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Co-ordination polymers of 7,7′-[1,4-N,N′-dimethylene piperazinylene]-8-quinolinol (DMPQ)

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Abstract

Attempts have been made to synthesize co-ordination polymers of a new bis oxine bidentate ligand, namely 7,7′-[1,4-N,N′-dimethylene piperazinylene]-8-quinolinol (DMPQ) with different metal ions. The bis bidentate ligand DMPQ polymer is synthesized by a Mannich base reaction of oxine with formaldehyde and piperazine dihydrochloride in the presence of acid catalyst. The co-ordination polymers of DMPQ with different metal ions like Cu^{+2}, Zn^{+2}, Co^{+2}, Mg^{+2}, Mn^{+2} and Cd^{+2} were prepared and characterized by their elemental analysis, IR spectral and magnetic moment studies. The metal content in all the polymers was found to be consistent with (1:1) metal:ligand stoichiometry. The thermal behaviour of each of these co-ordination polymers has been examined by TGA in air up to 600°C temperature.

1. Introduction

Oxine (8-quinolinol, 8-HQ) is considered a good metal precipitant and analytical reagent. Oxine-based polymers containing methylene bridge are also well known for their excellent chelating and ion exchange properties due to the strong tendency of oxine to form chelate [1–5]. Further, several attempts have been made to enhance the chelation property of oxine through formation of co-ordination polymers using bis oxine bidentate ligands [6–8] by simple polymerization reaction or by condensation reaction, one of the areas in which the formation of metal complexes from Mannich base derivatives of oxine has been reported in literature [9]. However, the way in which the formation of bis oxine bidentate polymers occurs through Mannich base reaction (Scheme 1) has not been investigated so far. Hence it was considered interesting to synthesize a novel Mannich base polymer containing bis oxine ligand with various divalent metal ions. Thus, the present paper comprises the synthesis of bis oxine bidentate ligand, namely bis(8-hydroxy-5-quinolyl methylene) piperazine (DMPQ) by Mannich base condensation of 8-hydroxy quinoline (oxine) with formaldehyde and piperazine dihydrochloride in presence of acid catalyst.

Co-ordination polymer of this novel DMPQ were prepared with different divalent metal ions and characterized for their metal:ligand stoichiometry, magnetic moment and thermal stability. The entire work accomplished is shown in Scheme 1.

2. Experimental

Piperazine, oxine (8-quinolinol), formaldehyde and ethanol were of LR grade and used without purification.

2.1. Preparation of piperazine dihydrochloride

Piperazine dihydrochloride was prepared by adding concentrated hydrochloric acid (120 mM) dropwise to an alcoholic solution of piperazine (60 mM). Upon cooling the fine precipitates of dihydrochloride formed were filtered and washed with alcohol. It is yellow coloured product.

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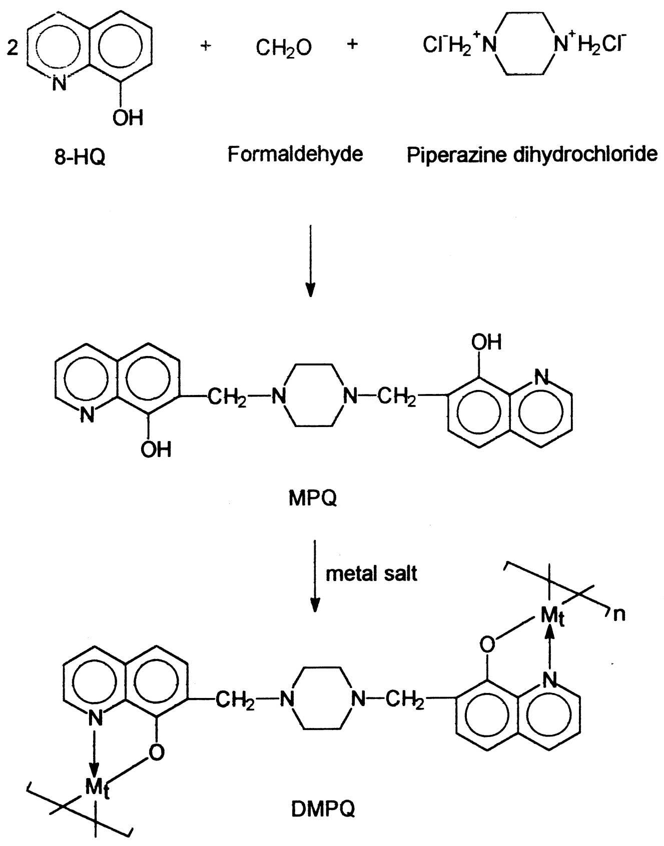

Scheme 1.

2.2. Synthesis of Mannich base DMPQ

This was prepared according to the method reported for Mannich base of phenol [10]. The oxine (60 mM), paraformaldehyde (60 mM) and piperazine dihydrochloride (30 mM) in 40 ml ethanol and 0.5 ml hydrochloric acid was refluxed at 110–120°C for 6 h. The resulting reaction mixture was cooled and washed with ether and large amount of boiling water. It was then neutralized with 10% aqueous sodium hydroxide solution. The solid buff-coloured product was filtered, washed with water and dried in air. The yield was 84%.

2.3. Preparation of co-ordination polymers

2.3.1. Co-ordination polymer of DMPQ with Cu(II):DMPQ–Cu^{2+}

To a warm and clear solution of DMPQ (2.55 g, 0.01 M) in 20% aqueous formic acid was added a solution of cupric nitrate (2.43 g, 0.01 M) in 50% aqueous formic acid with constant stirring. After completion of the addition of the metal ion solution it was adjusted to pH 5 with liquor ammonia and digested on a water bath for 1 h at 60–70°C temperature. The separated solid was filtered, washed with water followed by alcohol and dried at 100°C for about 24 h.

A similar procedure was followed to prepare other co-ordination polymers such as DMPQ-Zn^{2+}, DMPQ-Cd^{2+}, DMPQ-Co^{2+}, DMPQ-Mg^{2+} and DMPQ-Mn^{2+}.

2.4. Apparatus and methods of characterization

The carbon, hydrogen and nitrogen contents of DMPQ and its co-ordination polymers were determined on a C, H and N elemental analyzer. The metal content of co-ordination polymer was determined by decomposition of a weighed amount of the polymer followed by EDTA titration following standard procedures [11].

IR spectra of parent Mannich base DMPQ and each of the co-ordination polymers were scanned in KBr on a Perkin–Elmer spectrophotometer.

Measurements of magnetic susceptibility and electrical conductivity of all the co-ordination polymers were carried out by Gouy method and Millan megohmmeter, respectively. Mercury tetrathiocyanato cobaltate

(II), Hg[Co(CNS)$_4$], was used for calibration for the measurement of magnetic susceptibility.

Thermal behaviour of both parent Mannich base polymer DMPQ and its co-ordination polymers was investigated by conducting thermogravimetric analysis (TGA). TGA was carried out in a slow stream of air at 10°C/min heating rate. A Dupont thermogravimetric analyzer (TC-10ATA-3000) was used for TGA.

3. Results and discussion

Mannich base synthesis of DMPQ has not been reported earlier. However perusal of literature has revealed the applications of the Mannich base reaction to phenolic compounds like *p*-cresol and 8-hydroxy quinoline [12, 13]. On the basis of these reports the synthesis of ligand DMPQ was carried out with slight modification of reaction conditions. The bidentate DMPQ thus obtained is in the form of an amorphous buff-colour powder. It is insoluble in common organic solvents except formic acid. It is not melted up to 300°C temperature.

Results of C, H and N analysis of DMPQ are consistent with the predicted structure shown in Scheme 1. The IR spectrum of DMPQ is shown in Fig. 1. It shows characteristic vibrational frequencies due to 8-hydroxy quinoline moiety, methylene bridge and absence of N—H stretching frequency for the secondary amino group of piperazine. The important IR spectral features are a broad band in the region of 3300–3420 cm^{-1} corresponding to O—H stretching vibration of 8-hydroxy quinoline of Mannich base ligand DMPQ [6]. The weak band at 2960 cm^{-1} may be due to aliphatic stretching vibrations of bridge methylene group (—CH$_2$—) of 8-hydroxy quinoline and piperazine moieties. The bands around 1600, 1540, 1520 and 1460 cm^{-1} are attributed to the 8-hydroxy quinoline nucleus [14]. Lastly the absence of N—H stretching frequency for secondary amine, piperazine in the region of 3200–3600 cm^{-1} indicates the bond formation between N—H of piperazine and (—CH$_2$—) methylene bridge group, yielding the required Mannich base. In addition to this evidence, the structure of proposed DMPQ was confirmed by alkaline oxidation of DMPQ. Alkaline oxidation with potassium permanganate yielded 8-hydroxy quinoline-7-carboxylic acid due to the oxidation of methylene (—CH$_2$—) bridge of 8-hydroxy quinoline and piperazine. Formation of carboxylic acid derivative of 8-hydroxy quinoline was further confirmed by its m.p. (decomposed at 240°C) [15], chemical tests for —COOH group and IR spectral studies. Two main features of the IR spectrum of this acid are the presence of a small but strong peak at 1670 cm^{-1} due to an aromatic —COOH group, and the absence of a strong peak at 2960 cm^{-1} due to oxidation of the (—CH$_2$—) group to a —COOH group [16]. Thus all the above-mentioned features of the IR spectrum of DMPQ confirm the proposed structure of DMPQ.

The ability of bidentate DMPQ ligand to form co-ordination polymers was examined by preparing its co-ordination polymer with different divalent metal ions such as Cu^{+2}, Zn^{+2}, Cd^{+2}, Mn^{+2}, Mg^{+2} and Co^{+2}. These co-ordination polymers vary in colour from off-white to dark brown, as shown in Table 1, and are not softened up to 300°C upon heating. They are insoluble in common organic solvents and therefore it is not possible to characterize them by molecular mass using conventional methods like viscometry, osmometry etc. The metal content estimation of each of co-ordination polymer revealed 1:1 metal:ligand (M/L) stoichiometry.

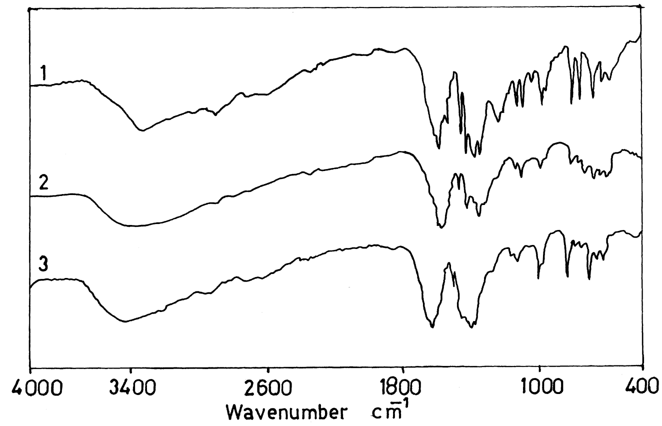

Fig. 1. IR spectra of DMPQ polymer and its metal chelates. (1) DMPQ polymer; (2) DMPQ-Cu(II) polymeric chelate; (3) DMPQ-Co(II) polymeric chelate.

Table 1
Characterization of DMPQs and their electrical properties and magnetic susceptibility

DMPQ and its metal chelates	Colour	Elemental analysis						Metal (%)		B.M. (μ_{eff})	Electrical conductivity at 35°C (Ω^{-1} cm^{-1})
		%C		%H		%N					
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found		
DMPQ	Buff	70.5	70.10	6.66	6.32	16.47	16.60	–	–	–	2.39×10^{-11}
DMPQ-Cu(II)	Green	63.0	63.10	5.60	5.25	14.70	14.70	11.11	11.00	1.80	3.55×10^{-11}
DMPQ-Cd(II)	Brown	57.83	57.50	5.46	5.75	13.49	13.55	18.06	18.00	Diamagnetic	1.35×10^{-11}
DMPQ-Mn(II)	Magenta	63.72	63.65	6.01	5.90	14.86	15.00	9.72	9.75	5.30	5.84×10^{-11}
DMPQ-Mg(II)	Off white	67.37	67.45	6.36	6.40	15.72	15.70	4.55	4.60	Diamagnetic	4.05×10^{-11}
DMPQ-Co(II)	Light green	63.27	63.15	5.97	6.00	14.76	14.72	10.35	10.30	4.18	5.20×10^{-11}
DMPQ-Zn(II)	Brown	62.56	62.75	5.90	6.10	14.59	14.60	11.36	11.30	Diamagnetic	5.90×10^{-11}

This is further supported by C, H, N contents in the polymers.

The IR spectra of selected co-ordination polymers are shown in Fig. 1. It is observed that they resemble each other in general shape while the comparison of IR spectra of parent DMPQ with its co-ordination polymers indicated certain characteristic differences.

One of the significant differences to be expected between IR spectra of parent polymer and its co-ordination polymers is the absence of broad band in the region of 3300–3420 cm^{-1} due to O—H stretching vibration frequency in the case of co-ordination polymers. This is because the oxygen of O—H group of parent polymeric ligand involves the co-ordination with metal ion. However in actual practice it has broadened more in the IR spectra of co-ordination polymers compared with parent polymer DMPQ. This is explained by the fact that water molecules might have strongly absorbed or co-ordinated to the polymer sample during the formation of co-ordination polymers. The other noticeable difference is the band in the IR spectrum of DMPQ due to C=N stretching at 1600 cm^{-1} shifted towards lower frequency. In addition to these the weak band around 1100 cm^{-1} is attributed to the C—O—M stretching frequency [14]. The band at 1430 cm^{-1} in the IR spectrum of DMPQ is assigned to in-plane OH deformation [14] and it is shifted towards higher frequency in the spectra of the co-ordination polymers, indicating the formation of a metal–oxygen bond. On the basis of the above-mentioned features the suggested structure of co-ordination polymer is shown in Scheme 1.

The thermal behaviour of the parent DMPQ polymer and its metal chelates is investigated by performing thermogravimetric analysis (TGA). The TGA data of all these samples are presented in Table 2. The weight loss of the polymer samples at different temperatures indicated that the degradation of the parent ligand is noticeable beyond 200°C and that of its co-ordination polymers is noticeable beyond 400°C. That rate of degradation becomes maximum at a temperature lying between 400–500°C and 500–600°C, respectively, for the parent ligand and its chelates. Each of the polymeric samples lost about 85% weight when heated up to 600°C. In addition to this the data of weight loss at different temperatures of all metal chelates of DMPQ revealed that all have similar mode of decomposition, indicating the thermal degradation of metal chelate is independent of the nature of the metal ion present in the polymeric ligand. Inspection of the thermograms of co-ordination polymers revealed that each of these samples decomposes very slowly initially up to 350°C compared with the parent ligand DMPQ, indicating that co-ordination polymers of DMPQ are more stable than the parent polymeric ligand. The

Table 2
Thermogravimetric analysis of DMPQ and its metal chelates

	Weight loss (%) at various temperatures (°C)						
DMPQ and its metal chelates	200	300	350	400	450	500	600
DMPQ	04.00	40.00	45.00	48.00	71.00	84.00	94.00
DMPQ-Mn(II)	04.00	09.00	22.00	35.00	40.00	49.00	86.00
DMPQ-Mg(II)	14.00	16.00	17.00	20.00	46.00	50.00	86.00
DMPQ-Cd(II)	16.00	10.00	15.00	32.00	45.00	60.00	85.00
DMPQ-Cu(II)	14.00	17.00	18.00	34.00	47.00	50.00	84.00
DMPQ-Zn(II)	08.00	11.50	20.00	37.00	52.00	56.60	81.00
DMPQ-Co(II)	07.00	11.00	19.00	37.00	51.00	56.00	80.00

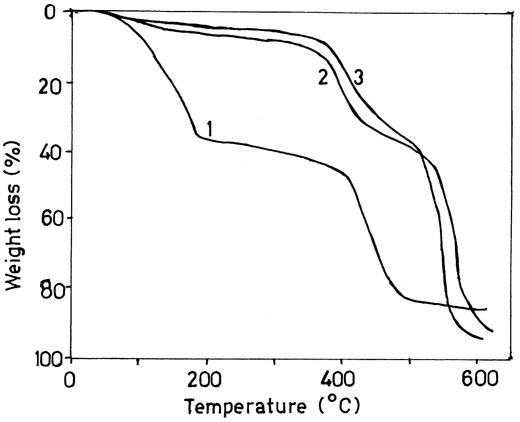

Fig. 2. Thermograms of DMPQ polymer and its metal chelates. (1) DMPQ polymer; (2) DMPQ-Cu(II) polymeric chelate; (3) DMPQ-Co(II) polymeric chelate.

thermograms of co-ordination polymers and the parent DMPQ are shown in Fig. 2.

The co-ordination polymers of DMPQ are further characterized in terms of their electrical and magnetic properties by measuring their electrical conductance and magnetic susceptibility. Examination of the data in Table 1 reveals electrical conductivity of co-ordination polymer in the range 1.35×10^{-9}–5.90×10^{-11}. The data of magnetic moment show that Cu(II), Mn(II) and Co(II) are paramagnetic, while Zn(II), Cd(II) and Mg(II) are diamagnetic.

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