

Volume 8, Issue 4 (IV)

ISSN: 2394 – 7780

October - December 2021



International Journal of
Advance and Innovative Research
(Conference Special)

Indian Academicians and Researchers Association
www.iaraedu.com

PREPARATION AND STRCUTURAL STUDIES OF SOME BIS POLYMERIC COMPLEXES

Vaishali P. Meshram

Department of Chemistry, Dharamph M. P. Deo Memorial Science College, RTM Nagpur University, Nagpur, Maharashtra, India

ABSTRACT

Synthesis of inorganic polymer is an emerging field that covers a wide range of disciplines including the frontiers of chemistry, materials, medicine, electronics, optics sensors, information storage, energy conversion, environmental protection aerospace and many more. Chelate polymers have important applications in medical sciences like controlled drug delivery, artificial organs and protein synthesis. Some polymers can be made to be electrically conductive and offer potential for the semiconductor industry and as lightweight electrodes and electrolytes for batteries for automotive and aerospace applications. Newly developed polymers exhibit unusual optical properties that have attracted significant interest from the defense industries. Besides the synthesis of chelate polymers and examination of their thermal stability, present work describes structural characterization of these chelate polymers on the basis of elemental analyses infrared and reflectance spectra, magnetic and thermal studies. Since polymeric chelates are thermally resistant and have a large number of practical applications. Recently some chelate polymers have been synthesized, characterized and their thermal stability has been studied. Ligands of hydroxamic acid with adipic acid, azelaic acid, succinic acid, sebasic acid and subaric acid have been prepared in benzene medium by condensation process Now a day's proton NMR technique can be used for determination of stereochemical structure and conformational analysis of polymer compounds. The chemical shift in NMR spectrum, indicates that what type of hydrogen atoms are present e.g., methylene, methyl groups, olefins, ethers, esters and aromatic compounds. 2D-NMR methods have been used as a powerful and reliable techniques for determination of compositional and configurationally structure of co-ordination polymer. Polyvinyl pyridine and its copolymers have important applications as polyelectrolyte, polymer reagents and in electrical applications. These ligands have been synthesized and characterized by various instrumental techniques.

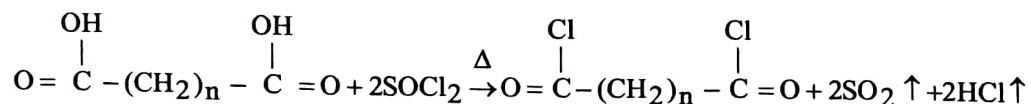
Keywords –complexes, polymeric ligands, IR studies, spectral studies.

EXPERIMENTAL

Chemicals: All the chemicals used were AR grade (Merck). The solvents used were doubled distilled before used.

Instrumentations: $^1\text{H-NMR}$ (CDCl_3 , DMSO-d_6) spectra were recorded on Bruker model DRX-30 NMR Spectrophotometer using TMS as internal reference (δ ppm) Carbon, Hydrogen and Nitrogen contents were analyzed on an EA 1108 Carlo Erba Elemental analyzer instrument at CDRI Lucknow. FTIR spectra were recorded on a Bruker IFS 66V Germany, spectrometer using the KBr technique at Regional Sophisticated Instrumentation Center, IIT Chennai. Reflectance spectra of the chelate polymers in solid state were recorded on a single beam Karl-Zeiss Jena, specord M-400 spectrophotometer, finely powdered barium sulphate was used as a reference material in the studies of reflectance spectra. Magnetic susceptibility of chelate polymers was determined by the Gouy's method at room temperature using mercury tetrathiocyanatocobaltate (II) as standard. The non-isothermal measurement of Mn (II), Co (II), Ni (II) and Zn (II) were carried out using a TGS-2 thermogravimetric analyzer along with a TADS computer system at the Regional Sophisticated Instrumental Center, Nagpur University, Nagpur. The thermocouple used was Pt-Pt-Rh with a temperature range of 20-1000 $^\circ\text{C}$, 12mg sample was taken and the heating rate 15 $^\circ\text{C}/\text{min}$ was employed. The thermal analyses were carried out in air atmosphere and mass loss was recorded continuously on the recorder.

Preparation of dichloride of adipic, azelaic, succinic, sebasic and subaric acid: A quantity of (0.1m mol) dry acid and (0.25m mol) double distilled thionyl chloride was taken in 100ml dry round-bottomed flask fitted with water condenser provided with guard tube containing anhydrous calcium chloride. Flask was heated on a water bath for about 2-3 hours, till clear solution was obtained. The reaction mixture was then refluxed under reduced pressure for 30 min. to remove sulphur dioxide, hydrogen chloride and unreacted thionyl chloride.



(1) $n=4$ for adipic acid (2) $n=7$ for azelaic acid (3) $n=2$ for succinic acid (4) $n=8$ for sebacic acid (5) $n=6$ for subaric acid.

Preparation of ligand: In present investigation, a modified method Priyadarshini and Tandon^[6] based on Schotten Baumann reaction, was used for the preparation of hydroxamic acid. In this procedure hydroxylamine hydrochloride and vacuum distilled acid chloride in stoichiometric ratio were reacted at low temperature 0°C or lower in diethylether medium containing aqueous suspension of sodium bicarbonate. Hydroxamic acid was prepared by the reaction of acid dichloride with excess of hydroxylamine hydrochloride in aqueous ethanol medium containing suspension of sodium bicarbonate, (0.25M) hydroxylamine hydrochloride A.R. grade, ethanol (50 ml) and sodium bicarbonate (0.5 M) and distilled water (25 ml) were placed in 500 ml beaker and acid dichloride was added (0.1 M) dissolved in 100 ml diethyl ether by dropping funnel during a period of 45 minutes with constant stirring. Mechanical stirrer was used for this. The stirring was further continued for 15 minutes. A granular solid mass was separated which was filtered and triturated with saturated solution of sodium bicarbonate in a porcelain mortar to remove any acidic impurities present and was then filtered and re-crystallized out in ethanol: DMF mixture. This ligand is reported first time in the present work and hence characterized by elemental and infrared spectral analyses[1-4]. The reaction of ligand formation has shown in Fig.1

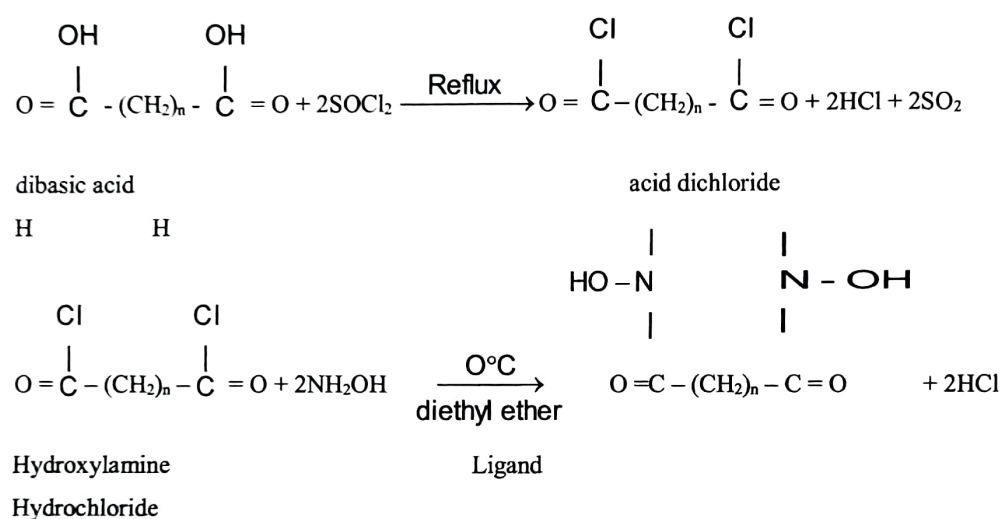


Fig. 1 - Synthesis of hydroxamic acid (ABHA)

Synthesis of chelate polymers of ligand

Chelate Polymers of with Mn (II), Co (II), Ni (II) and Zn (II) have been prepared by dissolving metal acetate (0.01M) separately in minimum amount of DMF and was added to a solution of hydroxamic acid (0.01 M) in (25 ml) DMF. The reaction mixtures were heated on an oil bath with constant stirring at 120°C temperature. The chelate polymers generally appeared after 24-hrs heating on an oil bath. These chelate polymers obtained were filtered, washed thoroughly first with hot DMF and then with absolute alcohol and dried.

RESULTS AND DISCUSSION:

The $^1\text{H-NMR}$ Spectrum of hydroxamic acid ligands with adipic acid, azelaic acid, succinic acid, sebacic acid and subaric acid in acetone solvent along with complete assignments of resonances signals for aliphatic and aromatic protons are shown[5-6]. The NMR signal around δ (chemical shift) 2.05-2.40 ppm is assigned to the over laps of $-\text{CH}_2$ -protons of Ligands^[7]. The aromatic protons of two phenyl groups are appeared at δ 7.48-7.63 ppm due to the presence of $(-\text{NHC}=\text{O})$ amide groups attached directly to benzene ring^[8] and other resonance signal around δ 7.35-7.47 ppm is assigned due to two protons of benzene ring at which bromine attached^[9-10].

The resonance weak signal around δ 4.54-5.64 ppm is assigned to $-\text{NH}$ -region of ligands and other weak signal around δ 8.24-8.27 ppm is assigned two protons of amide group $(-\text{NHC}=\text{O})$ ^[11]. In the infrared spectrum of the ligands a weak bands appeared from $3427\text{-}3480\text{ cm}^{-1}$ due to the presence of stretching vibration of the NH group^[12]. Another sharp bands observed from $1606\text{-}1700\text{ cm}^{-1}$ may be assigned due to the $\text{C}=\text{O}$ stretching vibration^[13]. A weak band appeared from $2882\text{-}2940\text{ cm}^{-1}$ may be assigned due to stretching vibrations of $-\text{CH}_2-$ groups.

Composition of the polymeric unit: the composition of the polymeric unit was assigned on the basis of detailed study of elemental analyses. The presence of water of crystallization was ascertained on the basis of thermal studies. The composition of polymeric unit is $[M(II)L]_n$, $\{[M'(II)(L)2H_2O]H_2O\}_n$ whereas ($M= Zn(II)$), ($M'= Mn(II)$, $Ni(II)$) and $Co(II)$) ($L = ABHA$ ligand). On the basis of elemental analyses, infrared spectra, reflectance spectra, magnetic measurements and thermal studies, the proposed structure of these chelate polymers .

Infrared spectral studies: In infrared spectra, a broad band appears at 3257 cm^{-1} in ABHA ligand may be assigned to the O-H stretching vibration ^[14]. A band appears at 1664 cm^{-1} in ABHA may be due to the resonating structure of the N-N-(C=O)-OH moiety. A band appears at 968 cm^{-1} may be assigned to the N-O stretching vibration.

The hydroxamic acids generally form five membered chelate ring with a metal ion and coordination takes place through >N-O and >C=O oxygen. As is anticipated, a band due to the O-H group disappears in polymers. Whereas a band due to the carbonyl group is shifted towards lower frequency side indicates that there is the formation of $C=O \rightarrow M$ coordinated bond. The N-O band in polymers found to have been shifted slightly to higher frequency side with increase in its intensity. A medium band appears in the region of lower frequency may be assigned to the M-O bonding in chelate polymers. Thus, from the above discussion and from the consideration of potential donor atoms of the polyligands, it can be concluded that the substituted-bis-hydroxamic acids act as bidentate ligands and participated in bonding through the phenolic oxygen and the oxygen of the C=O group to give neutral linear chain chelate polymers.

REFERENCES:

1. L.M.Jackman and S.Sternhell, Application of Nuclear Magnetic Resonance Spectroscopy in organic chemistry, 2nd Ed.(Oxford;Pergaman Press,1969).
2. J.S.Waugh, Analytical Chemistry, 65, no.17 (1993)725A-9A.
3. A.S.Brar and R.J.Kumar, Polym.Sci.Part A; Poly.chem. 84(2002)50.
4. A.S.Brar, Hooda S.and Kumar R., J.Polym.Sci. Part A; 84(2002)50.
5. Sunita Hooda, Rajeev Kumar and Manpreet Kumar, Indian J.of chemistry, 43 A (2004)527-531.
6. Vogels, Text book of Practical Organic Chemistry, Fifth Edition, Revised by Briam S. Furniss, Antoy J. Hannaford, Peter W. Smith and Austin R. Tatchell, 965.
7. R. J. Abraham, J.Fisher and P.Loftus, Introduction to NMR Spectroscopy (New York, Wiley, 1998).
8. Michael Mcgregor, NMR Spectroscopy, Hand book of instrumental Techniques for Analytical Chemistry, 316.
9. A. E. Tonelli, NMR Spectroscopy and Polymer Microstructure, The conformational connection (New York; VCH, 1989).
10. Laurent F.Groux,Thomas Weiss,Dastigin N.Reddy,Preston A.Chase,Warren E.Piers,Tom Ziegler,Masood Parvez and Jordi Benet-Buchhotz,J.AM.Chem.Soc.Vol.127,No.6(2005)1865.
11. Robert M.Silverstein, Francis X.Webster, Spectrometric Identification of Organic Compounds, John Wiley and Sons Inc.New York, 1998.
12. W. B. Gurnule, P.K.Rahangdale, L.J.Paliwal and K.B.Kharat, Reactive and Functional Polymers 55(2003)255-265.
13. Ashaq Hussain, Sheikh H. N.and Kalsotra B.L., J.Indian Chem. Soc., 83,531-535, (2006).
14. Azza A. A. Abu-Hussen, Journal of Coordination Chemistry, Vol. 59, No. 2, 157-176, (2006).