Syntheses, characterization and thermal decomposition studies of hydrazine complexes of transition metal phthalates

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INTRODUCTION

The ligational properties of hydrazine were extensively studied from the beginning of the 20th century but it took momentum in the latter half of the century[1]. The potent N-N bond has a positive heat of formation (AHf ~12 kcal mole-1) and is thus thermodynamically unstable[2]. The presence of carboxyl group adjacent to the hydrazine molecule in metal complexes gives interesting thermal behaviours like low-temperature oxide formation. This can produce oxide-particles of desirable properties in solid-state applications[1,3-9]. Among the reported thermal decomposition studies of metal complexes of hydrazine and carboxylates, complexes with dicarboxylates were only a few and aromatic dicarboxylates were not at all found. The kinetic analyses of the thermal decomposition studies were also scanty[10-13]. In this context, we selected the hydrazine complexes of transition metal phthalates, which is a part of a series of works being carried out in our laboratory.

EXPERIMENTAL

Materials

All the chemicals used were BDH/EMerck/Qualigen products, AnalAr-, Exceller or equivalent grade. Solvents used were purified by reported methods[14].

Preparation of complexes

For the preparation of the complexes, phthalic acid (8.3g, 50mmol) in ethanol (50mL) was used. To this solution, freshly prepared metal carbonate (50 mmol) was added slowly with constant stirring, at 30°C, until saturation and boiled. The mixture was filtered hot and hydrazine monohydrate (5g, 100mmol) in ethanol...
Studies of hydrazine complexes

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(20mL) was added drop by drop with constant stirring and allowed to cool to room temperature. The complexes precipitated after keeping for 24 h, were filtered, washed with water, ethanol and ether and dried under reduced pressure and kept in vacuum over fused calcium chloride. The formation of the complexes can be represented by the following equations.

\[
\text{MCO}_3 + \text{C}_8\text{H}_6\text{O}_4 \rightarrow \text{M(C}_8\text{H}_4\text{O}_4) + \text{H}_2\text{O} + \text{CO}_2
\]

\[
\text{M(C}_8\text{H}_4\text{O}_4) + 2\text{N}_2\text{H}_4 \rightarrow \text{M(C}_8\text{H}_4\text{O}_4)(\text{N}_2\text{H}_4)_2 + 2\text{H}_2\text{O},
\]

where \(\text{C}_8\text{H}_6\text{O}_4\) = phthalic acid and \(\text{M}=\text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)} \text{or Cd(II)}\).

Physical measurements

The percentages of metals were estimated by standard methods\[15\]. The percentage of hydrazine was estimated by titration with 25 mM solution of KIO\(_3\) under Andrews’ conditions\[15\]. Carbon, hydrogen, nitrogen and oxygen were estimated using a Hitachi C, H, N, O rapid analyzer. Electrical conductances of the saturated solutions of the complexes in DMSO were measured at room temperature in a direct-reading Systronix-305 conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy-type magnetic balance using Co[Hg(NCS)\(_4\)] as calibrant. Uv-Vis spectra of the complexes were recorded by the Nujol mull technique in a Shimadzu Uv-Vis1601 spectrophotometer. IR spectra were recorded on a Shimadzu FTIR-8101A spectrophotometer. X-ray diffraction in the powder method was done on a Bruker AXS-D5005 model diffractometer. Thermogravimetric analysis in static air was done on a Mettler Toledo Star system thermobalance, with a heating rate of 10°C min\(^{-1}\) and a sample size of 5 mg. Independent pyrolytic studies were also conducted to verify the TG results. A computer programme in Fortran 77 was used to calculate the kinetic parameters of the decomposition processes.

RESULTS AND DISCUSSION

All the complexes were non-hygroscopic, air- and photostable and sparingly soluble in methanol, ethanol, DMF, DMSO etc. The analytical- and magnetic data are given in TABLE 1. The non-conducting nature of the saturated solutions of the complexes in DMSO indicated the formation of neutral complexes.

Magnetic behaviour

The magnetic moment-values indicated the formation high-spin octahedral complexes for all the metals\[16\]. The Zn(II) and Cd(II) complexes were found diamagnetic indicating their d\(_{10}\) configuration.

Electronic spectra and ligand field parameters

The prominent electronic spectral bands and the ligand field parameters calculated are given in TABLE 2. The data corresponded to the formation of high-spin-octahedral complexes in all the cases. In the case of the Mn(II) complex, observed bands and the pale-pink color supported this view. For the Fe(II), Co(II) and Ni(II) complexes also, the data were in good agreement with the prediction\[17\]. The ligand field parameters calculated were ligand field stabilization energy (LFSE), ligand field splitting (\(\Delta J\)) and Racah parameter (\(B^1\)). The ratio \(B/B\), where \(B\) is the Racah parameter for free ion, is expressed as \(\beta\)[18]. The \(\beta\%\) were also calculated.

<table>
<thead>
<tr>
<th>Compd. (a)</th>
<th>Yield (%)</th>
<th>Colour</th>
<th>Melting point/ Decomposition temp. ((^o)C)</th>
<th>Found (calculated) %</th>
<th>(\mu_{\text{eff}}) (B.M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnL(_2)X</td>
<td>75</td>
<td>Pale-pink</td>
<td>&gt; 369</td>
<td>Metal</td>
<td>Hydrazine</td>
</tr>
<tr>
<td>FeL(_2)X</td>
<td>95</td>
<td>Brown</td>
<td>&gt; 360</td>
<td>(19.43)</td>
<td>(22.61)</td>
</tr>
<tr>
<td>CoL(_2)X</td>
<td>87</td>
<td>Pale-pink</td>
<td>&gt; 360</td>
<td>(19.67)</td>
<td>(22.54)</td>
</tr>
<tr>
<td>NiL(_2)X</td>
<td>88</td>
<td>Light-blue</td>
<td>300</td>
<td>(20.55)</td>
<td>(22.30)</td>
</tr>
<tr>
<td>ZnL(_2)X</td>
<td>79</td>
<td>Off-white</td>
<td>&gt; 360</td>
<td>(20.41)</td>
<td>(22.33)</td>
</tr>
<tr>
<td>CdL(_2)X</td>
<td>84</td>
<td>Off-white</td>
<td>&gt; 320</td>
<td>(22.68)</td>
<td>(21.81)</td>
</tr>
</tbody>
</table>

\(\text{L} = \text{N}_2\text{H}_4\) – hydrazine, \(\text{X} = \text{C}_8\text{H}_6\text{O}_4^2^-\) - phthalate, \(\text{D} = \text{diamagnetic}\)
and reported. All these values indicated to the highly covalent character of the metal-ligand bonds\cite{17}.

**Infra red spectra**

The significant IR spectral bands and assignments are given in TABLE 3. All the characteristic bands of the NH\textsubscript{2} and carboxyl groups are observed\cite{19}. The large difference between the asymmetric- and symmetric stretching frequencies of carboxyl groups (\(\Delta v\sim 200\text{ cm}^{-1}\)) indicated the monodentate behaviour of them towards the metals\cite{19}. All the complexes exhibited distinct absorptions in the 993-960 cm\(^{-1}\) region that were due to the N-N stretching\cite{20}. This indicated the presence of bridging hydrazine\cite{20}. This observation along with the insoluble nature indicated the polymeric nature of the complexes. The M-O stretching- and M-N stretching frequencies appeared in the 498-475 and 450-425 cm\(^{-1}\) regions respectively\cite{19}.

**X-ray diffraction**

The XRD analysis of the complexes in the powder method exhibited diffractograms with no specific signals characteristic of perfectly crystalline compounds. The lack of solubility in any solvents prevented the preparation of a perfect single crystal for analysis. The insoluble- and non-crystalline nature also indicated the polymeric nature of the complexes.
TABLE 4: Thermal decomposition pattern of hydrazine complex of Co(II) phthalate

<table>
<thead>
<tr>
<th>Stage</th>
<th>Mass-loss percentage</th>
<th>TG Temperature range (°C)</th>
<th>Decomposition pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>11.20</td>
<td>11.04</td>
<td>105-150 Co(C₂H₄O₂)(N₂H₄) → Co(C₂H₄O₂)(N₂H₄) + N₂H₄</td>
</tr>
<tr>
<td>II</td>
<td>22.88</td>
<td>22.08</td>
<td>207-293 Co(C₂H₄O₂)(N₂H₄) → Co(C₂H₄O₂) + N₂H₄</td>
</tr>
<tr>
<td>III</td>
<td>71.90</td>
<td>72.01</td>
<td>320-540 Co(C₂H₄O₂) → Co₃O₄</td>
</tr>
</tbody>
</table>

TABLE 5: Kinetic parameters of the thermal decomposition reactions of hydrazine complex of Cobalt(II) phthalate

<table>
<thead>
<tr>
<th>Stage</th>
<th>Method</th>
<th>ΔE (kcal mol⁻¹)</th>
<th>Z (sec⁻¹)</th>
<th>ΔS (kcal deg⁻¹mole⁻¹)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Coats-Redfern</td>
<td>25.29</td>
<td>1.33 x 10⁴</td>
<td>-48.11</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>Horowitz-Metzger</td>
<td>32.13</td>
<td>3.79 x 10⁵</td>
<td>-45.62</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>MacCallum - Tanner</td>
<td>28.55</td>
<td>2.32 x 10⁵</td>
<td>-38.25</td>
<td>0.997</td>
</tr>
<tr>
<td>II</td>
<td>Coats-Redfern</td>
<td>31.95</td>
<td>9.32 x 10⁷</td>
<td>-28.59</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>Horowitz-Metzger</td>
<td>35.20</td>
<td>8.16 x 10⁶</td>
<td>-32.90</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>MacCallum-Tanner</td>
<td>37.14</td>
<td>6.75 x 10⁷</td>
<td>-27.95</td>
<td>0.996</td>
</tr>
<tr>
<td>III</td>
<td>Coats-Redfern</td>
<td>52.08</td>
<td>1.80 x 10⁹</td>
<td>-11.20</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>Horowitz-Metzger</td>
<td>45.32</td>
<td>3.72 x 10¹¹</td>
<td>-17.21</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>MacCallum-Tanner</td>
<td>43.19</td>
<td>4.23 x 10¹⁰</td>
<td>-22.04</td>
<td>0.996</td>
</tr>
</tbody>
</table>

ΔE = energy of activation, Z = pre-exponential factor, ΔS = entropy change, r = correlation coefficient

Thermal behaviour

The thermogram for the decomposition of the Co(II) complex is exhibited in figure 1. The thermal decomposition pattern is explained in TABLE 4 and the kinetic parameters calculated are given in TABLE 5. The complex exhibited a three-stage decomposition pattern. The first stage started at 105°C and was complete by 150°C. The percentage mass-loss was found to be 11.20. One coordinated hydrazine molecule was expected to be eliminated in which the theoretical mass-loss was 11.04%. The second stage started at 207°C and was complete at 293°C. In this stage, the second hydrazine molecule was expected to be eliminated. The experimental mass-loss of 22.88% agreed well with the theoretical mass-loss of 22.08%. The third stage of decomposition started at 320°C and was complete at 540°C. In this stage, the cobalt phthalate was expected to have decomposed to Co₃O₄. The experimental mass-loss was 71.90% and the expected mass-loss, 72.02%. The decomposition pattern perfectly agreed with the proposed structure of the compound.

Decomposition kinetics

The non-isothermal method was used for the kinetic studies. The basic equations used for the calculation of kinetic parameters are given below.

Coats-Redfern equation

\[ \ln\left[ \frac{1-(1-\alpha)^{1-n}}{1-n} \right] = \ln\left( \frac{ZRT}{\phi E} \right) + \frac{\Delta E}{RT} + \frac{\Delta E}{R T} \]

Horowitz – Metzger equation

\[ \ln\left[ \frac{1-(1-\alpha)^{1-n}}{1-n} \right] = \ln\left( \frac{ZRT}{\phi E} \right) - \frac{\Delta E}{RT} \]

where \( \alpha \) is the weight-loss at time \( t \) and \( w_{\infty} \) the maximum weight-loss from the TG-curve. \( n \) is the order-parameter, \( Z \) is the pre-exponential factor, \( \Delta E \) the energy of activation, \( R \) the universal gas constant, \( T \) the absolute temperature, \( \phi \) the heating rate, \( T \) the temperature of maximum decomposition and \( \theta \) is \( T - T_f \).

\( \Delta S \), the entropy of activation is calculated from the expression

\[ Z = kT_s \exp(\Delta S/R)/h \]

where \( k \) is the Boltzmann constant and \( h \) the Planck's constant. In all the three methods, the equations represent straight lines and from the slope and intercepts, the parameters are calculated. The order parameter \( n \) was calculated by the method reported by Horowitz-Metzger.[22, 24]

The kinetic parameters calculated by the three different methods, Coats-Redfern, Horowitz-Metzger and MacCallum-Tanner, were in perfect agreement with good correlation coefficients. The large negative values of entropy of activation indicated that the activated states are more ordered than the initial states in all the steps of decomposition.

The final decomposition stage leading to the formation of metal oxide shows higher values of activation energy (~ 50 kcal mol⁻¹) than of the initial two steps (~...
30 kcal mol\(^{-1}\)). This is expected because the final stage involved the rupture of stronger bonds than the initial steps involving dehydradization. We have calculated pre-exponential factor values (Z sec\(^{-1}\)) for the process, they are in the limits \(10^4 < Z < 10^{12}\). A value \(Z \leq 10^{24}\) is believed to be real for the solid-state decomposition processes\(^{[25]}\).

**CONCLUSION**

All the complexes were octahedral in stereochemistry with metal ion in the high-spin state. Polymeric nature was also established. Based all the data, the general structure of the complexes is given in figure 2.

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**REFERENCES**