



SYNTHESIS, SPECTRAL, THERMAL AND X-RAY STUDIES OF SOME Cd(II) AND Hg(II) CHELATE POLYMERS

CHAUDHARY R.G.^{1*}, JUNEJA H.D.² AND GHARPURE M.P.²

¹Department of Chemistry, Seth Kesarimal Porwal College Kamptee, MS, India.

²Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, MS, India.

*Corresponding Author: Email- chaudhary_rati@yahoo.com

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Abstract- The bis-ligands adipoyl 1, 6 bis (4-methoxyphenylcarbamide) (ABMPC), azeloyl 1, 9 bis (4-methoxyphenylcarbamide) (AZBMPC) and sebacoyl 1, 10 bis (4-methoxyphenylcarbamide) (SBMPC) were synthesized and structurally elucidated on the basis of elemental analysis, IR, ¹H NMR and UV visible studies. Six chelate polymers of Cd(II) and Hg(II) with above three bis ligands have been prepared and were characterized by elemental analysis, FTIR, ¹H NMR, X-RD and TGA. On the basis of instrumental technique, the geometry of these chelate polymers has been reported.

Keywords- Chelate polymers, FTIR, TGA, IR, bis-ligand, spectral studies.

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Introduction

Research in the field of metal coordination polymers have attracted attention due to the promise of generating material with specific physical properties based on the chosen building blocks [1]. Such inorganic metal polymers provide an opportunity for expansion of fundamental knowledge, development of new material assisting in the advancement of technology and stimulating the thought of what might if organic and inorganic chemistry are combined in polymer science [2]. One of the most important thermally stable compounds in branch of organometallic chemistry is chelate compound; such chelate complexes having amide moieties are also interested to understand the role of metalloproteins in the control of cell metabolism [3]. Over the past few decades, great efforts have been made for the synthesis and investigation of new thermally stable chelate polymers. This applies especially to molecular bond magnetic compounds due to their impressive structural diversity and intriguing physical properties, as well as interesting magnets structural correlation. One of the major challenges is rational design of their compounds [4]. However, the studies of group 12 metal complexes carbamides give considerable attention because of various industrial and biological importances

[5]. These types of metal compounds are various and have been focus for their valuable properties in the field of electronic and optical applications [6]. However, various chelate polymers can be used as sensor, catalyst and adsorbent [7].

In the present work we have reported the synthesis of bis-ligands and their metal chelate polymers with Cd(II) and Hg(II). The newly synthesized polymers were characterized on the basis of elemental analyses, FTIR, ¹H NMR, thermogravimetric analysis and X-ray diffraction studies. The newly synthesized chelate polymers were insoluble in almost all organic solvents and have high thermal stability.

Experimental

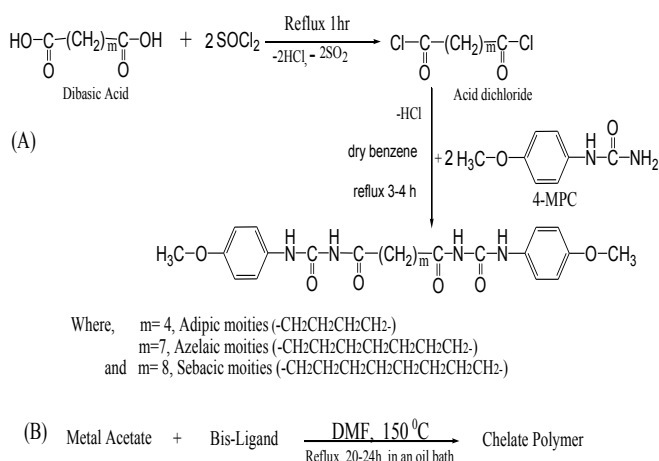
Materials and method

All the chemicals used for the synthesis of bis ligands and their metal chelate polymers were of analytical grade. The solvents were double distilled before used. The Bruker Advance Model II 400 MHz NMR spectrometer was used to measure the ¹H NMR spectra of bis-ligands. IR spectra were recorded on SHIMADZU Spectrophotometer FTIR-8101A. UV- visible spectra were carried out on SHIMADZU Double Beam UV-Vis Spectrophotometer. The

TGA were carried out at Perkin Elmer SII, Diamond TG/DTA. X-ray diffraction data was recorded on PAN Analytical X'pert PRO, Diffractometer. 4-methoxyphenylcarbamide (4-MPC) was prepared standard procedure "Scheme (1A)". The product was pale brownish in colour; m. p. 168 °C. The three aliphatic dibasic acids were converted into dichloride. These dichloride were prepared [8] by standard procedure "Scheme (1A)".

Synthesis of bis-ligands

The syntheses of bis-ligands were carried out by condensation method [9]. These bis-ligands were synthesized by the condensation reaction of acid dichloride (0.1 mmols) and 4-methoxyphenylcarbamide (0.2 mmols) in benzene medium "Scheme (1A)". The solution of acid dichloride were mixed dropwise into the solution of 4-methoxyphenylcarbamide with rigorously stirring. The reaction mixtures were transferred into 250 ml round bottom flask and were reflux for 3-4 h. The granular pale brown sticky solid products were obtained and were triturated with absolute alcohol and then washed with hot ethanol to remove the unreacted 4-methoxyphenylcarbamide. The yield obtained about 72-85%. The newly synthesized bis ligands were crystallized by ethanol: dimethylformamide mixture. Their elemental data have been given in "Table (1)". The obtained products were found to be soluble in organic solvents such as dimethylformamide, dimethylsulfoxide, m. p. 176 °C - 211 °C.



Scheme 1- Synthetic procedure for (A) Bis-ligands and (B) chelate polymers

Synthesis of chelate polymers

The six chelate polymers of Cadmium (II) and Mercury (II) were synthesized by dissolving metal acetate (0.01 mmols) and bis-ligands (0.01 mmols) separately in 50 ml hot dimethylformamide "Scheme (1B)".

Table 1- Elemental analysis of ligand and their chelate polymer

ligands/polymer	C%F(Cal)	H%F(Cal)	N%F(Cal)	M%F(Cal)
ABMPC	59.7(59.7)	5.86(5.8)	12.20(12.)	----
AZBMPC	62.5(62.6)	6.79(6.8)	11.20(11.)	----
SBMPC	62.6(62.8)	5.60(5.5)	9.10(9.14)	----
Cd (II) ABMPC	45.7(46.2)	4.59(4.6)	9.77(9.81)	18.1(19.4)
Hg (II) ABMPC	39.7(39.7)	3.90(3.9)	8.41(8.50)	28.2(30.4)
Cd (II) AZBMPC	48.7(48.7)	5.61(5.5)	9.10(9.14)	18.1(18.3)
Hg (II) AZBMPC	42.8(42.8)	4.59(4.6)	7.87(7.90)	28.4(28.6)
Cd (II) SBMPC	49.9(49.8)	5.70(5.4)	8.92(8.94)	17.8(17.9)
Hg (II) SBMPC	43.8(43.7)	4.97(5.0)	7.86(7.83)	27.8(28.0)

The solutions of metal acetate and bis-ligands were filtered and mixed in hot condition and, it was refluxed in an oil bath for 20-24 h. The temperature of reaction mixture was maintained 150 °C. The products obtained were filtered, washed thoroughly with hot dimethylformamide and alcohol to remove the unreacted reactants, if any. Finally, the polymers were dried. The chelate polymers were insoluble in almost all organic solvents [10]. The elemental data are given in "Table (1)".

RESULTS AND DISCUSSION

The bis-ligands were synthesized "Scheme (1A)" and characterised by elemental analyses, infrared, ¹H NMR and UV-Visible studies. These ligands were soluble in dimethylformamide. The presences of water of crystallization were determined on the basis of elemental analysis, thermal and infrared spectroscopy. The frameworks of chelate polymers "Fig. (2)" were deduced on the basis of elemental analyses "Table (1)", UV-Visible, FTIR, ¹H NMR, thermal and x-ray diffraction studies.

Spectroscopic analysis

The spectra of three bis-ligands have two main peaks at range of 264-266 nm and 294-300 nm and is attributed to π-π* and n-π* transition, for aromatic benzene ring this transition is shifted to lower wavelength with high intensity. This shift is indicated the donation of extra lone pair of electron of nitrogen in bis-ligand to central metal atom [11].

In the present investigation, the infrared spectra of bis-ligands exhibit sharp bands [12-13] in region of range 3245-3315 cm⁻¹ which may be due to the stretching vibration of the N-H group. A broad stretching frequency in metal chelate polymers at 3310-3410 cm⁻¹ may be due to of merging of N-H group and H₂O group [14]. A strong band observed in bis ligands around 1491-1542 cm⁻¹ which may be attributed to the C=C group stretching frequency, it supports the presence of aromatic ring [15, 16] and is also present in metal chelate polymers. The bis-ligand shows sharp band at 1667-1681 cm⁻¹ region which may be assigned to the stretching frequency of C=O vibration in -CONH₂ group [17]. The sharp band appeared at 2926-2932 cm⁻¹ may be due to the stretching frequency of -CH₂ group [13, 5]. It has been found that ABMPC, AZBMPC and SBMPC were undergoes keto-enol tautomerism during polymerization. As result of enolisation the C=O bond disappeared due to the formation of the C=N bond it has been confirmed by appearance of new band around at 1495-1580 cm⁻¹. The disappearance of -OH bond in chelate polymers indicates the formation of M-O bond through the oxygen of -OH group with the release of the proton, [18] and it is confirmed by the appearance of new weak band at 612 cm⁻¹ and 611 cm⁻¹ in metal chelate polymers of [Cd(II) ABMPC] and [Hg(II)ABMPC] while the M-N bond formation is confirmed by the presence of band at 493 cm⁻¹ and 502 cm⁻¹ in chelate polymers of [Cd(II) ABMPC] and [Hg(II) ABMPC] "Figure (1)" respectively. The broad band of free H-OH stretching vibration is exhibited at 3445-3510 cm⁻¹ due to presence of lattice water molecule [19]. Similarly M-O bond formation is confirmed by the appearance of weak band at 603 cm⁻¹ and 655 cm⁻¹ in chelate polymers of [Cd (II)AZBMPC] and [Hg(II) AZBMPC] while presence of weak band at 467 cm⁻¹ and 497 cm⁻¹ in chelate polymers of [Cd(II)AZBMPC] and [Hg(II) AZBMPC] may be assigned to the M-N bond respectively.

^1H NMR spectra of bis ligands were performed in deuterated dimethylsulfoxide (DMSO-d_6) solution using TMS as an internal reference. ^1H NMR signal of methylene proton shows multiplet for 8 H of methylene ($-\text{CH}_2$) of SBMPC at δ 1.4 - 2.5 ppm and methylene proton of AZBMPC shows multiplet for 7 H at δ 1.6-2.4 ppm, similarly ABMPC shows multiplet for 4 H at δ 1.8 -2.6 ppm. The signal of ABMPC, AZBMPC and SBMPC show singlet for 6 H at δ 3.6-4.2 ppm may be assigned to the methoxy proton ($-\text{CH}_3\text{O}$) [20] which is attached to the aromatic ring. The signal at range δ 5.2 - 5.8 ppm is observed due to singlet for 4H ($-\text{C-NH-}$) proton which may be due to the presence of amine group. ^1H NMR spectrums shows multiplet at δ 6.9 - 7.9 ppm which is due to the presence of aromatic protons (Ar-H) [13, 15]. These features confirmed the proposed structure of bis-ligands. Magnetic moment data depict the diamagnetic nature of chelate polymers due the paired electron in valence shell orbital, which in agreement with expected for tetrahedral geometry.

X-ray diffraction

X-ray diffractograms of chelate polymers have been, reported in the present work. In order to know the change in crystalline nature of bis-ligand on coordination with transition metal ions, X-ray diffraction pattern of bis-ligand and its chelate polymers have been examined. X-ray diffraction of bis-ligand shows amorphous in nature. X-ray analysis of Cd (II) chelate polymers were shown well defined sharp peaks whereas diffractogram of Hg (II) have weak peaks. The metal chelate polymers of Cd (II) are semicrystalline in nature, whereas Hg (II) polymers are amorphous.

Thermogravimetric analysis

The high thermal stabilities of chelate polymers due to their chelating effects are constantly required for various applications in various fields. The aromatic or heterocyclic rings as backbone in polymer chains are greatly enhance the thermal stability of metal chelate polymers. The examples of these heterocyclic compounds are imides, carbamides, imidazole and triazine etc. The thermal properties of chelate polymers also depend on the size of metals and nature of ligands. The various factors underlying the thermal stability of transition metals complexes are not well understood but generally stability follows the order $\text{Co} > \text{Ni} > \text{Cu}$ which inverse of Irving Williams series [21]. In general the water of hydration may be considered either crystal water or lattice water. In present work all the bis-ligands are carbamide and these are thermally stable having melting point at range of 176-211 $^\circ\text{C}$. The newly synthesized metal chelate polymers were found to be highly thermally stable as compare to its bis-ligands. Thermogram of all the metal chelate polymers shows two steps decomposition profile. The data clearly supports the proposed structure of metal chelate polymers. The thermograph $\{[\text{Cd}(\text{II})\text{ABMPC}]\text{H}_2\text{O}\}_n$ "Fig. (1)", $\{[\text{Cd}(\text{II})\text{AZBMPC}]\text{H}_2\text{O}\}_n$ and $\{[\text{Cd}(\text{II})\text{SBMPC}]\text{H}_2\text{O}\}_n$ were decomposed at two step at heating rate 5 $^\circ\text{C min}^{-1}$. At 120 $^\circ\text{C}$ -152 $^\circ\text{C}$ correspond to 2.80 % weight loss due to one molecule of crystal of water, it is also confirmed by elemental analyses and FTIR spectral broad band appeared at range of 3500-3332 cm^{-1} which may be due to merging of N-H group and H-OH lattice water. After 152 $^\circ\text{C}$ -280 $^\circ\text{C}$ no loss in weight was observed due to absence of water of coordination. Gradual decomposition with a rapid weight loss was occurred in the temperature range 280 $^\circ\text{C}$ to 585 $^\circ\text{C}$ correspond to 78.77 %. After 585 $^\circ\text{C}$ the decomposing stop and no loss in weight

was observed may be due to formation of metal oxide. The decomposition temperature of $\{[\text{Cd}(\text{II})\text{ABMPC}]\text{H}_2\text{O}\}_n$, $\{[\text{Cd}(\text{II})\text{AZBMPC}]\text{H}_2\text{O}\}_n$ and $\{[\text{Cd}(\text{II})\text{SBMPC}]\text{H}_2\text{O}\}_n$ are found to be 399 $^\circ\text{C}$, 450 $^\circ\text{C}$ and 455 $^\circ\text{C}$ respectively.

Thermogram of $\{[\text{Hg}(\text{II})\text{ABMPC}]\text{H}_2\text{O}\}_n$, $\{[\text{Hg}(\text{II})\text{AZBMPC}]\text{H}_2\text{O}\}_n$ and $\{[\text{Hg}(\text{II})\text{SBMPC}]\text{H}_2\text{O}\}_n$ also decomposed at two step. At 90 $^\circ\text{C}$ - 150 $^\circ\text{C}$ correspond to 2.73 % (ABMPC), 2.56 % (AZBMPC) and 2.52 % (SBMPC) due to loss of one molecule of crystal of water which is also confirm by elemental analyses and FTIR spectra. But no weight losses were observed up to 252 $^\circ\text{C}$, may be due to absence of water of coordination. At 264 $^\circ\text{C}$ to 515 $^\circ\text{C}$ correspond to 69.89 % weight loss due to gradual loss of mass of ABMPC and 70.08 % in case of AZBMPC. After 515 $^\circ\text{C}$ the degradation is terminate and no loss of weight is observed hence it indicates that the formation of stable metal oxide. The decomposition temperature of $\{[\text{Hg}(\text{II})\text{ABMPC}]\text{H}_2\text{O}\}_n$, $\{[\text{Hg}(\text{II})\text{AZBMPC}]\text{H}_2\text{O}\}_n$ and $\{[\text{Hg}(\text{II})\text{SBMPC}]\text{H}_2\text{O}\}_n$ chelate polymer were found to be 392 $^\circ\text{C}$, 345 $^\circ\text{C}$ and 349 $^\circ\text{C}$ at heating rate 5 $^\circ\text{C min}^{-1}$ respectively.

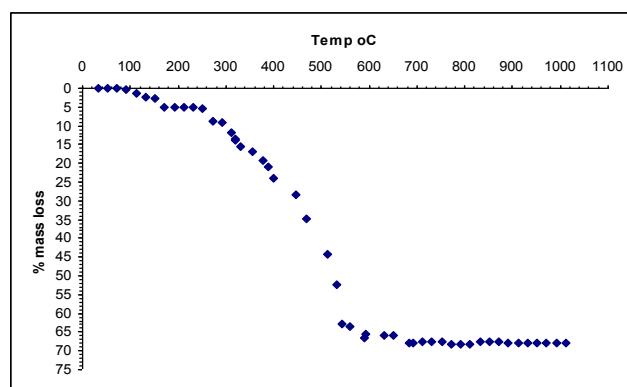


Fig. 1- Thermogram of $\{[\text{Cd}(\text{II})\text{ABMPC}]\text{H}_2\text{O}\}_n$ chelate polymers at 5 $^\circ\text{C min}^{-1}$

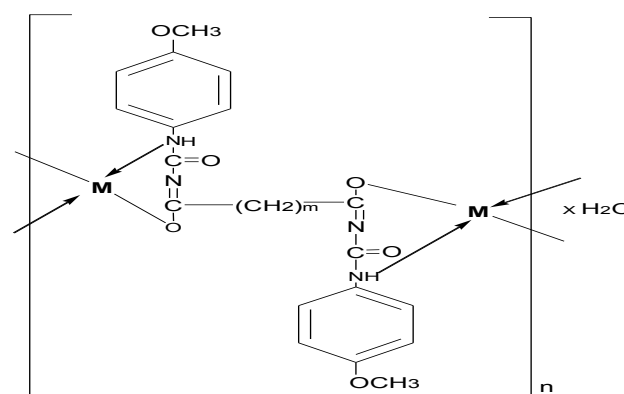


Fig. 2- Proposed structure of chelate polymers, where $m=4$ (ABMPC), 7(AZBMPC), 8(SBMPC); $M= \text{Cd}(\text{II}), \text{Hg}(\text{II})$; $x=1, \text{H}_2\text{O}$ = lattice of water

Conclusion

We have successfully synthesized and characterized six chelate polymers of cadmium and mercury with bis-ligands. The TGA data of polymer found high thermal stability; hence they can be used as high thermal stable materials. By performing the spectral and analytical data it has been observed that the ligand coordinated to

central metal atoms in tetradentate manner and thus probably suggested tetrahedral geometry for all chelate polymers. On the basis of C H N, TGA, FTIR, ¹H NMR and X-RD analysis, the proposed structure of chelate polymers has shown in "Fig. (2)".

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