On the basis of the proposed structure as shown in Scheme 1, the molecular formula of the BHQTN ligand is $C_{24}H_{24}N_2O_5$, which upon chelation coordinates with one central metal atom at four coordination sites and with two water molecules. Therefore, the general molecular formula of the resulting coordination polymer is given by $C_{24}H_{24}N_2O_5M{\cdot}2H_2O$. This has been confirmed by the results of elemental analyses of all five coordination polymers and their parent ligand (Table 1). They resemble each other in their general shape. But the comparison of the IR spectrum of the parent ligand BHQTN with those of its coordination polymers has revealed certain characteristic differences.

One significant difference to be expected between the IR spectrum of the parent ligand and its metal coordinated polymers is the presence of more broadened bands in the region of $3300–3650\,cm^{-1}$ for the coordination polymer, as the oxygen of the O−H group of the ligand forms a coordination bond with the metal ions. This is explained by the fact that water molecules may have strongly absorbed to the polymers during their formation. Another noticeable difference is that the band due to the C=N stretching vibration of 8-hydroxyquinoline at $1600\,cm^{-1}$ in the IR spectrum of BHQTN is shifted to lower frequency, where as the band at $1420\,cm^{-1}$ in the IR spectrum of BHQTN assigned to in-plane −OH deformation [14] is shifted

TABLE 1 Analytical and Spectral Data of the Coordination Polymers of BHQTN (H_2L)

Compound	Empirical formula	Yield (%)	Analyses % Found/(Calcd.)				Absorption band (cm^{-1})	Transitions	μ_{eff} (B.M.)
			% C	% H	% N	% M			
H_2L	$C_{24}H_{24}N_2O_5$	65	68.29 (68.57)	5.28 (5.71)	6.16 (6.66)	—	—	—	—
$[CuL(H_2O)_2]_n$	$Cu{\cdot}C_{24}H_{22}N_2O_5{\cdot}H_2O$	78	57.06 (57.65)	4.71 (4.80)	5.51 (5.60)	12.23 (12.73)	24,500 15,625	Charge transfer $^2B_{1g}\rightarrow{}^2A_{1g}$	1.73
$[CoL(H_2O)_2]_n$	$Co{\cdot}C_{24}H_{22}N_2O_5{\cdot}2H_2O$	80	56.00 (56.14)	4.90 (5.60)	5.10 (5.45)	11.10 (11.50)	22,727 15,384 9,550	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ $^4T_{1g}(F)\rightarrow{}^4T_{2g}$ $^4T_{1g}(F)\rightarrow{}^4T_{2g}(P)$	3.87
$[NiL(H_2O)_2]_n$	$Ni{\cdot}C_{24}H_{22}N_2O_5{\cdot}2H_2O$	92	56.19 (56.17)	4.95 (5.07)	5.20 (5.46)	11.20 (11.45)	23,105 15,535	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$ $^3A_{1g}\rightarrow{}^3T_{1g}(F)$	3.3
$[MnL(H_2O)_2]_n$	$Mn{\cdot}C_{24}H_{22}N_2O_5{\cdot}2H_2O$	82	56.15 (56.58)	5.00 (5.10)	5.20 (5.50)	10.30 (10.81)	22,955 18,650 16,000	$^6A_{1g}\rightarrow{}^4A_{1g}.{}^4E_g$ $^6A_{1g}\rightarrow{}^4T_{2g}(4G)$ $^6A_{1g}\rightarrow{}^4T_{1g}(4G)$	5.92
$[ZnL(H_2O)_2]_n$	$Zn{\cdot}C_{24}H_{22}N_2O_5{\cdot}2H_2O$	85	55.14 (55.45)	4.02 (4.23)	5.00 (5.39)	12.02 (12.58)	—	—	D



SCHEME 1

toward higher frequency in the spectra of the coordination polymers. This may be due to chelation of metal with 8-hydroxyquinoline. This has been further confirmed by a weak band at 1105 cm^{-1} corresponding to C–O–M stretching [14] and the bands around 770 and 650 cm^{-1} correspond to the M–N vibration. Thus, all of these characteristic features of the IR studies suggest the structure of the coordination polymer as shown in Scheme 1. Examination of data of the metal content in each polymer (Table 1) revealed a 1:1 metal:ligand (M/L) stoichiometry in all the coordination polymers.

Magnetic moments (μ_{eff}) of the coordination polymer are given in Table 1. Examination of these data reveals that all coordination polymers other than that of Zn^{+2} are paramagnetic while that of Zn^{+2} is diamagnetic.

The diffuse electronic spectrum of all the coordination polymers are shown in Table 1, suggesting an octahedral structure for all the polymers. However, [CuL(H$_2$O)$_2$] shows a distorted octahedral structure. As the spectrum of the [ZnL(H$_2$O)$_2$] polymer is not well resolved, it is not interpreted but its μ_{eff} value shows that it is diamagnetic as expected.

The thermal behavior of the coordination polymers and their parent ligand was investigated by thermogravimetric analysis (TGA) and the thermograms are shown in Figure 1. Scrutiny of these thermogram indicates that the degradation in coordination polymers as well as in unchelated bis ligand has initiated at almost the same temperature, near about 25–50°C (T$_0$). A very slight decrease in weight loss (3–4%) found from the thermogram in the temperature range 25–150°C for

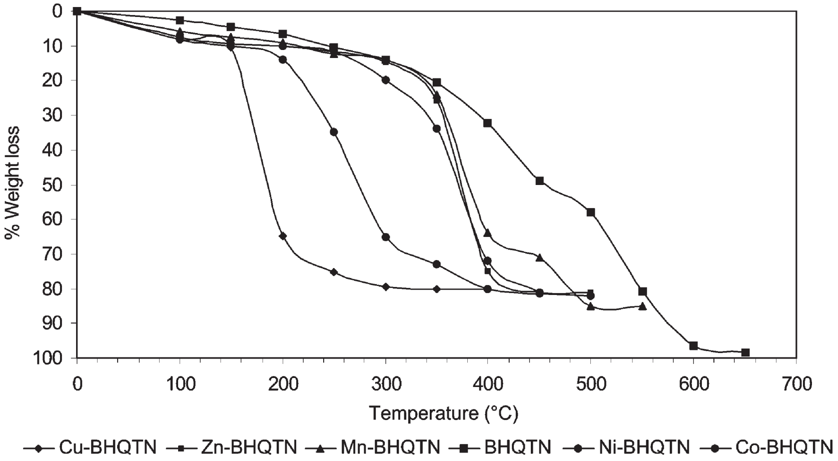


FIGURE 1 Thermograms of BHQTN ligand and its coordination polymers.

the parent ligand may be attributed to loosely held moisture present in the bis ligand. On the other hand, the gradual weight loss initially occurred below 150°C in all of the coordination polymers may be due to removal of hydrated water, whereas that obtained in the temperature range 150–200°C might be due to metal coordinated water molecules [15].

The rate of decomposition for the entire coordination polymer is initially low, up to 180°C and gradually increases to a maximum in the range 280–400°C temperatures at which almost 80% weight loss occurred. A remarkable difference is observed in the mode of thermal degradation for parent ligand and its coordination polymers. The bis (bidentate) ligand follows a two-step thermal degradation as compared to a single step thermal degradation occuring in each of the five coordination polymers. The two steps of thermal degradation in the parent bis (bidentate) ligand can be explained as:

- The first slow step of thermal degradation in the temperature range of 330–450°C may be due to decomposition of a more labile aliphatic bridge present between the two 8-hydroxyquinoline units as compared to the aromatic nature of oxine.
- The second step of thermal degradation may be in 8-hydroxyquinoline, initiated at the temperature of 480°C and then lose the weight rapidly around 550°C and completed to about 98.5% weight loss at 650°C.

Examination of the percentage weight loss as a function of temperature in all coordination polymer reveals that all the coordination polymer decompose in a single step and have an almost similar mode of decomposition, indicating that the thermal decomposition reactions in these coordination polymers are independent of the nature of the metal ion present. However, the rate of thermal decomposition in each sample is remarkably different, indicating that the thermal degradation is also dependent on an efficiency of a central metal atom to act as a catalyst in the thermal decomposition. On the basis of these criteria, the order of thermal stability among these five coordination polymers is;

$$\begin{aligned}&\mathrm{Mn^{+2}\text{-}BHQTN} > \mathrm{Zn^{+2}\text{-}BHQTN} > \mathrm{Ni^{+2}\text{-}BHQTN}\\ &> \mathrm{Co^{+2}\text{-}BHQTN} > \mathrm{Cu^{+2}\text{-}BHQTN}.\end{aligned}$$

Thus, the unchelated bis(bidentate) ligand and coordination polymers begin to decompose at almost the same temperature but in the polymer chelates this decomposition propagates very fast compared to that in the parent ligand. Consequently, one may conclude that the present ligand is thermally more stable than its coordination polymers. These results of thermal behavior can be explained by the fact that the decomposition in metal coordinated polymers was catalytically induced by the metal ions [16] and/or the introduction of the metal ion into the polymer backbone chain may develop a considerable strain in the coordination polymer of bis(bidentate) ligand than that of the strain of the free bis(bidentate) ligand molecule.

A comparative study of thermal stability of coordination polymers has also been carried out with a view to examine structure-property relationship. For this purpose the thermal parameters such as T_0, T_{10}, PDT, IPDT are estimated and are furnished in Table 2. A significant differences is observed for the temperatures corresponding to T_{10}, PDT, and IPDT. The values of these temperatures are higher in the case of unchelated bis(bidentate) ligand as compared to those of its

TABLE 2 Thermal Parameters of BHQTN Coordination Polymers

Compounds	T_0°C	T_{10}°C	PDT	IPDT	Activation energy (E_a) Kcal/mol
H_2L	25	340	480	518	10.10
$[CuL(H_2O)_2]_n$	25	160	175	250	7.5
$[CoL(H_2O)_2]_n$	25	200	250	350.80	8.6
$[NiL(H_2O)_2]_n$	25	230	340	380.25	8.5
$[MnL(H_2O)_2]_n$	25	240	400	415.25	8.9
$[ZnL(H_2O)_2]_n$	25	235	380	410	8.7

PDT = Temperature for maximum rate of thermal degradation.
IPDT = Integral procedural decomposition temperature.

metal coordination polymers, indicating that the parent bis(bidentate) ligand is thermally more stable than its coordination polymers. Scrutiny of PDT and IPDT values of coordination polymers have indicated that the Cu-coordinated polymer has the least thermal stability whereas the Mn-coordination polymer is the most stable.

In conclusion, the results of thermogravimetric analyses of bis(bidentate) ligand and its coordination polymers reveal that the unchelated bis(bidentate) ligand is thermally more stable than its coordination polymers. Further, Mn-BQDO coordination polymer is the most stable of the five metal coordination polymers and its thermal stability is comparable to that of parent bis(bidentate) ligand (BQDO). It is also revealed from the shape of the thermogram that the thermal degradation is a function of temperature in case of bis (bidentate), but not in case of the coordination polymers. Therefore, Mn-BQDO coordination polymer may be used as heat resistant material up to 300°C.

Broido method was followed for estimation of energy of activation of thermal decomposition of all samples. The energy of activation E_a was computed from the slope of the plot of ln(ln 1/y) versus (I/T) and reported in Table 2.

$$\text{Slope} = -E_a/R$$

Where, $R = 1.987$ kcal/mole, and it is 10.10 Kcal/mole for the bis ligand whereas the activation energies observed for the coordination polymers are in the range of 7.5–8.9 kcal/mole.

A comparison of the thermal stability of the present coordination polymers with the reported thermal stability of coordination polymers having bis(8-hydroxyquinolinyl)methane (MBQ) [4] and bis(8-hydroxy quinolin-5-ylmethylene)ether (BHQE) [7] reveals that the polymers of this study, containing $-CH_2-O-(CH_2)_4-O-CH_2-$ bridges, are thermally less stable than those containing methylene ($-CH_2-$) or dimethylene oxide ($-CH_2-O-CH_2-$) bridges. It may be due to the higher aliphatic character of the bridge, $-CH_2-O-CH_2)_4-O-CH_2-$, containing two ether oxygen atoms making it more labile to undergo decomposition.

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