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E-Journal of Chemistry
Vol 1, No. 3, pp 158-163, May 2004

Coordination Polymers of 4,4'-(8-Quinolinyloxy)-5-methylenoxy diphenyl sulfide

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Received 13 March 2004; Accepted 1 May 2004

Abstract Coordination polymers containing a novel bis(oxine) bidentate ligand, namely 4,4'[(8-Quinolinyloxy)-5-methylenoxy] diphenyl sulfide H_2L 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 4,4'-dihydroxy diphenyl sulfide in the presence of a base catalyst. 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 (M_n) 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

Key words: Coordination polymers, bis(oxine) bidentate ligand 4,4'-(8-Quinolinyloxy) diphenyl sulfide., diffuse reflectance spectra,

Introduction

The coordination chemistry of bis(oxine), a bidentate ligand, has been extensively investigated for their chelating properties.¹⁻³ In this context bis(oxine) ligands with two oxine 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 $-CH_2-O-CH_2-$ are reported in literature.⁴⁻¹⁰ Recently we have reported^{11,12} the synthesis and characterization of coordination polymers based on the bis-oxine ligand joined with a bridges, $-H_2C-O-Ph-O-CH_2-$ (Ph = 1,3-phenylene) and $H_2CO-Ph-C(CH_3)_2-Ph-OCH_2$. This work has been further extended with the view of investigating the chelating ability of a *bis*-8-quinolinol *bis*(bidentate) ligand by introducing the bridge of 4,4' dihydroxy diphenyl sulfide between two 8-hydroxyquinoline moieties. Accordingly, the present work deals with the synthesis and characterization of a bis(oxine) ligand, namely 4,4'-(8-Quinolinyloxy)-5-Methylenoxy diphenyl sulfide. [H_2L] and its coordination polymers with Zn(II), Cu(II), Ni(II), Co(II) and Mn(II) metal ions.

Experimental

Materials

All chemicals were of analytical grade. The synthesis of 4,4'-(8-Quinolinyloxy-5-Methylenoxy) diphenyl sulfide (H_2L) was carried out in two steps. The preparation of 5-chloromethyl-8-hydroxyquinoline hydrochloride According to a literature method.¹²

Preparation of polymers of 4,4'-(8-Quinolinyloxy-5-Methylenoxy) diphenyl sulfide (QMDS)

QMDS (i.e. H_2L) was prepared using the method reported for 5-alkoxy methylene-8-quinoline.¹³ For example, to a suspension of 5-chloromethyl-8-hydroxyquinoline hydrochloride (23 g, 0.01 mol), 4,4'-dihydroxy diphenyl sulfide-A (17.5 g, 0.1 mol) in an acetone–water mixture was added. The resulting mixture was refluxed for 3 h with occasional shaking. The resulting suspension, which contained of a green precipitate, was made alkaline with dilute aqueous ammonia and then filtered. The solid product was collected and dried to give QMDS (70% yield). The product melted with decomposition at 220–222°C (uncorrected). Analysis for $C_{32}H_{24}S N_2 O_2$; Calculated (%): C, 76.8; H, 4.8; N, 5.6; Found: %C, 76.5; H, 4.5; N, 5.3; S;6.1.

Preparation of coordination polymers

For example, Cu (II): A solution of copper acetate (1.99 g, 0.01 mol) in aqueous formic acid (50 ml, 50%) was added dropwise to a solution of QMDS (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 0.5 h. The reaction mixture was made alkaline by the addition of dilute aqueous ammonia until the precipitation was completed. The polymer separated out in the form of a suspension and was digested on boiling water bath for about 1 h. Finally, the resultant solid brownish yellow was collected by filtration and washed with hot water, dimethylformamide (DMF) and then acetone. The polymer [QMDS-Cu(II)] was air-dried. A similar procedure was used to prepare the QMDS-Co(II), QMDS-Ni(II), QMDS-Mn(II), and QMDS-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 procedure.¹⁴ The percentage composition (C, H and N) for the coordination polymers was determined with a Carlo Erba C,H,N Elemental Analyzer (Table I). The IR spectra of the *bis*-ligand QMDS and of each of the coordination polymers samples were scanned as KBr pellets using a NICOLET – 900 DR FTIR spectrophotometer. The solid diffusion reflectance spectra of all the coordination polymers were recorded on a Beckman DU 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.^{15,16}

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 calibration.¹⁹ Molar susceptibilities were corrected for diamagnetism of the component atoms using Pascal's constant.¹⁹

Thermogravimetry of all these coordination polymers was carried out using a Dupont 950 Thermogravimetric Analyzer (TGA). The data are reported in Table III.

Results and Discussion

The synthesis of the *bis*(bidentate) ligand, 4,4'-(8-Quinolinyloxy-5-Methylenoxy) diphenyl sulfide (H_2L), has not been previously reported. The synthesis H_2L was performed by chloromethylation of the oxine followed by condensation with disodium salt 4,4'-dihydroxy diphenyl sulfide (Scheme I).

The IR spectrum of H_2L is shown in Fig. 1. The important IR spectral features are (i) a broad band from 3550 cm^{-1} to 3200 cm^{-1} that is attributed to the hydrogen bonded-OH group,¹⁸ (ii) the weak bands near 2950 cm^{-1} and 2800 cm^{-1} that are due to asymmetric and symmetric stretching vibrations of methylene groups (CH_2) of the $-CH_2-O-CH_2-$ bridge, (iii) the weak band at 1110 cm^{-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-hydroxyquinoline nucleus.¹⁸ The weak band around 1085 and

1118 cm^{-1} may also be attributed to the ether group bridge. It was also observed that H_2L has numerous IR spectral features in common with those of 5,5-methylene bis(8-hydroxyquinoline).¹ These features support the proposed structure of H_2L . The coordination polymers derived from H_2L are insoluble in common organic solvents. All these coordination polymers decomposed at approximately 250°C. 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 ($\bar{M}_n$) of coordination polymers.^{19,20} This may be due to the insolubility in common organic solvents and instability of coordination polymers in acidic or basic medium. However, efforts are made by the present authors to estimate $\bar{M}_n$ of the H_2L coordination polymers by utilizing the non-aqueous conductometric titration method under controlled experimental conditions.²³ 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 more volume of NaOMe may cause de-coordination of polymer of NaOMe. The addition of NaOMe did not (appear to) alter the properties of coordination polymer. A discernible break was observed in the titration curve and the molecular weights were calculated as shown in Table I. Examination of the metal content in the polymers (Table I) reveals a 1:1 metal : ligand (M/L) stoichiometry for all the polymers.

Table I Analytical data for co-ordination polymer of QMDS.

Co-ordination polymers	Colour	Elemental Analysis				μ^{eff}	$\overline{\text{Mn}}$
		N%		M%			
		Calc	Found	Calc	Found		
QMDS – Cu ⁺²	Dark green	5.2	5.1	11.31	11.16	1.98	5331
QMDS – Ni ⁺²	Green	5.2	5.1	10.54	10.39	3.37	5890
QMDS – Co ⁺²	Brown	5.2	5.1	10.58	10.43	4.56	5487
QMDS – Mn ⁺²	Brown	5.3	5.1	9.93	9.78	5.6	5850
QMDS – Zn ⁺²	Pale green	5.2	5.1	11.60	11.45	Diamagnetic	5347

The IR spectra of all the coordination polymers of H_2L are not shown. Comparison of the IR spectrum of the ligand H_2L (see above) and those of the coordination polymers reveal certain characteristic differences. Thus, the broad band in the region from 3550 to 3200 cm^{-1} for H_2L is absent in the spectra of the polymers. This is consistent with the involvement of -OH groups in a coordinate interaction with the polymers. However, the weak band near 3400 cm^{-1} in $\text{H}_2\text{L-Mn(II)}$ indicates that water molecules might be strongly absorbed by the polymer sample. This point will be discussed later. The band in H_2L 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 frequency.¹⁷ The band at 1430 cm^{-1} in QMDS is assigned to the in-plane OH deformation.¹⁷ This band is shifted toward higher frequency (1468 cm^{-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 I. The diffuse electronic spectrum of QMDS-Cu(II) coordination polymer shows two broad bands near 15,625 cm^{-1} and 22,222 cm^{-1} . The first band may be due to $2\text{T}_{\text{g}} \rightarrow 2\text{E}_{\text{g}}$ transition while the second may be due to charge transfer. The first band shows some structural characteristics that suggest a distorted octahedral geometry. The higher theoretical value of μ_{eff} of the QMDS-Cu(II) polymer supports this view. The QMDS-Ni(II) and QMDS-Co(II) polymers exhibit two absorption bands at 16,000 and 23,809 cm^{-1} , respectively. These bands are assigned to the $4\text{T}_{\text{1g}} \rightarrow 2\text{T}_{\text{2g}}$, $4\text{T}_{\text{1g}} \rightarrow 2\text{T}_{\text{2g}}$ (P) transitions, respectively.²³ Both the absorption bands and the values of μ_{eff} are consistent with an octahedral structure for QMDS-Ni(II) and QMDS-Co(II). Since the spectra of QMDS-Mn(II) and QMDS-Zn(II) were not well resolved, no analysis was attempted.

As expected the QMDS-Zn(II) polymer is diamagnetic and the QMDS-Mn(II) polymer has a value of μ_{eff} lower than required for a spin value only state.

The TGA thermograms of the polymers are shown in Fig. 4 and the data are summarized in Table II. The coordination polymers are as thermally stable as *bis*(8-hydroxy-5-quinolymethylene) sulfide (BHQs) and 5,5'-methylene *bis*(oxine) (MBQ).^{1,3} The decomposition of the Cu(II) polymer occurred at a lower temperature ~100°C than the other coordination polymers, ~125°C. The lower thermal stability of the copper-containing polymer may be due to oxidation by the catalytic action of Cu(II) ion as suggested by .¹⁴ The relative order of thermal stability of the coordination polymers is Cu < Co < Ni < Mn.

Table II Reflectance spectral and magnetic moment data of the QMDS co-ordination polymers

Coordination polymers	Absorption band (cm ⁻¹)	Transitions	Magnetic moment (μ_{eff}) BM
Cu-QMDS	22,221	Charge transfer	1.98
	15,626	${}^2T_g \rightarrow {}^2E_g$	
Ni-QMDS	23,810	${}^4T_{1g} \rightarrow {}^2T_{2g}(\text{P})$	3.37
	16,008	${}^4T_{1g} \rightarrow {}^2T_{2g}$	
Co-QMDS	23,805	${}^4T_{1g} \rightarrow {}^2T_{2g}(\text{P})$	4.56
	16,001	${}^4T_{1g} \rightarrow {}^2T_{2g}$	

Zn-QMDS is Diamagnetic in nature.

Table II Infrared Frequencies (cm⁻¹) of QMDS ligand and its coordination polymers.

Bis ligands and their coordination polymers	V(O-H)	V(C-N)	V(C-O-C)	V(C-O)	V(M-N)	V(M-O)
QMDS	3341(S)	1588(S)	1115(S)	1380(S)	----	----
Zn-QMDS	3448-3338(br)	1600(S)	1198(S)	1412(S)	794(W)	500(m)
Cu-QMDS	3520-3300(br)	1600(S)	1100(S)	1362(S)	762(W)	500(m)
Ni-QMDS	3448-3342(br)	1573(S)	1111(S)	1392(S)	769(W)	482(m)
Co-QMDS	3492-3350(br)	1582(S)	1100(S)	1373(S)	762(W)	482(m)
Mn-QMDS	3450-3382(br)	1581(S)	1100(S)	1373(S)	789(W)	478(m)

Table III Thermogravimetric Analysis (TGA) of the co-ordination polymer of QMDS

Co-ordination polymers	% weight loss at temperature T (°C)						
	100	150	175	200	250	300	350
QMDS – Cu ⁺²	3.3	5.0	10.1	70.00	90.00	91.00	--
QMDS – Ni ⁺²	3.0	8.1	8.1	9.0	85.00	90.00	--
QMDS – Co ⁺²	3.1	5.0	6.0	7.2	15.00	40.00	80.00
QMDS – Mn ⁺²	2.0	3.3	4.2	6.10	15.00	25.00	60.00
QMDS – Zn ⁺²	2.1	4.2	5.1	6.5	15.10	30.00	60.00

Scheme - II*Acknowledgement*

We are thankful to Dr. D. I Desai, Principal of V.P. & R.P.T.P. Science College, Vallabh Vidyanagar for providing research facilities.

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