Research Article

TG, DTA Pyrolytic Analysis of Cobalt, Nickel, Copper, Zinc, and 5,8-Dihydroxy-1,4-Naphthoquinone Chelate Complexes

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The solid state reactions identified on the TG traces with correspondence to DTG peaks consequent to the nonisothermal decomposition of polymetallic chelates of the naphthazarin with Zn(II), Co(II), Ni(II), and Cu(II) over the temperature range ambient to 800°C have been studied kinetically following the Dave and Chopra method as these solid state reactions exhibited their resemblance with the Freeman recommended reaction for kinetic studies. The solid state reactions as described followed first order kinetics. The kinetic data showed the very low value of Z for each of the solid state reaction in reference, concluding on the solid state reactions (the nonisothermal decomposition of polymetallic chelate of Zn(II), Co(II), Ni(II), and Cu(II) as slow reactions).

1. Introduction

Due to automation in the recent times, the instruments have become capable of self-operation, improving both accuracy and precision of measurements, as well as relinquishing both investigator’s time and patience.

Besides other instruments, the thermal methods provide today the means of solving existing chemical as well as creating new ones. These methods can provide rapid information concerning the thermal stability, composition of pyrolysis intermediates, and composition of the final product as a compound is heated to elevated temperature.

Borrel and Paris [1] carried out the synthesis and stoichiometry of some metal oxinate complexes and their associated thermal stability by using thermogravimetric analysis. The effect of alpha methyl substitution on the oxide ligand in Cu(II) and Zn(II) complexes [2] over the solubility products of Cu(II) and Zn(II) oxinates and methyloxinates was studied by potentiometric neutralization of acid solutions containing oxine or methyloxine and metallic cations [3]. The thermal stability and volatilization on vacuum of metallic chelates which are derivatives of 8-hydroxyquinoline have been studied by Charles and Langer [4]. Also, it had been observed that the temperature range of volatilization depends on metallic ion electronegativity for the divalent metal 8-hydroxyquinolinates. The thermal stability analysis of these complexes was studied by Wendlandt and Horton [5] using differential thermal analysis (DTA). These 8-hydroxyquinolinates hydrates were also studied by Gore and Wendlandt [6] by using thermogravimetry, differential scanning calorimetry, and reflectance spectra.

The crystalline structures study of this kind of complex [7–9] notifies monoclinic in the a and b forms for the copper (II) complexes regardless of the hydration degree. Zn (II) and Cd (II) complexes [10, 11] have been found to be monoclinic, but it had been found that these structures depend on the hydration. The zinc (II) and cadmium (II) hydrated complexes show the same b form found for the copper (II) complexes. Several studies have indicated characteristic IR bands for these compounds [12–18]. An attractive group of natural 1,4-naphthoquinones is spinochrome, i.e., the pigments of echinoderms with naphthazarin 1 (5,8-dihydroxy-1,4-naphthoquinone) core.
[19–22]. Naphthoquinones in association with various metals have many medicinal properties [23–26].

The chelating agents are capable of chelating the metal cations having 2–4 valencies in line with the ligancy of metals involved, but the hydroxynaphthoquinone, namely, 5,8-dihydroxy-1,4-naphthoquinone (naphthazarin), a synthetic hydroxynaphthoquinone, appears to be able to form polymetallic chelates with different metal cations due to the presence of an additional hydroxyl group at carbon 8 as compared to its family member: 5-hydroxy-1,4-naphthoquinone (juglone) with the capability to chelate two metal cations initially forming the two six member rings with the progression of more six member ring formation in line with the metal ligancy involving either ligand molecule(s) or coordinated water molecules as the satisfaction of metal ligancy a prerequisite in the chelation process.

The literature survey has provided information on the little work performed so far on the chelating properties of naphthazarin molecule (Scheme 1).

This work centers around the synthesis of polymetallic chelates of different metal cations (Zn(II), Co(II), Ni(II), and Cu(II)) with naphthazarin and their pyrolysis mapping with emphasis on the detection of stability and instability zones, composition of the pyrolysis intermediates and the synthetic metal chelates, as well, and the kinetics of the nonisothermal decomposition of the polymetallic chelates involving the decomposition reactions detected on the pyrolysis traces with agreement to the type of reaction.

A (s) → B (s) + C (g).

It was recommended by Freeman and Carrol [27] for the study of the kinetics of the reaction. The Dave and Chopra procedure [28] was applied to study the nonisothermal decomposition reactions kinetically.

2. Materials and Methods

The chemicals of high purity were used in the study of chelation of metal cations and naphthazarin at pH 6. For the synthesis of metal chelates, equal molar of aqueous metal salt solution and ethanolic solution of naphthazarin were mixed and buffered at pH 6. The resultant mixture was allowed to stand for a period of at least ten days. The crystals so formed were filtered, washed with double distilled water, and shade dried and finally bottled. The process of preparation of chelate complexes was carried out without using any external catalyst. The process takes place via the autocatalytic mechanism.

For pyrolysis mapping, the dried solid mass of metal chelate of naphthazarin with metal cations Zn (II)/Co (II)/Ni (II)/Cu (II) was subjected to thermal analysis in nitrogen atmosphere with reference weight of 10.500 mg and reference name alumina powder and temperature program as EXSTAR TG/DTA 6300. The samples of polymetallic chelates of naphthazarin with Zn (II) or Co (II) or Ni (II) or Cu (II) cations were run on EXSTAR TG/DTA 6300 in nitrogen (100/200 ml/min) atmosphere with reference weight of 10.500 mg and reference name alumina powder and temperature program as

Cal Cal Cal/min min S
31 800 10 0 0.5

The sample weights ranging from 1 mg to 3 mg were employed. The small sample size within the limits of sensitivity of balance was so used as to ensure that the heating rate (10°C/min) could not depart from its constant value.

The polymetallic chelates of naphthazarin with Zn (II), Co (II), Ni (II), and Cu (II) were mapped thermally, structurally, and compositionally employing the thermal database generated with the use of instrument “EXSTAR TG/DTA 6300.”

3. Results and Discussion

The nonisothermal decomposition reactions with correspondence to the well-defined sigmoidal TG traces had been kinetically studied employing the peaks on DTG trace with complete correspondence to sigmoidal on TG traces.

Scheme 1: The systematic representation of naphthoquinone.

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Table 1: Analytical data on nonisothermal decomposition of \([(C_{10}H_{6}O_{4})_3 (Zn)_2] 2\frac{1}{2} H_2O\).

| Reaction               | Loss          | Composition                  | Found   | Calc   |
|------------------------|---------------|------------------------------|---------|--------|
| Plateau I, ambient at 24.1°C | —             | \((C_{10}H_{6}O_{4})_3 (Zn)_2 2\frac{1}{2} H_2O\) | —       | —      |
|                         | Sigmoid I     | \(2\frac{1}{2}H_2O\)         |         |        |
| 24.1°C–100°C            | \(T_i \ °C\)  | 24.1                         | —       | —      |
|                         | \(T_f \ °C\)  | 100                          | —       | —      |
|                         | Loss to       | \((C_{10}H_{6}O_{4})_3 (Zn)_2\) | 6.30    | 6.37   |
| Plateau II, 100°–150°C  |               | \((C_{10}H_{6}O_{4})_3 (Zn)_2\) |         |        |
|                         | Sigmoid II    | \(\frac{5}{2}C_{10}H_6O_4\)  |         |        |
| 150°–200°C              | \(T_i \ °C\)  | 150                          | —       |        |
|                         | \(T_f \ °C\)  | 200                          | —       |        |
|                         | Loss to       | \((C_{10}H_{6}O_{4})_2 (Zn)_2\) | 17.80   | 18.12  |
| Plateau III, 200°–500°C |               | \(\frac{5}{2} (C_{10}H_{6}O_4) (Zn)_2\) |         |        |
|                         | Sigmoid III   | \(\frac{5}{2}C_{10}H_6O_4\)  |         |        |
| 500°–529°C              | \(T_i \ °C\)  | 500                          | —       |        |
|                         | \(T_f \ °C\)  | 529                          | —       |        |
|                         | Loss to       | \((C_{10}H_{6}O_{4})_2 (Zn)_2\) | 29.90   | 31.54  |
| Plateau IV, 529°–600°C  |               | \((C_{10}H_{6}O_4)_2 (Zn)_2\) |         |        |
|                         | Sigmoid IV    | \(c_{10}H_6O_4\)            |         |        |
| 600°–700°C              | \(T_i \ °C\)  | 600                          | —       |        |
|                         | \(T_f \ °C\)  | 700                          | —       |        |
|                         | Loss to       | \((C_{10}H_{6}O_4) (Zn)_2\)  | 55.76   | 57.05  |
| 700° onwards            |               |                              |         |        |

Table 2: Analytical data on the nonisothermal decomposition of \([(C_{10}H_{6}O_4)_3 (Co)_2 \cdot 4H_2O] \cdot 3H_2O\).

| Reaction               | Loss          | Composition                  | Found   | Calc   |
|------------------------|---------------|------------------------------|---------|--------|
| Plateau I, ambient at 100°C | —             | \([(C_{10}H_{6}O_4)_3 (Co)_2 \cdot 4H_2O] \cdot 3H_2O\) | —       | —      |
|                         | Sigmoid I     | 7H_2O                        |         |        |
| 100°C–169°C             | \(T_i \ °C\)  | 100                          | —       | —      |
|                         | \(T_f \ °C\)  | 169                          | —       | —      |
|                         | Loss to       | \((C_{10}H_{6}O_4)_3 (Co)_2\) | 15.17   | 15.46  |
| Plateau II, 169°–200°C  |               | \((C_{10}H_{6}O_4)_3 (Co)_2\) |         |        |
|                         | Sigmoid II    | \(3/2C_{10}H_6O_4\)         |         |        |
| 200°–363°C              | \(T_i \ °C\)  | 200                          | —       |        |
|                         | \(T_f \ °C\)  | 363                          | —       |        |
|                         | Loss to       | \((C_{10}H_{6}O_4)_2 (Co)_2\) | 49.08   | 49.26  |
| Plateau III, 363°–500°C |               | \((C_{10}H_{6}O_4)_2 (Co)_2\) |         |        |
|                         | Sigmoid III   | \(3/2C_{10}H_6O_4\)         |         |        |
| 500°–600°C              | \(T_i \ °C\)  | 500                          | —       |        |
|                         | \(T_f \ °C\)  | 600                          | —       |        |
|                         | Loss to       | Co_3O_8                      | 83.56   | 87.78  |
|                         |               | Co_3O_8                      | 16.44   | 12.19  |
3.1. Polymetallic Chelate of Naphthazarin with Zn (II).
The thermal database resulted in the leads on the tentative structural pattern of this polymetallic chelate, consisting of 0.2 moles of Zn (II) and 0.3 moles of naphthazarin and 2 ½ water molecules as lattice water (Figure 2).
Composition: \([(\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Zn})_2]\) 2 ½\text{H}_2\text{O}.

3.1.1. Proposed Structure. Initially, the thermal stability of metal chelate \([(\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Zn})_2]\) 2 ½\text{H}_2\text{O} exhibited ambient at 24.1°C as first plateau temperature range with 24.1°C as procedural decomposition temperature (pdt as its acronym). The solid mass began to lose lattice water 2 ½\text{H}_2\text{O}, and the loss was complete at 100°C, after which the TG trace levelled off with extension to 150°C (second plateau: 100°C–150°C).

With the increase of temperature beyond 150°C, the intermediate composition of structure \((\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Zn})_2\) was reduced to \((\text{C}_{10}\text{H}_6\text{O}_4)_{2}(\text{Zn})_2\) with the departure of half molecule of \text{C}_{10}\text{H}_6\text{O}_4 in the temperature range 150°C–200°C.

### Table 3: Analytical data on the nonisothermal decomposition of \([(\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Ni})_2\text{H}_2\text{O}]\) 1½\text{H}_2\text{O}.

| Reaction | Loss | Composition | Found | Calc. |
|----------|------|-------------|-------|-------|
| Plateau I, ambient at 99.9°C | — | \([(\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Ni})_2\text{H}_2\text{O}]\) 1½\text{H}_2\text{O} | — | — |
| Sigmoid I \(99.9^\circ\text{C–136}^\circ\text{C}\) | \(5\frac{1}{2}\text{H}_2\text{O}\) | 12.98 | 12.60 |
| \(T_i^\circ\text{C}\) | 99.9 | | |
| \(T_f^\circ\text{C}\) | 136 | | |
| Loss to \((\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Ni})_2\) | | | |
| Plateau II, \(136^\circ\text{C–300}^\circ\text{C}\) | \(1\frac{1}{2}\text{C}_{10}\text{H}_6\text{O}_4\) | 43.28 | 42.84 |
| Sigmoid II \(300^\circ\text{C–365}^\circ\text{C}\) | \((\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Ni})_2\) | 99.9–136°C | |
| \(T_i^\circ\text{C}\) | 300 | | |
| \(T_f^\circ\text{C}\) | 365 | | |
| Loss to \(7/4(\text{C}_{10}\text{H}_6\text{O}_4) (\text{Ni})_2\) | | | |
| Plateau III, \(365^\circ\text{C–500}^\circ\text{C}\) | \(7/4\text{C}_{10}\text{H}_6\text{O}_4\) | 77.73 | 81.17 |
| Sigmoid III \(500^\circ\text{C–600}^\circ\text{C}\) | \((\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Ni})_2\) | 300°–400°C | |
| \(T_i^\circ\text{C}\) | 500 | | |
| \(T_f^\circ\text{C}\) | 600 | | |
| Loss to \text{NiO} | | | |
| \text{NiO} (600°C onwards) | 22.27 | 18.83 |

### Table 4: Analytical data on the nonisothermal decomposition of \([(\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Cu})_2\text{H}_2\text{O}]\) 4\text{H}_2\text{O}.

| Reaction | Loss | Composition | Found | Calc. |
|----------|------|-------------|-------|-------|
| Plateau I ambient at 26.5°C | — | \([(\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Cu})_2\text{H}_2\text{O}]\) 4\text{H}_2\text{O} | — | — |
| Sigmoid I \(26.5^\circ\text{C–71}^\circ\text{C}\) | \(4\text{H}_2\text{O}\) | 26.5 | — |
| \(T_i^\circ\text{C}\) | 26.5 | — |
| \(T_f^\circ\text{C}\) | 71 | — |
| Loss to \((\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Cu})_2\) | | 9.52 | 9.38 |
| Plateau II, \(71^\circ\text{C–300}^\circ\text{C}\) | \(\text{C}_{10}\text{H}_6\text{O}_4\) | \((\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Cu})_2\) | 35.64 | 34.11 |
| Sigmoid II \(300^\circ\text{C–400}^\circ\text{C}\) | \((\text{C}_{10}\text{H}_6\text{O}_4)_{3}(\text{Cu})_2\) | 300°–400°C | |
| \(T_i^\circ\text{C}\) | 300 | | |
| \(T_f^\circ\text{C}\) | 400 | | |
| Loss to \((\text{C}_{10}\text{H}_6\text{O}_4)_{2}(\text{Cu})_2\) | | 9.52 | 9.38 |
| Plateau III, \(400^\circ\text{C–500}^\circ\text{C}\) | \(3/2(\text{C}_{10}\text{H}_6\text{O}_4)\) | \((\text{C}_{10}\text{H}_6\text{O}_4)_{2}(\text{Cu})_2\) | 500°–545°C | |
| Sigmoid III \(500^\circ\text{C–545}^\circ\text{C}\) | \((\text{C}_{10}\text{H}_6\text{O}_4)_{2}(\text{Cu})_2\) | 500°–545°C | |
| \(T_i^\circ\text{C}\) | 500 | | |
| \(T_f^\circ\text{C}\) | 545 | | |
| Loss to \(1/2\text{C}_{10}\text{H}_6\text{O}_4\) \text{Cu}_2 | | 68.63 | 70.57 |
The weight constancy of the second intermediate \((5/2 \text{ (C}_{10}\text{H}_{6}\text{O}_{4})_3 (\text{Zn})_2)\) was exhibited in the temperature 200°–500°C (third plateau). The second intermediate \((5/2 \text{ (C}_{10}\text{H}_{6}\text{O}_{4}) (\text{Zn})_2)\) lost further half molecule of \(\text{C}_{10}\text{H}_{6}\text{O}_{4}\) in 500°–520°C temperature range generating still another (third intermediate) intermediate \((\text{C}_{10}\text{H}_{6}\text{O}_{4})_2 (\text{Zn})_2\) showing weight constancy from 529° to 600°C. With further supply of energy, the \((\text{C}_{10}\text{H}_{6}\text{O}_{4})_2 (\text{Zn})_2\), departed a molecule of \(\text{C}_{10}\text{H}_{6}\text{O}_{4}\), leaving behind \((\text{C}_{10}\text{H}_{6}\text{O}_{4})_2 (\text{Zn})_2\) (forth intermediate) showing weight constancy in temperature range of 700°C onwards till 800°C, the other extreme of the temperature range over which the sample was pyrolysed.

The sample could not be further pyrolysed beyond 800°C due to the instrumental limitation. It showed that the sample could not be led to the complete combustion level, the stage of complete departure of organic matter from the sample mass, leaving behind \(\text{ZnO}\) (zinc oxide).

The possible nonisothermal decomposition reactions identified on TG trace (Figure 6) are described as follows:

(I) \([\text{C}_{10}\text{H}_{6}\text{O}_{4})_3 (\text{Zn})_2] 2\text{H}_{2}\text{O} \xrightarrow{241°–100°C} [2\text{C}_{10}\text{H}_{6}\text{O}_{4})_3 (\text{Zn})_2] + 2\text{H}_{2}\text{O}\)

(II) \([\text{C}_{10}\text{H}_{6}\text{O}_{4})_3 (\text{Zn})_2] \xrightarrow{150°–200°C} 5/2\text{C}_{10}\text{H}_{6}\text{O}_{4})_2 (\text{Zn})_2 + 1/2\text{C}_{10}\text{H}_{6}\text{O}_{4}\)

(III) \([\text{C}_{10}\text{H}_{6}\text{O}_{4})_3 (\text{Zn})_2] \xrightarrow{500°–529°C} (\text{C}_{10}\text{H}_{6}\text{O}_{4})_2 (\text{Zn})_2 + 1/ \text{C}_{10}\text{H}_{6}\text{O}_{4}\)

(IV) \([\text{C}_{10}\text{H}_{6}\text{O}_{4})_3 (\text{Zn})_2] \xrightarrow{600°–700°C} (\text{C}_{10}\text{H}_{6}\text{O}_{4})_2 (\text{Zn})_2 + \text{C}_{10}\text{H}_{6}\text{O}_{4}\)

The sample could not be pyrolysed further due to instrumental limitation.

The analytical data on the pyrolysis journey on the polymetallic chelate of naphthazarin with zinc as shown by TG mapping are given in Table 1.

### 3.2. Polymetallic Chelate of Naphthazarin with Co (II).
Composition: \([\text{C}_{10}\text{H}_{6}\text{O}_{4})_3 (\text{Co})_2 \cdot 4\text{H}_{2}\text{O}) 3\text{H}_{2}\text{O}\).
3.2.1. Proposed Structure. The \([(C_{10}H_6O_4)_3(Co)_2H_2O]3H_2O\) had been found composing of 02 moles of cobalt cation, 03 moles of \(C_{10}H_6O_4\) (naphthazarin molecules), 04 coordinated water molecules, and 03 lattice water molecules. This polymetallic chelate on its formation under the applied condition composed of additional 04 six membered rings in addition to the 02 six membered rings of the chelating agents (Figure 3).

The nonisothermal decomposition of the thermal mapping spectrum showed the thermal stability at initial states as ambience to 100°C (pdt: 100°C). Beyond 100°C, with the increase of temperature, the structural degeneration occurred, proceeding slowly to 169°C with the loss of 7H_2O including lattice and coordinates water molecules. The TG trace was levelled off between 169° and 200°C showing weight constancy range with correspondence to \((C_{10}H_6O_4)_3(Co)_2\), the intermediate composition. The further incremental increase of temperature beyond 200°C registered the further departure of organic matter and stopped at 363°C, with departure of 1½ \((C_{10}H_6O_4)_3(Co)_2\) between 200° and 363°C. The plateau 363°–500°C had a match with another intermediate composition, 1½ \((C_{10}H_6O_4)_3(Co)_2\). This intermediate 1½\((C_{10}H_6O_4)\) lost, with the rise of temperature slowly to 600°C, the organic residue 1½ \((C_{10}H_6O_4)\), leaving behind \(Co_3O_8\). The calculated data on the periodic losses covering thermal spectrum had a close agreement to the experimental data. The data compilation is given in Table 2.

The thermal spectrum recorded on \([(C_{10}H_6O_4)_2(Co)_2H_2O]3H_2O\) exhibited 04 plateaus, the constant weight zones, and 03 sigmoids (100°–169°C, 200°–363°C, and 500°–600°C). The sigmoids on TG trace had corresponding peaks recorded on DTG (Figure 7).
Figure 6: Simultaneous pyrolysis mapping of polymetallic chelates of zinc with naphthazarin TG/DTA.

Figure 7: Simultaneous pyrolysis mapping of polymetallic chelates of cobalt with naphthazarin TG/DTA.

Figure 8: Simultaneous pyrolysis mapping of polymetallic chelates of nickel with naphthazarin TG/DTA.
**Figure 9:** Simultaneous pyrolysis mapping of polymetallic chelates of copper with naphthazarin TG/DTA. Rxn: \[ (C_{10}H_6O_4)_3(Zn)_2 \cdot 21/2H_2O \xrightarrow{241^\circ-100^\circ C} (C_{10}H_6O_4)_3(Zn)_2 \cdot 21/2H_2O \]\n
**Figure 10:** Dave and Chopra plot applying DTG traces (P I). Rxn: \[ 5/2(C_{10}H_6O_4)_{1/2}(Zn)_2 \xrightarrow{500^\circ-529^\circ C} (C_{10}H_6O_4)_{1/2}(Zn)_2 + 1/2C_{10}H_6O_4. \]
The DTA spectrum analysis led to believe "No Visible deviation" from the baseline.

The possible nonisothermal decomposition reactions identified on TG trace (Figure 7) are described as follows:

\[
\begin{align*}
\text{TG Peaks:} & \\
156^\circ C (33.9 \mu g \text{ min}^{-1}) & \\
48^\circ C (35.1 \mu g \text{ min}^{-1}) & \\
557^\circ C (38.5 \mu g \text{ min}^{-1}) & 
\end{align*}
\]

3.3. Polymetallic Chelate of Naphthazarin with Ni (II).

3.3.1. Proposed Structure. The \([\text{Ni}(10\text{H}_6\text{O}_4)_2 \cdot 4\text{H}_2\text{O}]\) \(1\frac{1}{2}\text{H}_2\text{O}\) exhibited thermally the initial plateau, ambience to 99.9°C, showing the structural stability, which showed the
Figure 15: Dave and Chopra plot applying DTG traces (P VI). Rxn: 
\[ [(C_{10}H_{6}O_4)_3(Ni)_24H_2O]11/2H_2O \rightarrow (C_{10}H_{6}O_4)_3(Ni)_2 + 11/2H_2O. \]

Figure 16: Dave and Chopra plot applying DTG traces (P VII). Rxn: 
\[ (C_{10}H_{6}O_4)_3(Ni) \rightarrow 5/4(C_{10}H_{6}O_4)_3(Ni)_2 + 13/4C_{10}H_6O_4. \]

Figure 17: Dave and Chopra plot applying DTG traces (P VIII). Rxn: 
\[ 5/4(C_{10}H_{6}O_4)_3(Ni)_2 \rightarrow NiO + 5/4C_{10}H_6O_4. \]

Figure 18: Dave and Chopra plot applying DTG traces (P IX). Rxn: 
\[ (C_{10}H_{6}O_4)_3(Cu)_24H_2O \rightarrow (C_{10}H_{6}O_4)_3(Cu)_2 + 4H_2O. \]

Figure 19: Dave and Chopra plot applying DTG traces (P X). Rxn: 
\[ (C_{10}H_{6}O_4)_3(Cu)_2 \rightarrow NiO + 5/4C_{10}H_6O_4. \]

Figure 20: Dave and Chopra plot applying DTG traces (P XI).
degeneration with the rising temperature above 99.9°C (pdt: 99.9°C). The structural degeneration ended at 136°C with the departure of coordinated and lattice water molecules, ending at the intermediate composition, (C_{10}H_{6}O_{4})_3(Ni)\_2, showing weight constancy in temperature range 136°C–300°C. Further supply of energy to (C_{10}H_{6}O_{4})_3(Ni)\_2 caused more degeneration in the structural design of the intermediate composition in the temperature of 300°–365°C, leaving behind 5/4 (C_{10}H_{6}O_{4})_3(Ni)\_2 with the loss of 1/4 C_{10}H_{6}O_{4} molecule. The 5/4 (C_{10}H_{6}O_{4})_3(Ni)\_2 intermediate composition (stable at 365°–500°C) could not tolerate the impact structurally at the temperature above 500°C. The residual organics attached with the metal was lost in the temperature range of 500°–600°C, leaving finally the mass with correspondence to NiO.

The peaks recorded on DTG traces (132°C (4.12 μg/min), 350°C (7.7 μg/min), and 577°C (8.4 μg/min)) had the clear tally with the corresponding sigmoids on TG traces (99.9°–136°C, 300°–365°C, and 500°–600°C).

The possible nonisothermal decomposition reactions identified on TG trace (Figure 8) are described as follows:

(VIII) [(C_{10}H_{6}O_{4})_3(Ni)_2(4H_{2}O)]\_11/2H_{2}O \xrightarrow{99.9°–136°C} (C_{10}H_{6}O_{4})_3(Ni)_2 + 51/2H_{2}O

(IX) (C_{10}H_{6}O_{4})_3(Ni)_2 \xrightarrow{300°–365°C} 7/4(C_{10}H_{6}O_{4})_3(Ni)_2 + 11/4C_{10}H_{6}O_{4}

(X) 7/4(C_{10}H_{6}O_{4})_3(Ni)_2 \xrightarrow{500°–600°C} NiO + 7/4C_{10}H_{6}O_{4}

The analytical data on the pyrolysis journey on the polymetallic chelate of naphthazarin with nickel as shown by TG mapping are given in Table 3.

3.4. Polymetallic Chelate of Naphthazarin with Cu (II)

Composition: [(C_{10}H_{6}O_{4})_3(Cu)_2] 4H_{2}O.

3.4.1. Proposed Structure. The spread of temperature range ambience at 800°C, the instrumental condition could not cause complete combustion, that is, the departure of 03C_{10}H_{6}O_{4} molecules and 04 lattice water molecules from the parent polymetallic chelate, [(C_{10}H_{6}O_{4})_3(Cu)_2] 4H_{2}O, with the initial range ambience, 26.5°C, as the initial thermal stability of the metal chelate. The incremental rise of temperature till 71°C (pdt: 71°C) caused 04 H_{2}O lattice water to depart, leaving behind [(C_{10}H_{6}O_{4})_3(Cu)_2], the structural intermediate composition, showing weight constancy between 71°C and 300°C. The sigmoid II began at 300°C and ended at 400°C agreeing analytically with loss of C_{10}H_{6}O_{4} molecule. The plateau 400°–500°C had been found analytically true with the [(C_{10}H_{6}O_{4})_3(Cu)_2] composition, which assumed structural degeneration when the temperature began to increase slowly above 500°C. The departure of 1/2 C_{10}H_{6}O_{4} molecules ended at 545°C leaving behind 1/2(C_{10}H_{6}O_{4})_3(Cu)_2, agreeably true to the last plateau at 545°–800°C. The last plateau (545°C–800°C), beyond which the pyrolysis could not be extended (780°C), clearly indicated the incomplete combustion of the metal chelate in reference under the applied instrumental conditions. The 03 sigmoids traces on the TG spectrum had the correspondence to the peaks registered on DTG trace of the metal chelate. The instrument registered 2nd peak contiguous to the 3rd peak on DTG trace showing near correspondence to the sigmoid tracing on TG traces (Figure 9).

| Reaction | E (kcal.mol\(^{-1}\)) | Z | DTG peak |
|----------|------------------------|---|----------|
| I        | 2.25                   | 2.8×10\(^{-2}\) | P I (Figures 3–6) |
| II       | 1.75                   | 4.78×10\(^{-2}\) | P II (Figures 3–6) |
| III      | 1.6                    | 5.4×10\(^{-4}\) | P III (Figures 3–6) |
| IV       | 4.75                   | 1.51×10\(^{-3}\) | P IV (Figures 3–6) |
| V        | 5.5                    | 1.09×10\(^{-3}\) | P V (Figures 3–7) |
| VI       | 16                     | 15.8×10\(^{-3}\) | P VI (Figures 3–7) |
| VII      | 8.0                    | 1.0×10\(^{-3}\) | P VII (Figures 3–7) |
| VIII     | 6.0                    | 3.63×10\(^{-3}\) | P VIII (Figures 3–8) |
| IX       | 6.6                    | 2.5×10\(^{-2}\) | P IX (Figures 3–8) |
| X        | 22                     | 8.7×10\(^{-0.7}\) | P X (Figures 3–8) |
| XI       | 2.0                    | 79.4×10\(^{-2}\) | P XI (Figures 3–9) |
| XII      | 0.8                    | 60.5×10\(^{-2}\) | P XII (Figures 3–9) |
| XIII     | 6.1                    | 36.3×10\(^{-2}\) | P XIII (Figures 3–9) |

The possible nonisothermal decomposition reactions identified on TG trace (Figures 3–8) are described as follows:

(XI) (C_{10}H_{6}O_{4})_3(Cu)_2 4H_{2}O \xrightarrow{265°–71°C} (C_{10}H_{6}O_{4})_3(Cu)_2 + 4H_{2}O

(XII) (C_{10}H_{6}O_{4})_3(Cu)_2 \xrightarrow{300°–400°C} (C_{10}H_{6}O_{4})_3(Cu)_2 + C_{10}H_{6}O_{4}

(XIII) (C_{10}H_{6}O_{4})_3(Cu)_2 \xrightarrow{545°C} 1/2(C_{10}H_{6}O_{4})_3(Cu)_2 + 3/2(C_{10}H_{6}O_{4})

The analytical data on the pyrolysis journey on the polymetallic chelate of naphthazarin with copper as shown by TG mapping are given in Table 4.

**Figure 21:** Dave and Chopra plot applying DTG traces (P XII).
3.5. Kinetics and Solid State Reactions. The I–XIII solid state reactions identified on the TG traces with correspondence to DTG peaks consequent to the nonisothermal decomposition of polymetallic chelates of the naphthazarin with Zn (II), Co (II), Ni (II), and Cu (II) over the temperature range ambient at 800°C have been studied kinetically following the Dave and Chopra method as these solid state reactions exhibited their resemblance with the Freeman recommended reaction for kinetic studies.

\[ A(s) \rightarrow B(s) + C(g) \]

The sigmoid sandwiched between two plateaus represents a solid state reaction (Scheme 2).

For each solid state reaction, the terms \( A, a, \) and \( \frac{dx}{dt} \) at various \( T \) values employ DTG traces corresponding to sigmoids on TG trace. The plot of \( \log k \) (where \( k = \frac{dx}{dt} \)) against the reciprocal of absolute temperature (\( T \)) gave a straight line relationship justifying the assumption of order of reaction (\( n \)) as one.

Figures 10–21 represent the Dave and Chopra plots for \( n = 1 \) for different solid state reactions (I–XIII), giving slope (\( tan \theta \)) as \( E/2.3R \) and intercept as \( log Z \). The characteristics terms \( E \) and \( Z \) for solid state reactions (I–XIII) are tabulated in Table 5.

It is an established fact that the velocity rate increases with the rise of temperature according to collision theory for reactions, justifying more collisions among the involved molecules. This means that the \( Z \) (frequency factor or collisions number) value rises with more collisions among the molecules describing the reactions involved as fast reaction, but the lower values of \( Z \) may help conclude the reaction under study as slow in nature. The kinetic data showed the very low value of \( Z \) for each of the solid state reaction in reference (Table 5), concluding on the solid state reaction (I–XIII) (the nonisothermal decomposition of polymetallic chelate of Zn(II), Co(II), Ni(II), and Cu(II) as slow reactions).

The DTG traces on the polymetallic chelates of naphthazarin with Zn (II), Co (II), Ni (II), and Cu (II) are shown in Figures 6–9, respectively.

4. Conclusion

The pyrolysis spectrum of each of the polymetal chelates exhibiting plateaus and sigmoids with correspondence on the DTG traces but with no responses on DTA traces have led us to conclude on the structures of the polymetal chelates tentatively.

The unidentified nonisothermal decomposition of polymetallic chelates of naphthazarin with resemblance to \( A(s) \rightarrow B(s) + C(g) \) (reaction: sigmoid flanked by plateaus on the trace) has been studied kinetically applying the Dave and Chopra method and DTG traces. The solid state reactions described followed first order kinetics. The kinetic data showed the very low value of \( Z \) for each of the solid state reaction in reference, concluding on the solid state reactions (the nonisothermal decomposition of polymetallic chelate of Zn (II), Co (II), Ni (II), and Cu (II) as slow reactions).

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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