PREPARATION AND CHARACTERIZATION OF HYDROXAMIC ACID BIS LIGAND AND THEIR CHELATE POLYMERS

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ABSTRACT

The bis–ligand was synthesized by condensation of acidic dichloride with bis tolyl hydroxamic acid in stoichiometric ration of 1:2. The recrystallized ligand was structurally elucidated on the basis of elemental analysis. IR, NMR and UV visible studies. Four metals chelate polymers were synthesized and characterized on the basis of elemental analyses, reflectance spectra and magnetic susceptibility data, FTIR, X-RD, SEM, TGA and DSC . The nature of bonding has been further discussed on the basis of infrared spectral data. The water of hydration as well as water of coordination has been ascertained on the basis of thermal analyses.

KEY WORDS: Azelaoyl bis-N-tolyl hydroxamic acid, chelate polymers, transition metal ions, thermal properties

INTRODUCTION

Chelate polymer has attention due to promise of generating material with specific properties based on chosen building blocks.Polymers are important materials for use in commodity products such as texties, tires, and packaging. Polymers, particularly thermosets, also have widespread use as composite materials in transportation, including automotive, marine, and aerospace. Most of these markets are now mature and future growth is expected to be small; however, there are many more application for polymers that may be less obvious but have great potential and offer challenges for new technology and growth into the twenty-first century. This communication describes the synthesis and characterization of chelate polymers of Mn(II), Co(II), Ni(II) and Zn(II) with azelaoyl bis-N-tolyl hydroxamic acid[1-6].

EXPERIMENTAL

Chemicals

All the chemicals used were AR grade. The solvents used were doubled distilled before used.

PREPARATION OF ACID DICHLORIDE FOR LIGAND PREPARATION

Azelaic acid (0.1M) and thionyl chloride (0.2M) was placed in a dry 250 ml round bottomed flask fitted with a perfectly dry Leibig water condenser with a guard tube containing calcium chloride. The mixture was heated on a water bath till a yellow clear liquid was obtained. An air condenser was then used and the mixture was heated to 70-80 ^{o}C for half an hour for complete evolution of HCl gas. Then the acid dichloride was distilled off under reduced pressure.

SYNTHESIS OF CHELATE POLYMERS

Chelate Polymers of ABTHA with Mn(II), Co(II), Ni(II) and Zn(II) were prepared by dissolving metal acetate (0.01M) separately in minimum amount of DMF were added to a solution of azelaoyl bis-N-tolyl hydroxamic acid, ABPHA ligand (0.01 M) in (25 ml) DMF. The reaction mixtures were then heated on an oil bath with constant stirring till the polymers separated as an insoluble solid, they were then digested on an oil bath for about 24 hrs at 120 ^{o}C to 160 ^{o}C . The chelate polymers generally appeared after 24-hrs heating in an oil bath. These chelate polymers were filtered, washed thoroughly first with hot DMF and then with absolute alcohol and dried. These newly synthesized chelate polymers were found to be insoluble in almost all organic solvents such as alcohol, acetone, chloroform, carbon tetrachloride, dimethyl formamide, dioxane, dimethyl sulphoxide etc. The purity of these chelate polymers were ascertained by repeated washing, as recrystallization was not possible.

The final products appeared as amorphous powder. The chelate polymers were all stable at room temperature.

RESULTS AND DISCUSSION

On the basis of elemental analyses, infrared spectra, reflectance spectra and thermal studies, the proposed structures of these chelate polymers have shown octahydral geometry. The presences of water of crystallization as well as water of coordination were ascertained on the basis of thermal studies [7-9]

INFRARED SPECTRAL STUDIES: -

Infrared spectra of the chelate polymers are practically identical ,The frequencies of some significant bands of the free ligand and of the metal polymer are reported in the Table 2. The free O-H stretching frequency appears at 3260 cm^{-1} in ABTHA ligand[15]. Sharp band at 1628 cm^{-1} in ABTHA is assigned to the C=O stretching vibration. Two consecutive bands at 1624-1720 cm^{-1} in ABTHA ligand are due to various resonation structures of ligand. The N-O stretching vibration is observed at 984 cm^{-1}. As anticipated, the O-H band disappears in the polymers. The carbonyl band is found to have been displaced towards lower frequency side with an increase in intensity. The same is observed in case of ABTHA polymers. The presence of bands in the region 3379-3412 cm^{-1}in chelate polymers indicates the O-H stretching vibration of lattice or coordinated water wherever it is present. In all the cases the evidence of metal to oxygen (of the ligand) bonding is observed around 630-702cm.$^{-1}$

ELECTRONIC SPECTRAL STUDIES AND MAGNETIC SUSCEPTIBILITY DATA OF THE GBTHA CHELATE POLYMERS

In $[Mn (II)(ABTHA)]_n$ chelate polymer a band appears at 30.25 kK may be assigned due to $6A_1 \rightarrow 4E$ (P) transition in octahedral field. The magnetic moment value also supported octahedral geomentry of $\{[Mn(II)(ABTHA)(H_2O)_2\ ]\ (H_2O)\}_n$ chelate polymer.

In case of $\{[Co(II)(ABTHA)(H_2O)_2\ ]\ (H_2O)\}_n$ chelate polymer bands appear at 16.80 kK and 14.85 kK may be attributed to $4T_{1g} \rightarrow 4T_{1g}$ (P) and $4T_{1g} \rightarrow 4A_{2g}$ transition in octahedral field, the octahedral geomentry is futher supported by magnetic moment value.

In $[Ni(II)(ABTHA)(H_2O)_2]_n$ chelate polymer bands appears at 20.45 kK and 16.62 kK may be assigned to $3A_{2g} \rightarrow 3T_{1g}$ (P) and $3A_{2g} \rightarrow 3T_{1g}$ (F) transition in octahedral field respectively, which is futher supported by magnetic moment value and thermal analysis.

Since $[Zn(II)(ABTHA)]_n$ is a d^{10} system and hence is diamagnetic. However, from elemental analyses, infra red spectra, magnetic measurement and thermal decomposition data, its most probable geometry suggested to be tetrahedral.

THERMAL ANALYSES OF THE ABTHA CHELATE POLYMERS

In the present study of chelate polymers, no sharp loss in weight have been observed in the TG curve indicated their polymeric nature. After the loss of lattice/coordinated water molecules the chelate polymers gradually degrade. In case of two-step degradation, the first step is faster than the second step. This may be due to the fact that non-coordinated part of the ligand decomposes first, while the actually coordinated part decomposes later. This step, in most cases leads to the formation of stable metal oxide; mostly higher oxides are formed. [10-11]

CONCLUSION

In summary, we report synthesis and thermogravimetric studies of metal chelate polymers. Newly prepared chelate polymers are coloured and insoluble in almost all the organic solvents. On the basis of elemental analyses, infrared spectra, reflectance spectra, magnetic moment data and thermal studies the $[Zn(II)(ABTHA)]_n$ chelate polymer has tetrahedral geometry whereas $\{[Mn(II)(ABTHA)(H_2O)_2](H_2O)\}_n$, $[Ni(II)(ABTHA)(H_2O)_2]_n$ and $\{[Co(II)(ABTHA)(H_2O)_2](H_2O)\}_n$ chelate polymers have octahedral geometry and order of reactions are found to be approximately one.

References

[1] C. Kaiser , J. E. sonier and D. B. Leznoff , Inor Chem 48 (2009)

[2] J. E. Mark, H. R. Allcock and R. West Inorg. Polmer, Prentice- Hall 141-185 (1920)

[3] B. Dangel, M. Clarke,J. Haley, D. Sames and R. Polt, J. Am. Chem Soc, 119 (1997)

[4] J. Rogan and D. poleti , Thermochim Acta 413 (2004)

[5] B. Singh , B. V. Agrawal , P. l. maurya and A. K. Dey , J ind. Chem. Soc. 59 (1982)

[6] A. V. nikolaev, V. A. Logovienko and L. I. Machina Therm Anal. Acad. Press: New York, 2(1969)

[7] Gupta V. K. and Tandon S. G., J of Chem. Society, 883(1969)

[8] Tandon S. G. and Bhattacharya S C., Analytical Chemistry, 1267(1961)

[9] Ukey V. V. and Juneja H. D., J. of Applied polymer Sci. Vol.99,1,273-278(2005)

[10] Shukla J. P., Agrawal Y.K. and Kuchya K. P., J. Indian chem. Soc, 51,143(1954)

[11] Nakamoto K., " Infrared Spectra of Inorganic and Coordination Compounds, John Wiley", New York 270(1970)

[7] Lever A. B. P.,"Inorganic Electronic spectroscopy" , Elsevier publishing company, New York 297(1668)