Available online at www.elixirpublishers.com (Elixir International Journal)

Chemical Physics

Elixir Chem. Phys. 44 (2012) 7378-7381

Elixir ISSN: 2229-712X

Novel co-ordination polymers of 8-hydroxyquinoline

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ARTICLE INFO

Article history:
Received: 31 October 2011;
Received in revised form:
5 March 2012;
Accepted: 17 March 2012;

Keywords
Heteronuclear bisligand,
Co-ordination polymer,
Antimicrobial activities.

ABSTRACT

The reaction between 5-(4-phenyl carbonyl methyl amino) 8-hydroxyquinoline(PHQ) and melic anhydride afforded heteronuclear bisligand namely 4-(4-(2-(8-hydroxyquinolin-5-ylamino)acetyl)phenylamino)-4-oxobut-2-enoic acid(CMHQ). The bisligand was designated as CMHQ and its co-ordination polymers with Cu^{+2}, Zn^{+2}, Co^{+2}, $Mn^{+2}$and Ni^{+2} metal ions were prepared. The co-ordination polymers and parent ligand were characterized by elemental analysis, IR, NMR spectral studies, thermogravimetry, number-average molecular weights ($\overline{Mn}$), diffuse reflectance spectral studies and magnetic susceptibilities. All co-ordination polymers and parent ligand were also monitored for microbicidal activity.

Introduction

The study of co-ordination polymers has made much progress [1]. These polymers are known for their semiconducting catalytic properties, waste water treatment for metal recovery, in protective coating, as antifouling paints and anti fungal properties [1, 2]. Such co-ordination polymers are mostly derived from bi-chelating ligands in which metal ions and chelating agents are arrayed alternatively. Most of bichelating ligands are derived from well known chelating agents like 8-hydroxy quinoline and salicylic acid etc [3, 6]. The joining segment of these two similar ligands are mainly –N=N-, SO_2, -CH_2 -, -O- [3-9]. The area in which the co-ordination polymers having bis-azo dye containing ligands has not been developed so far. Such ligand may afford the co-ordination polymer with different properties. Hence, it was thought interesting to explore the field of co-ordination polymers based on hetronuclearting bis ligands having 8-hydroxy quinoline and amic acid. Though the amic acid is generally derived by condensation of amines with anhydrides having carboxylic and amide group. Such amic acid may afford metal complex with metal ions. The metal complexation study of various amic acids has been reported recently from scientist [10-13], so the proposed present work is in connecting with the co-ordination polymers based on hetronuclearting bisligands. The synthetic route is shown in Scheme-1.

Experimental

Materials

All the chemicals used were of analytical grade and obtained from local market.

Synthesis of 4-(4-(2-(8-hydroxyquinolin-5-ylamino)acetyl)phenylamino)-4-oxobut-2-enoicacid (CMHQ)

The precursor 5-amino-8-hydroxyquinoline hydrochloride (AHQ) was prepared by reported method [14, 15]. The 4-chloro acetamido phenacyl chloride (APC) was prepared by reported method [16].

Preparation of 5-(4-phenyl carbonyl methyl amino)-8-hydroxyquinoline(PHQ): This was prepared by following method. The solution of 4-chloro acetamido phenacyl chloride (APC) (24.6*g*, 0.1 mole) in acetone was treated with 5-amino-8-hydroxyquinoline hydrochloride (AHQ) (23.1*g*, 0.1 mole) in acetone at room temperature. The resultant product was filtered and hydrolyzed by 50:50 HCl: Ethanol mixture.

Preparation of 4-(4-(2-(8-hydroxyquinolin-5-ylamino)acetyl)phenylamino)-4-oxobut-2-enoic acid (CMHQ): The CMHQ was prepared by the solution of 5-(4-phenyl carbonyl methyl amino)-8-hydroxy quinoline(PHQ) (36.9*g*,0.1mole) in acetone was cooled to 10^oC, to this solution the melic anhydride (9.8,0.1mole) was added with stirring , The resulting product was then filtered and air-dried. The yield of CMHQ was 73% and m.p.185-187^0C (uncorrected). IR [ν,cm^{-1},KBr]: 1638, 1575, 1500, 1450 (8-Hydroxy quinoline moiety);3040,1520,1665(Aromatic);1725(CO);3440-3180(OH);3400(Sec.NH); 2895, 2960 (CH_2) ; 1690 (COOH); 1650,1620,1530 (amide group). ^{1}HNMR [400 MHz, δ,ppm, DMSO- d_6] : 7.98 -7.80 (m,4H,Ar-H); 6.89-8.92 (m,5H,Quinoline); 3.92 (s,2H, CO-CH_2-NH);4.22 (s,1H, OH);8.82-8.64(d,2H,CH); 8.4,3.26 (s,2H,NH); 11.72 (s,1H, COOH). Anal. Calc. for $C_{21}H_{17}N_3O_5$ (391) C, 64.45; H, 4.38; N, 10.74.Found; C, 64.4; H, 4.3; N, 10.7. The predicted structure and formation of polymeric ligand is shown in Scheme-1.

Preparation of Co-ordination Polymers

All co-ordination polymers were synthesized by using metal acetates in a general method described as follows:

A warm clear solution of CMHQ in 20% aq. formic acid (200ml) was added to a solution of metal acetate (0.01mole) in 50% aq.formic acid (50ml) 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 is 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 dimethyl formamide (DMF) and then dried in air at room temp. The yields of all co-ordination polymers were almost quantitative.

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Measurements

Elemental analysis of CMHQ and its co-ordination polymers were carried out on a C,H,N elemental analyzer (Italy). IR spectra of H_2L and the polymeric chelates were scanned on a Nicolet-760D FTIR spectrophotometer in KBr. The metal content analyses of the polymeric chelates were performed by decomposing a weighed amount of each polymeric chelates followed by EDTA (disodium ethylendiamine tetra acetate) titration as reported in the literature [8]. Magnetic susceptibility measurements of all the polymeric chelates were carried out at room temperature by the Gouy method. Mercury tetrathiocynatocobaltate (II), Hg[Co(NCS)], was used as a calibrant. Molar Susceptibilities were corrected for diamagnetism of component atoms using Pascal's constant. 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.

The number average molecular weight ($\overline{Mn}$) of all the co-ordination polymers were determined by method reported in earlier communications [17].

Thermogravimetric analysis of co-ordination polymers were carried on DuPont 950 TGA analyzer in air at a heating rate of 20C/min.

Antibacterial activities

Antibacterial activity of CMHQ ligand and its co-ordination 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 50µg/ml by agar cup plate method. Methanol system was used as control in this method. The area of inhibition of zone measured in mm.

Antifungal activities

The fungicidal activity of all the compounds was 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 co-ordination polymers was measured on each of these plant pathogenic strains on a potato dextrose agar (PDA) medium. Such a PDA medium contained potato 200gm,dextrose 20gm,agar 20gm and water one liter. Five days old cultures were employed. The compounds to be tested were suspended (1000ppm) in a PDA medium and autoclaved at 120° C for 15 min.at 15atm.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:

Percentage of Inhibition = 100(X-Y) / X

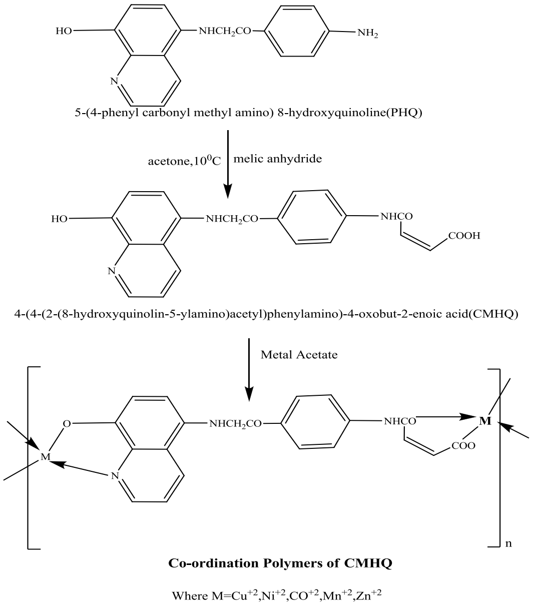
Where, X = Area of colony in control plate
Y = Area of colony in test plate

Results and Discussion

The synthesis of the bisbidentate ligand, 5-[4-(2-carboxyphenyl carbonyl amino) phenyl carbonyl methyl amino)-8-hydroxyquinoline (CMHQ) has not been reported in the literature. The ligand CMHQ was isolated in the form of a yellowish powder. It is soluble organic solvents such as in dioxane, DMSO (dimethyl sulfoxide), DMF. The results of elemental analyses of the CMHQ ligand (Table-1) are agreed with those predicted on the basis of formula.

The IR spectrum of CMHQ features are a broad band extending from 3440-3180 cm^{-1} with maximum at 3310 cm^{-1} attributed to the OH group [3]. The weak bands around 2895 and 2960 cm^{-1} may be due to asymmetric and symmetric stretching vibrations of methylene groups($-CH_2-$). The bands at 3400cm^{-1} and at 1725cm^{-1} are respectively due to NH (Sec) and CO group respectively. The bands around 1638, 1575, 1500 and 1450 cm^{-1} are attributed to the 8-hydroxyquinoline nucleus [18]. The band at 1690 cm^{-1} due to COOH group. The band around 1650, 1620 and 1530 are attributed to amide group. The others bands are at their respective positions.

The ^1H NMR(δ ppm) spectrum of CMHQ also show the signals 3.92 ($2H,s,CH_2$) ;8.82-8.64(d,2H,CH) ; 8.4,3.26 (s,2H,NH); 4.22 (1H,s,OH) ; 7.98 -7.80 (m,4H,Ar-H); 6.89-8.92(5H,m,Quinoline) ; 11.72 (1H,s, COOH). These features confirm the proposed structure of ligand CMHQ. The NMR Data of CMHQ shown in experimental part are also confirming the structure of CMHQ.



SCHEME 1

The co-ordination polymers derived from CMHQ are insoluble in common organic solvents. Hence it is not possible to characterized the co-ordination polymers by molecular mass using conventional methods like osmometry, viscometry etc. These co-ordination polymers do not melt up to 360°C.

On the basis of the proposed structure shown in Scheme-1, the molecular formula of the CMHQ ligand is $C_{21}H_{17}N_3O_5$, which, upon chelation coordinates with two central metal atom at four co-ordination sites and two water molecules. Therefore, the general molecular formula of the resulting co-ordination polymer is given by $[M(CMHQ).2H_2O]$ as shown in Scheme-1. This has been confirmed by the results of elemental analyses of all of the five co-ordination polymers and their parent ligand. The data of elemental analyses reported in Table I are in agreement with the calculated values of C , H and N based on the above mentioned molecular formula of the parent ligand as well as co-ordination polymers. Examination of data of the metal content in each polymer (Table 1) revealed a 1:1 metal:ligand (M/L) stoichiometry in all of the co-ordination polymers. Comparison of the IR spectrum of the ligand CMHQ and those of the co-ordination polymers reveals certain characteristic differences. The broad band at 3400-3100 cm^{-1} for CMHQ has almost disappeared for the spectra of polymers. However, the weak bands around 3200 cm^{-1} in the spectra of CMHQ-Co^{2+}, CMHQ-Ni^{2+}, CMHQ-Mn^{2+} indicate the presence of water molecules which may have been strongly absorbed by the polymer sample. The weak band around 1110 cm^{-1} is attributed to the C-O-M stretching frequency [18].The band at 1430 cm^{-1} in the IR spectrum of CMHQ is attributed to the in-plane OH deformation [18]. 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 co-ordination polymer.

The value of the degree of polymerization of all the co-ordination polymers listed in Table-1 suggest that the average Dp for all the polymers in a range of 5 to 6.Magnetic moments (μ_{eff}) of polymeric chelate are given in Table-1.

The diffusion electronic spectrum of CMHQ-Cu^{2+} co-ordination polymers shows two broad bands around 15,392 cm^{-1} and 22,744 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 CMHQ-Co^{2+} polymers. The higher value of μ_{eff} of the CMHQ-Cu^{2+} polymer support this view [19]. The CMHQ-Ni^{2+} and CMHQ-Co^{2+} polymers give two absorption bands respectively at 17,250 and 24,000 cm^{-1} and at 17,248and 23746 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 CMHQ-Ni^{2+} and CMHQ-Co^{2+} polymers [20].The spectrum of [MnCMHQ $(H_2O)_2$] show weak bands at 16,480, 17,697 and 23,168 cm^{-1} assigned to the transitions $6_{A1g} \rightarrow 4_{T1g}(4G)$, $6_{A1g} \rightarrow {}_{4T2g}(4G)$ and $6_{A1g} \rightarrow 4_{A1g}, 4_{Eg}$ respectively, suggesting an octahedral structure for the [MnCMHQ $(H_2O)_2$] polymer. As the spectrum of the [ZnCMHQ $(H_2O)_2$] polymer is not well resolved, it is not interpreted, but its μ_{eff} value shows that it is diamagnetic as expected.

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 CMHQ-Co2+,CMHQ-Mn2+ and CMHQ-Ni2+ samples revealed that these samples suffered appreciable weight loss in the range 150 to 280oC. 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:

Cu < Ni < Co < Mn

This trend also coincides with the stability order already reported for the metal oxinates [19] and for co-ordination polymers of CMHQ [3].

The antimicrobial activity of CMHQ and its co-ordination 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 % age of bacteria or fungus is inhibited in the range of 55 to 82% depending upon the biospecies and co-ordination polymers.

Conclusion

The research described in the present article revels the following conclusion:

Polycondensation of 5-(4-phenyl carbonyl methyl amino) 8-hydroxyquinoline (PHQ) with melic anhydride in the presence of a base catalysed yielded a novel 4-(4-(2-(8-hydroxyquinolin-5-ylamino)acetyl)phenylamino)-4-oxobut-2-enoic acid(CMHQ) polymeric ligand. The applicability of the polymeric ligand was explored by preparing polymeric chelates using different divalent metal ion indicating that the CMHQ polymeric ligand has good chelating property and high thermal stability.

Further, the polymeric ligand is thermally more stable than its polymeric chelates. Among the five polymeric chelates, M-CMHQ chelate is least stable, whereas M-CMHQ polymeric chelates is the most stable having a thermal stability comparable to that of chelates may be used as heat resistant material up to 350oC. The polymeric ligand follows a two steps thermal degradation whereas polymeric chelates follow a single step thermal degradation.

A comparison of the thermal stability of the present polymeric chelates with those of 5-(4-phenyl carbonyl methyl amino) 8-hydroxyquinoline (PHQ) with melic anhydride as a pendent groups of polymeric chelates revels that the CMHQ polymeric chelates are thermally more stable. Finally, the maganetic susceptibility results indicate that polymeric chelates of Cu+2, Ni+2 and Co+2 are paramagnetic, whereas that of Zn+2 is diamagnetic in nature. All the polymers have good microbicidal activity.

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TABLE 1. Analytical and spectral data of the co-ordination polymers of CMHQ (h_2l)

Ligand/ Co-ordination polymers	Empirical Formula	Formula Weight	Analyses %Found(Calculated)				$\mu_{eff.}$ (B.M.)	$(\overline{Mn}) \pm 60$	$\overline{Dp}$
			%M	%C	%H	%N			
H_2L	$C_{21}H_{17}N_3O_5$	391	-	64.4 (64.45)	4.3 (4.38)	10.7 (10.74)	-	-	-
$[Cu(CMHQ)(H_2O)_2]_n$	$Cu.C_{21}H_{15}N_3O_5.2H_2O$	488.54	12.9 (13.00)	51.5 (51.58)	3.8 (3.88)	8.5 (8.59)	2.03	2512	5
$[Co(CMHQ)(H_2O)_2]_n$	$Co.C_{21}H_{15}N_3O_5.2H_2O$	483.94	12.1 (12.17)	52.1 (52.11)	3.9 (3.92)	8.6 (8.67)	2.92	2490	5
$[Ni(CMHQ)(H_2O)_2]_n$	$Ni.C_{21}H_{15}N_3O_5.2H_2O$	483.71	12.1 (12.13)	52.0 (52.09)	3.9 (3.92)	8.6 (8.68)	4.04	2976	6
$[Mn(CMHQ)(H_2O)_2]_n$	$Mn.C_{21}H_{15}N_3O_5.2H_2O$	479.94	11.4 (11.44)	52.4 (52.50)	3.9 (3.95)	8.7 (8.75)	4.87	2468	5
$[Zn(CMHQ)(H_2O)_2]_n$	$Zn.C_{21}H_{15}N_3O_5.2H_2O$	490.38	13.3 (13.33)	51.3 (51.38)	3.8 (3.87)	8.5 (8.56)	Diamagnetic	3012	6

Table 2. Thermo gravimetric analysis co-ordination polymers of CMHQ

Ligand/ Co-ordination polymers	% weight loss at temperature T(^0C)					
	100	200	400	500	600	700
H_2L	-	5.5	10.4	40.7	45.9	48.4
$[CuL(H_2O)_2]_n$	2.8	5.2	13.3	42.8	48.2	53.5
$[CoL(H_2O)_2]_n$	4.9	8.9	16.8	22.1	43.7	59.6
$[NiL(H_2O)_2]_n$	4.8	8.8	15.4	26.9	45.6	59.5
$[MnL(H_2O)_2]_n$	5.1	6.9	9.5	15.7	24.9	36.5
$[ZnL(H_2O)_2]_n$	2.3	3.6	4.9	15.5	23.7	35.6

Table 3. Antibacterial activity of co-ordination polymers

Compounds	Zone of Inhibition			
	Gram +Ve		Gram –Ve	
	Bacillus subtilis	*Staphylococcus aureus*	*Salmonella typhi*	*E.coli*
$[CuL(H_2O)_2]_n$	59	66	65	65
$[CoL(H_2O)_2]_n$	61	70	59	65
$[NiL(H_2O)_2]_n$	62	66	70	79
$[MnL(H_2O)_2]_n$	60	67	81	82
$[ZnL(H_2O)_2]_n$	63	61	72	62

Table 4. Antifungal activity of co-ordination polymers

Compounds	Zone of Inhibition at 1000 ppm (%)			
	Penicillium Expansum	*Nigrospora Sp.*	*Trichothesium Sp.*	*Rhizopus Nigricum*
$[CuL(H_2O)_2]_n$	71	69	55	52
$[CoL(H_2O)_2]_n$	62	63	58	69
$[NiL(H_2O)_2]_n$	70	75	64	66
$[MnL(H_2O)_2]_n$	69	63	79	71
$[ZnL(H_2O)_2]_n$	55	69	64	68