Preparation, spectral, thermal and magnetic studies of some coordination polymers synthesized from adipyl bis-$p$-ethoxyphenyl carbamide

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Abstract - In the current article we depict combination and interpretation of some coordination polymers of adipyl bis-$p$-ethoxyphenylcarbamide (ABPEPC) with first transition series metal particles, for example, Mn(II), Co (II), Ni(II) and Zn. The structure and organization coming about coordination polymers is affirmed by natural investigation, reflectance spectra and FTIR examines. Further the warm investigation and active boundaries were dissected by Sharp-Wentworth and Freeman-Carroll strategies.

Index Terms - Coordination polymers, Elemental analysis, Thermal studies, Magnetic studies.

I. INTRODUCTION

Coordination polymer of divalent progress metal with chelating ligand is an intriguing point with regards to the part of coordination science because of its particular properties and high warm strength than standard edifices. During the most recent twenty years, scientists demonstrated a great deal of revenue in the coordination science of d10 framework divalent metal in coordination polymers and organometallic polymers [1-4]. In the course of recent a very long time all through the world the strong state science was being given incredible significance by the specialists to recognize the water hydration, soundness, warm deterioration of natural moiety in coordination polymers by utilizing different warm strategies for example, thermogravimetry, subsidiary warm investigation, differential warm investigation, differential scanning colorimetry [5-7]. Chaudhary and coworkers reported seven thermally stable coordination polymer compounds of bis(bidentate) ligand and compared their thermal properties by TG/DTG/DTA techniques at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere [8-9]. Earlier workers from our laboratories synthesized coordination polymers of bis ligand with transition metals and reported [10]. The excellence of coordination polymer is warm strength. The nanoscale particles of progress metal coordination polymers have immense warm dependability and huge expected applications [11-12]. In addition, aromatic polyamide a compound of amide bunches is – high performance polymeric materials with remarkable mechanical properties, and great warm and synthetic secure qualities [13-17].

In this work, we have analyzed warm investigation of four novel coordination polymers of d10 divalent c metals. The goal of present work was to depict the similar warm practices by utilizing TG–DTG and DTA procedures under different warming rates. Further, we have assessed warm deterioration energy and thermodynamic boundaries including enactment energy, order of reaction, enthalpy change, entropy change and free energy change by utilizing the Sharp-Wentworth and Freeman-Carroll strategy for each progression of debasement bend with the assistance of TG–DTG and DTA information. Surely, above strategies were altogether discovered supportive to look at the warm dependability and to choose whether water atoms were available at either inward or external circle of coordination polymers.

II. EXPERIMENTAL

A. CHEMICALS
Entire chemicals used were Analytical Reagent grade. The solvents used were purified before use.

B. INSTRUMENTS
Carbon, hydrogen, and nitrogen content were inspected on an EA 1108 Carlo Erba basic analyzer from CDRI Lucknow (India). FTIR spectra of ligand and coordination polymers were recorded at the Regional Sophisticated Instrumentation Center, Nagpur, India, on a Bruker IFS 66V spectrometer (Germany), utilizing the KBr pellet in the scope of 400–4000 cm\(^{-1}\). Reflectance spectra of the coordination polymers in strong state were recorded on a solitary shaft Karl-Zeiss Jena, Specord M-400 spectrophotometer in the reach 250–600 nm. Finely powdered magnesium oxide was utilized as a source of perspective material. Attractive powerlessness of the coordination polymers was dictated by Gouy's technique at room temperature utilizing mercury tetra(thiocyanato)cobaltate (II) as the norm. Thermogravimetric examination was done at RSIC; RTM Nagpur University, Nagpur, India on a TGA/SDTA-851, Mettler Toledo. The thermocouple utilized was Pt-Pt-Rh with a temperature scope of 20°C–1000°C at a warming pace of 15°C/min. A 12-mg test was utilized in the warm investigations, which were done in an air environment. Mass misfortune was recorded constantly on the recorder.

C. SYNTHESIS OF LIGAND
In a broiler dried round base cup an amount of 30 g (2 m mol) of finely powdered of adipyl bis-p-ethoxyphenylcarbamido was taken and 50ml sodium dried benzene was applied. The relating corrosive chloride was then added to it while the benzene–ethoxy carbamido was gradually whirled. Thereafter it was fitted with completely dry Leibag water condenser with anhydrous CaCl\(_2\) filled in gatekeeper tube. The response starts quickly with the HCl gas advancement. On a water shower, the response combination was then refluxed and vigoursly shaken. The items acquired after 4-5 h was sifted, washed with hot benzene and kept in a broiler at 100°C.

D. SYNTHESIS OF COORDINATION POLYMERS
Four coordination polymers were composed in the current work. Coordination polymers were combined independently by dissolving metal acetic acid derivation (10 m mol) and ligand (5 m mol) (Scheme 1) in 25 ml of hot dimethylformamide. Metal acetic acid derivation and bis-ligand arrangements were filtered in hot conditions and the blend was refluxed in an oil shower. The temperature of the response blend was kept up at 120–140 °C. Thereafter 20–24 h the coordination polymers arise out. The items got were separated, completely washed with hot dimethylformamide, dimethylsulphoxide, and liquor was utilized to oust the lethargic reactant, if any present. At last, the polymers were dried. Continued washing with hot DMF and ethanol has decided the immaculateness of items. At room temperature, the polymers acquired were steady. They were portrayed...
by basic examination, IR spectroscopy, diffuse reflectance and attractive estimations were characterized by blended coordination polymers to distribute the calculation.

![Synthesis of coordination polymer](image)

**Fig 2 Synthesis of coordination polymer**

### III. RESULTS AND DISCUSSION

#### A. ELEMENTAL EXAMINATION

The prepared coordination polymers were examined for C, H, N at SICART, Vallabh Vidyanagar Anand, Gujrat. The findings were tabulated in Table 1. The elemental analysis data are in good agreement with the theoretical (calculated) data. The elemental analysis data were used to assign empirical formula and empirical weight to ligand and coordination polymer.

<table>
<thead>
<tr>
<th>Proposed Polymeric Unit</th>
<th>Elemental Analysis</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Experimental</td>
</tr>
<tr>
<td></td>
<td>% C</td>
<td>% H</td>
</tr>
<tr>
<td>[Mn(II)(ABPEPC)]n</td>
<td>48.08</td>
<td>5.38</td>
</tr>
<tr>
<td>[Co(II)(ABPEPC)(H2O)2]n</td>
<td>51.16</td>
<td>5.74</td>
</tr>
<tr>
<td>[Ni(II)(ABPEPC(H2O))2]n</td>
<td>51.18</td>
<td>5.73</td>
</tr>
<tr>
<td>[Zn(II)(ABPEPC)]n</td>
<td>53.99</td>
<td>5.29</td>
</tr>
</tbody>
</table>

#### B. INFRARED SPECTRAL STUDIES

The infrared spectra of the coordination polymers were almost indistinguishable (Figure 3). The frequencies of some critical groups of the free ligand and of the coordination polymers are accounted for in Table 2. IR groups saw at 3435 cm\(^{-1}\) in the ligand might be relegated to the N-H extending recurrence. At 1660 cm\(^{-1}\) sharp band of C=O extending is noticed. The medium band appeared at 2885 cm\(^{-1}\) allotted to fragrant CH\(_2\) gathering. Medium band acquired in the reach 1565 cm-1 may be because of C-N gathering. It has been discovered that bis-ligand shows keto-enol tautomerism during polymerization as follows.

This has been demonstrated by the reality by that the band saw at 1691 cm1 because of C=O extending mode if there should be an occurrence of ligand vanishes and new band is seen around 1555-1570 cm\(^{-1}\) in polymers plainly showed that the C=O band vanishes because of the arrangement of C=N because of enolization. This is additionally upheld by the presence of C-O band around 1105 cm\(^{-1}\) if there should arise an occurrence of polymers. The powerless groups showing up at 631-665 cm\(^{-1}\) in polymers are allotted because of the M-O bond cooperation. While the presence of band around 450-509 cm\(^{-1}\) can be allotted to the M-N bond.
Table 2 IR spectral assignments of the ligand and coordination polymers (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Coordination polymers</th>
<th>H-O-H</th>
<th>-NH-</th>
<th>C=O-</th>
<th>-C=O-</th>
<th>M-O</th>
<th>M(\rightarrow)N</th>
<th>(\text{CH}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABPEPC Ligand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mn (II)(ABPEPC)](_n)</td>
<td>--</td>
<td>3435(b)</td>
<td>1660 (s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2885</td>
</tr>
<tr>
<td>[Co (II)(ABPEPC)(H(_2)O)](_n)</td>
<td>805 (w)</td>
<td>3425 (b)</td>
<td>-</td>
<td>1570</td>
<td>1105</td>
<td>665</td>
<td>509</td>
</tr>
<tr>
<td>[Ni(II)(ABPEPC)(H(_2)O)](_n)</td>
<td>785 (w)</td>
<td>3400 (b)</td>
<td>-</td>
<td>1558</td>
<td>1129</td>
<td>640</td>
<td>438</td>
</tr>
<tr>
<td>[Zn(II)(ABPEPC)](_n)</td>
<td>--</td>
<td>3405 (b)</td>
<td>-</td>
<td>1555</td>
<td>1125</td>
<td>631</td>
<td>450</td>
</tr>
</tbody>
</table>

C. ELECTRONIC SPECTRAL STUDIES AND MAGNETIC SUSCEPTIBILITY DATA OF COORDINATION POLYMERS

A band showed up at 28.05 kK in the [Mn(II)(ABPEPC)]\(_n\) coordination polymer that could be assigned in a tetrahedral field due to the \(^6\text{A}_1\rightarrow\text{E}(g)(D)\) transition. The tetrahedral geometry of the [Mn(II)(ABPEPC)]\(_n\) coordination polymer was likewise upheld by the attractive second worth. The groups that showed up at 17.40 kK in the [Co(II)(ABPEPC)(H\(_2\)O\)]\(_n\) coordination polymer can be because of the \(^4\text{T}_{1g}\rightarrow\text{T}_{1g}\) (P) progress in the octahedral field [18]. The octahedral math was additionally upheld by the attractive second worth. The groups that showed up at 19.00 kK in the [Ni(II)(ABPEPC)(H\(_2\)O\)]\(_n\) coordination polymer, might be doled out to the \(^3\text{A}_2\rightarrow\text{T}_{1g}\) (P) advances, separately, in octahedral field, which was additionally upheld by the attractive second worth. Since [Zn (II) (ABPEPC)]\(_n\) is a d10 framework, it is diamagnetic. In any case, the aftereffects of essential examinations, an infrared range, and warm disintegration investigation proposed that its most likely calculation was tetrahedral. The electronic indistinct (Figure 4) and attractive helplessness information of the coordination polymers are given in the Table-3.
Table 3: Electronic spectral and magnetic susceptibility data of coordination polymers

<table>
<thead>
<tr>
<th>Coordination polymers</th>
<th>Colour</th>
<th>μ(\text{eff}) (B. M.)</th>
<th>Electronic spectra</th>
<th>Assignments</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(II)(ABPEPC)](_n)</td>
<td>Light pink</td>
<td>5.82</td>
<td>28.05</td>
<td>(^6\text{A}<em>1\rightarrow^\text{E}</em>{\text{g}}(\text{D}))</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>[Co(II)(ABPEPC)(H(_2)O)](_n)</td>
<td>Pink</td>
<td>5.10</td>
<td>17.40</td>
<td>(^4\text{T}<em>{1g} \rightarrow^\text{T}</em>{1g}(\text{P}))</td>
<td>Octahedral</td>
</tr>
<tr>
<td>[Ni(II)(ABPEPC)(H(_2)O)](_n)</td>
<td>Green</td>
<td>3.28</td>
<td>19.00</td>
<td>(^3\text{A}<em>{2g} \rightarrow^\text{T}</em>{1g}(\text{P}))</td>
<td>Octahedral</td>
</tr>
<tr>
<td>[Zn(II)(ABPEPC)](_n)</td>
<td>White</td>
<td>Diamagnetic</td>
<td>-</td>
<td>-</td>
<td>Tetrahedral</td>
</tr>
</tbody>
</table>

D. THERMOGRAVIMETRIC STUDIES OF ADBPU COORDINATION POLYMERS

The presence of water of crystallization has been affirmed dependent on TGA and DTA investigation; the discoveries got for these polymers are introduced in Table 4. The delegate warm debasement bends for Co- ABPEPC polymer appeared in figure 5.

The rate mass misfortune relating to composed water particles was considered at around 220 °C. Past this a progressive mass misfortune is seen up to 660 °C, which can be credited to disintegration of coordination polymers. The bend by and large does not show any sharp change yet a progressive decay, which is trademark highlight of these mixes. Co(II)- ABPEPC and Ni(II)- ABPEPC coordination polymers show nonappearance of grid water while; there is presence of two particles of composed water. Along these lines TG examination, IR spectra, electronic spectra and attractive second worth upheld octahedral calculation for Co(II)- ABPEPC and Ni(II)- ABPEPC coordination polymers. Anyway Mn(II) and Zn(II) polymers are tetrahedral in nature because of nonappearance of water of coordination. Various stages engaged with thermogram for the coordination polymers are arranged in Table 4.
E. EVALUATION OF KINETIC PARAMETERS

The kinetic parameters controlled by Sharp-Wentworth and Freeman-Carroll strategies are given in table-5. A delegate sharp-Wentworth plot, warm enactment energy plot and Freeman-Carroll of Ni (II) ABPEPC polymer. Thermodynamic boundaries have been determined based on warm initiation energy.

The assessment of TGA information and from the idea of thermograms, the warm disintegration can be clarified by considering monomeric unit of the polymer. Based on deterioration temperature information given in table 4, the request for warm strength of coordination polymers are discovered to be Zn> Co > Ni > Mn.

IV. CONCLUSIONS

In the current investigation of warm deterioration of some metal coordination polymer accumulates and of a specific ligand with various metal particles under nitrogen climate at warming rate 10°C min-1. Near investigations were accounted for from the perspective. In practically all the natural solvents, recently combined coordination polymers are hued and insoluble. TG, DTA, CHN and IR spectroscopy have affirmed the presence of number of cross section and facilitated water. The coordination polymer mixes are discovered to be thermally steady based on TG/DTA investigation, however Ni (II) was to some degree exceptionally thermally stable contrasted with other coordination polymer mixes. The warm security of coordination polymers follows the request: Co (II) > Zn (II) >Ni (II)>Mn (II)
REFERENCES