

SYNTHESIS AND CHARACTERIZATION OF SOME HYDRAZINE DERIVATIVES
WITH α , β UNSATURATED ACIDS

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ABSTRACT : Some new metal cinnamate monohydrazinate, $M(\text{cin})_2\text{N}_2\text{H}_4$ ($M = \text{Co}$ or Zn), metal cinnamate dihydrazinates, $M(\text{cin})_2(\text{N}_2\text{H}_4)_2$ ($M = \text{Co}, \text{Ni}, \text{Zn}$ or Cd), metal crotonate dihydrazinates, $M(\text{crot})_2(\text{N}_2\text{H}_4)_2$ ($M = \text{Co}$ or Ni), nickel crotonate monohydrazinate monohydrate $\text{Ni}(\text{crot})_2\cdot\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and $\text{Cd}(\text{crot})_2(\text{N}_2\text{H}_4)_2\cdot\text{H}_2\text{O}$ have been prepared and characterized by physico – chemical studies. Electronic spectral data suggest that the octahedral environment around the central metal ion. The IR spectral data confirm the bridging bidentate coordination of hydrazine molecules ($\nu_{\text{N-N}}$ 976 – 959 cm^{-1}). The $\Delta\nu$ ($\nu_{\text{asy}} - \nu_{\text{sym}}$) separation suggest that the carboxyl group is monodentatively coordinated in metal cinnamate and crotonate dihydrazinate complexes, whereas monohydrazinate complexes show smaller $\Delta\nu$ separation, indicating chelate bidentate coordination of the carboxylate groups to the central metal ion. All the complexes undergo two or three steps exothermic or endothermic decomposition to give respective carboxylates through metal carboxylate intermediate. X – ray powder diffraction pattern reveal that complexes with same formulation possess isomorphism.

Key words: Physico–chemical studies; electronic spectral data; IR spectral data; X – ray powder diffraction

INTRODUCTION

Hydrazine complexes of the first row transition metal ions with a variety of carboxylic acids have been reported in the literature [12]. These include simple aliphatic monocarboxylic acids [11, 13, 14, 15], aliphatic dicarboxylic acids [3, 16, 8, 25, 4], aromatic mono and dicarboxylic acids [5, 6, 23, 24], aliphatic and aromatic hydroxyl acids [24, 26], halo acids [18], amino acids [19, 21] and heterocyclic carboxylic acids [10]. However hydrazine complexes of first row transition metal with unsaturated carboxylic acids are limited except maleate and fumarate derivatives [4]. The coordinating ability of the acids are also of interest which have two different donor sites for forming bond with metal ions, the double bond between the carbon atoms and the oxygen atoms of the carboxylate group. Hence an attempt has been made to study the metal hydrazine complexes of simple unsaturated acids like cinnamic and crotonic acids. In this paper the preparation, spectral and thermal properties of some new metal cinnamate monohydrazinates, metal cinnamate and crotonate dihydrazinates, metal crotonate monohydrazinate monohydrate and metal crotonate dihydrazinate monohydrate are reported.

EXPERIMENTAL**Preparation of Metal cinnamate monohydrazinates** **$M(\text{cin})_2\cdot\text{N}_2\text{H}_4$ ($M = \text{Co}$ (or) Zn)**

The cobalt and zinc complexes are prepared by the addition of an aqueous solution (50 mL) of hydrazine hydrate (1 mL, 0.02 mol) and cinnamic acid (0.74 g, 0.005 mol) to the corresponding aqueous solution (50 mL) of metal nitrate hexahydrates ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 0.73 g, 0.002 mol; $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 0.73 g, 0.002 mol). The complexes are precipitated immediately. They are washed with water, alcohol followed by diethyl ether and air dried.

Preparation of metal cinnamate dihydrazinates **$M(\text{cin})_2(\text{N}_2\text{H}_4)_2$ [M = Co, Ni, Zn (or) Cd]**

The cobalt and nickel complexes are prepared by the addition of an aqueous solution (50 mL) of hydrazine hydrate (0.5 mL, 0.001 mol) and cinnamic acid (0.74g 0.005 mol) to the corresponding aqueous solution (50 mL) of metal nitrate hexahydrates [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.73 g, 0.002 mol; $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.73 g, 0.002 mol]. The complexes are formed immediately. They are kept aside for an hour to digestion, then filtered and washed with water, alcohol followed by diethylether and air dried.

The zinc and cadmium complexes are prepared by the same procedure with the molar ratio of metal nitrate hydrates : cinnamic acid : hydrazine hydrate, respectively given in parentheses [For zinc, 0.7437 g, 0.002 mol: 0.74 g, 0.005 mol: 2 mL, 0.4 mol] [for cadmium 0.77 g, 0.002 mol: 0.74 g, 0.055 mol: 1 mL, 0.01 mol].

Preparation of metal crotonate dihydrazinates **$M(\text{crot})_2(\text{N}_2\text{H}_4)_2$ [M = Co (or) Ni]**

The cobalt, nickel crotonate dihydrazinates are prepared by heating aqueous suspension of the corresponding metal carbonates (CoCO_3 , 1 g, 0.008 mol; $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, 1 g, 0.002 mol) and crotonic acid (3.44 g, 0.03 mol) in 50 mL of water. It is filtered and cooled. To this resulting clear solution aqueous solution (50 mL) of hydrazine hydrate (2.5 mL, 0.05 mol) is added. Cobalt and nickel crotonate dihydrazinates are formed after few minutes. They are kept an hour for digestion, then filtered and washed with water, alcohol followed by diethylether and air dried.

Preparation of Nickel crotonate monohydrate monohydrate **$\text{Ni}(\text{crot})_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$**

Nickel crotonate is prepared by the same procedure as above. To this an aqueous solution (25 mL) of hydrazine hydrate (1.25 mL, 0.02 mol) is added. The complex is separated out after 10 minutes from the clear solution. Then it is kept aside half an hour for digestion, filtered and washed with water, alcohol followed by diethylether and air dried.

Preparation of Cadmium crotonate dihydrazinate monohydrate **$\text{Cd}(\text{crot})_2 \cdot (\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{O}$**

This complex is also prepared by the same procedure as above with molar ratio of CdCO_3 , 1 g, 0.006 mol: Crotonic acid, 3.44 g, 0.04 mol: hydrazine hydrate, 2.5 mL, 0.05 mol. The colourless spongy crystals of Cadmium complex formed slowly.

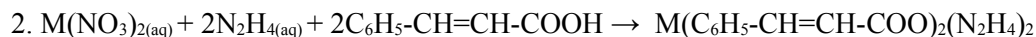
The complexes obtained as polycrystalline powders insoluble in water, alcohol, diethyl ether and other organic solvents, but decompose in dilute HCl. This is only to be expected these types of complexes prefer to exist in polymeric structures. All the complexes are stable in air and insensitive to light.

RESULTS AND DISCUSSION

Cobalt, nickel and cadmium cinnamate monohydrazinates, dihydrazinates are prepared by the reaction of the aqueous solution of the corresponding metal nitrate hydrate, aqueous solution of hydrazine hydrate and cinnamic acid.

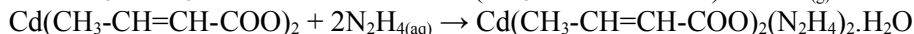
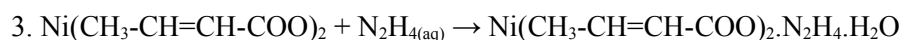
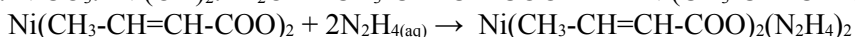
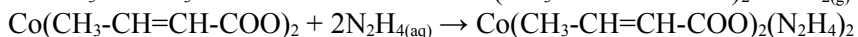


Where M = Co or Zn



+ 2HNO₃ Where M = Co, Ni, Zn or Cd

Metal crotonate complexes are prepared from the corresponding aqueous solution of metal crotonates and aqueous solution hydrazine hydrate. Metal crotonates are prepared from aqueous suspension of corresponding metal carbonates and crotonic acid.



All the metal hydrazine carboxylates prepared are insoluble in water, alcohol and other organic solvents. The compositions of these complexes are assigned on the basis of hydrazine and metal contents (Table 1)

Table 1. Analytical and Electronic Spectral Data

Compound	Analytical Data			Electronic Spectral Data	
	Hydrazine (%) Obsd. (Calcd.)	Metal (%) Obsd. (Calcd.)	Yield (%)	Absorption Maxima (cm ⁻¹)	Assignments
Co(cin) ₂ ·N ₂ H ₄	09.00 (08.31)	14.80 (15.31)	90	20000	⁴ T _{1g} (F) → ⁴ T _{1g} (P)
Co(cin) ₂ ·(N ₂ H ₄) ₂	14.90 (15.35)	14.00 (14.13)	90	20202	⁴ T _{1g} (F) → ⁴ T _{1g} (P)
Ni(cin) ₂ ·(N ₂ H ₄) ₂	15.00 (15.36)	14.10 (14.08)	90	13514, 20408	³ A _{2g} (F) → ³ T _{1g} (F), ³ A _{2g} (F) → ³ T _{1g} (P)
Zn(cin) ₂ ·N ₂ H ₄	08.49 (08.18)	16.10 (16.70)	83	-	-
Zn(cin) ₂ ·(N ₂ H ₄) ₂	14.50 (15.12)	15.00 (15.44)	85	-	-
Cd(cin) ₂ ·(N ₂ H ₄) ₂	13.70 (13.61)	23.60 (23.90)	82	-	-
Co(crot) ₂ ·(N ₂ H ₄) ₂	21.80 (21.83)	19.70 (20.11)	85	21053	⁴ T _{1g} (F) → ⁴ T _{1g} (P)
Ni(crot) ₂ ·(N ₂ H ₄) ₂	21.50 (21.85)	20.40 (20.04)	83	13158, 20408	³ A _{2g} (F) → ³ T _{1g} (F), ³ A _{2g} (F) → ³ T _{1g} (P)
Ni(crot) ₂ ·N ₂ H ₄ ·H ₂ O	11.10 (11.47)	20.90 (21.05)	90	-	-
Cd(crot) ₂ ·(N ₂ H ₄) ₂ ·H ₂ O	17.30 (17.56)	31.00 (30.84)	80	-	-

Electronic spectra

The electronic spectrum of the cobalt cinnamate monohydrate, cobalt cinnamate and crotonate dihydrazinates, display a broad band at 20000, 20202 and 21053 cm⁻¹ respectively (Table 1), which is assigned to the transition ⁴T_{1g}(F) → ⁴T_{1g}(P). This band and pink colour of the complex are indicative of the octahedrally coordinated Co(II) ion [8]. All nickel complexes exhibit two bands at 20408 and 13158-13154 cm⁻¹, which are attributed to ⁴T_{1g}(F) → ⁴T_{1g}(P), and ³A_{2g} → ³T_{1g}(P), respectively. These transitions are characteristics of octahedral environment around Ni(II) ion [8].

Infrared spectra

The important IR absorption frequencies of prepared complexes are studied and are assigned on the basis of earlier studies [22, 27, 2]. Mono hydrated cadmium crotonate dihydrazinate and nickel crotonate monohydrazinate displays a broad band in the region, 3680 – 3300 cm^{-1} , due to O-H stretching of water. The N-H stretching frequency of all the complexes appears in the region 3380 - 3148 cm^{-1} . The metal complexes show a band in the region 1663 -1636 cm^{-1} , which is assigned to the stretching frequency of C=C vibration of the unsaturated system [1]. There is no reduction or increase in the ν (C=C) band of the metal complexes indicate that the coordination does not take place between the π electron system of the C=C bond and the metal ion due to more effective coordinating property of carboxylate ions. In all the complexes, the carbonyl asymmetric and symmetric stretching frequencies are observed in the range, 1612-1541 and 1420-1384 cm^{-1} , respectively. The $\Delta\nu$ ($\nu_{\text{asy}} - \nu_{\text{sym}}$) separation is in between 288 - 180 cm^{-1} suggest that carboxylate group is monodentatively coordinated to the central metal ion [9] in metal cinnamate and crotonate dihydrazinate complexes, whereas the monohydrazinate complexes show small separation between asymmetric and symmetric stretching i.e., 160–147 cm^{-1} indicating chelate bidentate coordination of the carboxylate groups to the central metal ion [9]. The N-N stretching frequency of the complexes appears in the range, 976 - 959 cm^{-1} , confirming the bridging bidentate coordination of hydrazine molecules.

Thermal studies

The thermal decomposition patterns of all the complexes are listed in Table 2. The observed mass losses from TG coincide well with the theoretical mass losses. Thermogravimetric results are in good agreement with the DTA data. All the metal complexes yield their oxides as the final residue.

M(cin)₂.N₂H₄, Where M = Co or Zn

Both the complexes undergo two step decomposition through metal cinnamate intermediate. The first step, i.e., dehydrazination in cobalt compound is obtained as an exotherm, whereas in the zinc compound, it is observed as an endotherm. The variation in the thermal nature of transformation may be due to the catalytic activity difference of the metal ion in the complexes. In both the complexes, the disproportionation of the metal cinnamate intermediate decomposes exothermically yielding the respective metal oxide as the final residue. The CoO is formed with in 450°C observed from TG, whereas ZnO is formed only at 530°C.

Zn(cin)₂.(N₂H₄)₂

The thermograms of this complex show a distinct three step decomposition. In the first step, one of the hydrazine molecules is lost between 142-201°C. The corresponding peak in DTA is observed as an endotherm in contrast to nickel and cobalt complexes at 173°C. The zinc cinnamate monohydrazinate formed in the first step undergoes a further decomposition yields the second intermediate as zinc cinnamate. In the second step also, the thermal nature of transformation is endothermic, and observed at 219°C from DTA. The decomposition of zinc cinnamate takes place exothermically in the third step, giving zinc oxide as the final residue in the temperature range, 231-525°C.

Table 2. Thermal Decomposition Data

Compound	DTA Peak Temp./ ° C	Thermogravimetry (TG)		Decomposition Product
		Temp.range/ ° C	Mass loss(%) Obsd. (Calcd.)	
Co(cin) ₂ N ₂ H ₄ Mol. Wt : 387.31	208 (-)	188 – 212	08.50(08.31)	Co(cin) ₂ CoO
	415 (-)	212 – 450	80.00(80.65)	
Co(cin) ₂ .(N ₂ H ₄) ₂ Mol. Wt : 419.37	211 (-)	195 - 251	15.50(15.35)	Co(cin) ₂ Co ₂ O ₃
	426 (-)	251 - 470	60.00(60.45)	
Ni(cin) ₂ .(N ₂ H ₄) ₂ Mol. 419.13	246 (-)	222 - 256	15.00(15.36)	Ni(cin) ₂ NiO
	416 (-)	256 - 465	81.07(82.17)	
Zn(cin) ₂ N ₂ H ₄ Mol. Wt : 393.77	226 (+)	200 – 240	07.50(08.18)	Zn(cin) ₂ ZnO
	511 (-)	240 - 530	73.34(79.33)	
Zn(cin) ₂ .(N ₂ H ₄) ₂ Mol. Wt : 425.83	173 (+)	142 – 201	6.50(07.56)	Zn(cin) ₂ .N ₂ H ₄ Zn(cin) ₂ ZnO
	219 (-)	201 – 231	14.50(15.12)	
	505 (-)	231 – 525	80.00(80.55)	
Cd(cin) ₂ .(N ₂ H ₄) ₂ Mol. Wt : 472.85	193 (+)	166 – 297	14.00(13.61)	Cd(cin) ₂ Cd(CH ₃ COO) ₂ CdO
	333 (-)	297 – 395	51.00(51.02)	
	507 (-)	395 – 536	74.00(72.84)	
Co(crot) ₂ .(N ₂ H ₄) ₂ Mol. Wt : 295.23	181 (-)	158 – 233	22.00(21.83)	Co(crot) ₂ CoO _{1.5}
	383 (-)	233 – 398	69.24(71.91)	
Ni(crot) ₂ .(N ₂ H ₄) ₂ Mol. Wt : 284.99	231 (-)	207 – 237	26.00(21.85)	Ni(crot) ₂ NiO
	378 (-)	237 – 390	74.00(74.68)	
Ni(crot) ₂ N ₂ H ₄ H ₂ O Mol. Wt : 280.93	55 (+)	37 – 100	06.00(06.45)	Ni(crot) ₂ .N ₂ H ₄ NiO
	375 (-)	141 - 385	76.43(73.41)	
Cd(crot) ₂ .(N ₂ H ₄) ₂ .H ₂ O Mol. Wt : 366.71	66 (+)	50 – 77	05.50(04.94)	Cd(crot) ₂ .2N ₂ H ₄ Cd(crot) ₂ .N ₂ H ₄ CdO
	168 (+)	151 – 181	12.00(13.71)	
	454 (-)	181 - 474	62.93(64.98)	
Zn(crot) ₂ H ₂ O Mol. Wt : 255.57	193 (-)	166 – 201	08.00(07.10)	Zn(crot) ₂ ZnO
	485 (-)	201 – 496	71.43(68.15)	

Cd(cin)₂.(N₂H₄)₂

The TG-DTA curves of this complex shows a three step decomposition. Dehydrazination of two hydrazine molecules is observed endothermically in the first step. The unstable cadmium cinnamate gives cadmium acetate as the intermediate exothermically in the temperature range, 297-395°C. Our attempt to separate the cadmium acetate intermediate was unsuccessful since the decomposition is continuous and is proposed from the percentage weight loss which best fit with the TG curve. The proposed intermediate undergoes exothermic decomposition to give CdO as the end product

Ni(crot)₂. N₂H₄.H₂O

This compound decomposes in two steps. The dehydration in the first step at 37°C confirms the presence of water molecule as lattice water. The anhydrous hydrazinate is stable upto 140°C, then it is decomposed in a single step to yield nickel oxide with at 385°C.

Cd(crot)₂.(N₂H₄)₂.H₂O

This compound decomposes in three steps. The dehydration in the first step at 66°C (from DTA) confirms the presence of water molecules as a lattice water. The endothermic disproportionation of the anhydrous dihydrazinate loses its one molecule of hydrazine, yielding cadmium crotonate monohydrazinate, which on exothermic decomposition directly affords CdO as the final residue.

$\text{MX}_2(\text{N}_2\text{H}_4)_2$, where $\text{M}=\text{Co}$ or Ni and $\text{X} = \text{cinnamate}$ or crotonate .

The simultaneous TG-DTA curves of all the four complexes show two step decomposition. In the first step, of TG, dehydrazination of two hydrazine molecules occurs in the temperature range of 158-256°C. In DTA, the corresponding decomposition is observed as an exotherm within the temperature range of TG inflexion. The intermediate formed in all the complexes is the respective metal carboxylate. The metal carboxylate intermediates are not thermally stable, which undergo gradual decomposition exothermically to yield corresponding metal oxide as the end product.

In order to confirm the intermediates, end products proposed and the fueling nature of hydrazine, the TG-DTA analysis of zinc crotonate hydrate has been carried out, which is obtained as a stable product during the attempts to prepare the hydrazine derivatives. The water molecule is lost exothermically at 193°C, (from DTA), which shows the presence of water molecule as a coordinated one. In the second step, the anhydrous zinc crotonate continuously decomposes to yield zinc oxide as the final product, in the temperature range 201-496°C.

The formation of zinc oxide as the final residue authenticates the oxide end products in the hydrazine derivatives. It is worth mentioning that the reported simple cobalt and nickel cinnamates and crotonates yielded only their metal oxides as the final residue during thermal analysis [26]. However, the fueling nature of hydrazine is observed in the prepared hydrazine derivatives [26].

All the complexes the thermogravimetric analysis, thermogram is found to have increase in mass after the decomposition of the complex to the corresponding metal oxides, this may be due to decomposition of carbon particles, at the end of the thermal analysis. The TG – DTA pattern of the some prepared complexes are given in the figure 1 – 8 as examples.

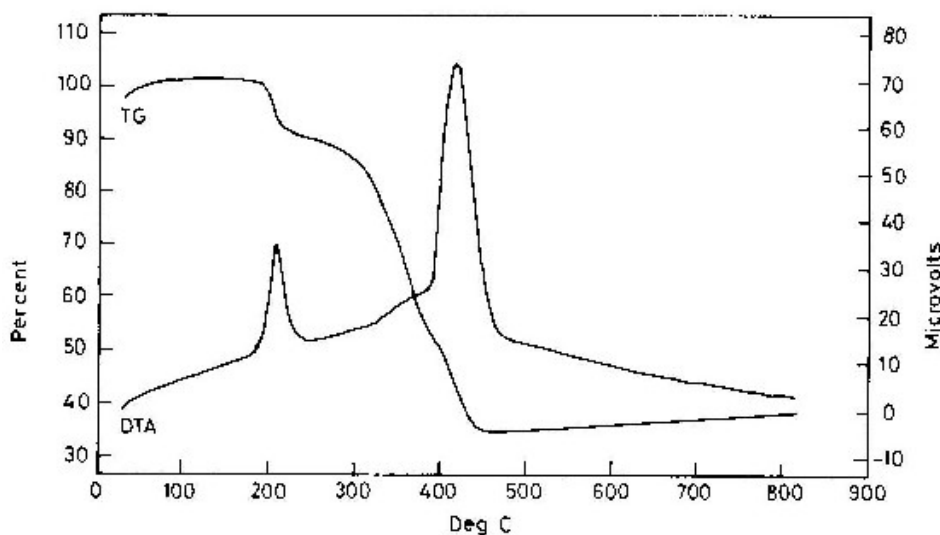


Fig 1. TG – DTA of $\text{Co}(\text{cin})_2\text{N}_2\text{H}_4$

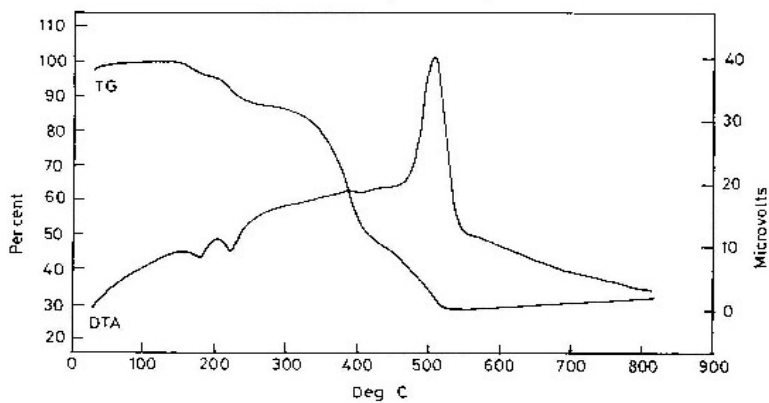


Fig 2. TG – DTA of $Zn(cin)_2 \cdot (N_2H_4)_2$

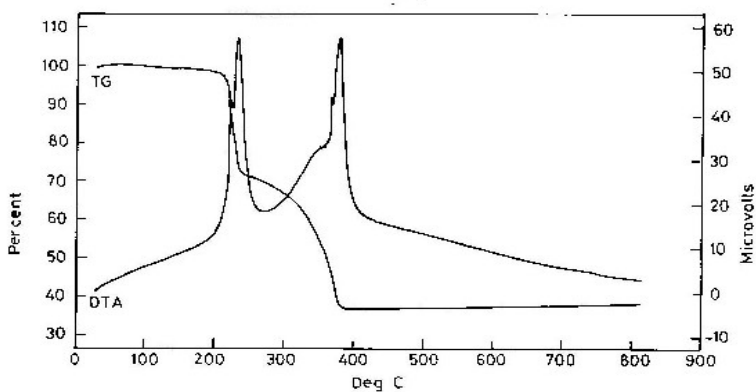


Fig 3. TG – DTA of $Ni(crot)_2 \cdot (N_2H_4)_2$

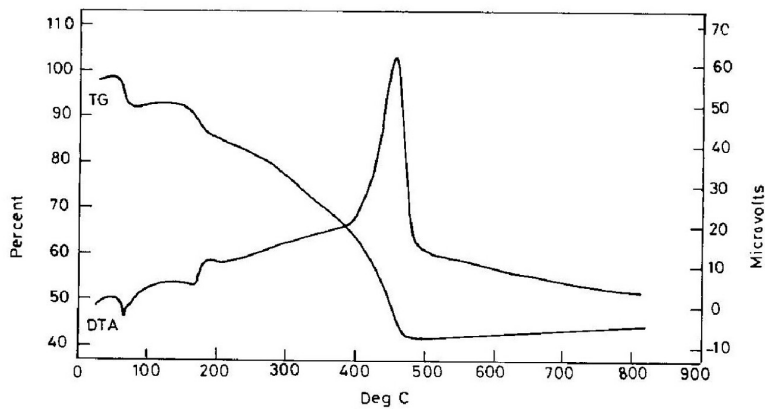


Fig 4. TG – DTA of $Cd(crot)_2 \cdot (N_2H_4)_2 \cdot H_2O$

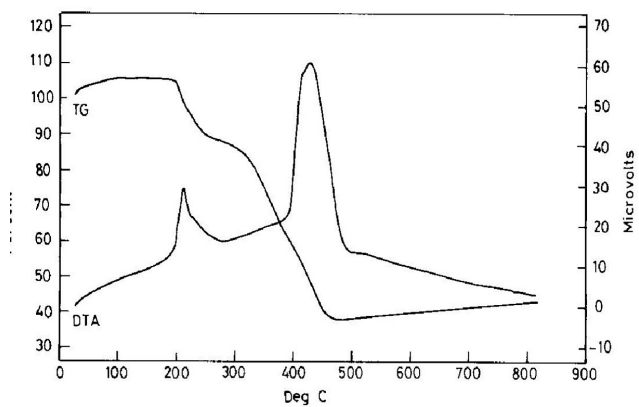


Fig 5. TG – DTA of $\text{Co}(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$

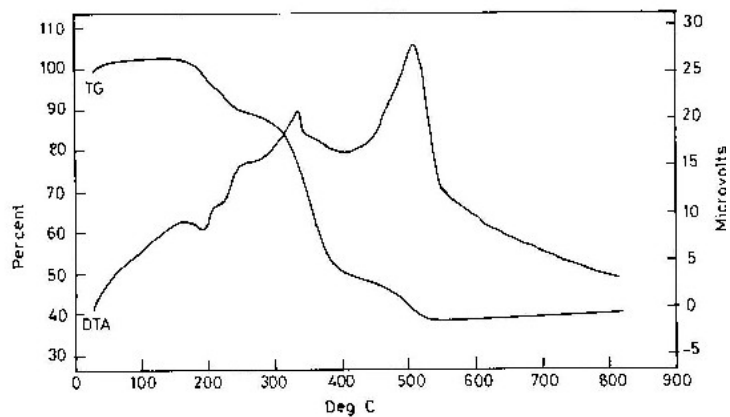


Fig 6. TG – DTA of $\text{Cd}(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$

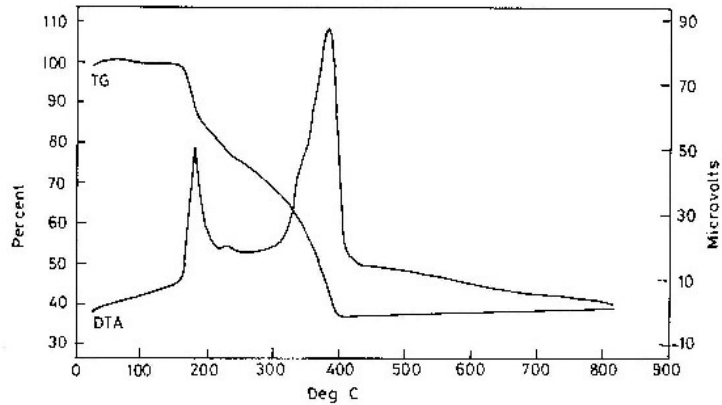


Fig 7. TG – DTA of $\text{Co}(\text{crot})_2 \cdot (\text{N}_2\text{H}_4)_2$

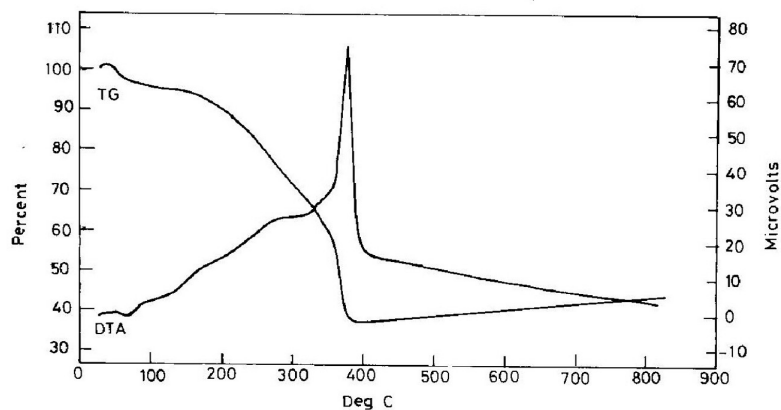


Fig 8. TG – DTA of $\text{Ni(crot)}_2\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$

X - ray diffraction studies

In order to compare and also to confirm the structural similarity among the complexes, the 'd spacing' of $\text{Co(cin)}_2\text{.(N}_2\text{H}_4)_2$ and $\text{Ni(cin)}_2\text{.(N}_2\text{H}_4)_2$ have been compared. Similar complexes have almost same values of d-spacing and number of peaks. Hence these are isomorphous in nature. The X – ray pattern of $\text{Co(cin)}_2\text{.(N}_2\text{H}_4)_2$ and $\text{Ni(cin)}_2\text{.(N}_2\text{H}_4)_2$ are given in fig 9.

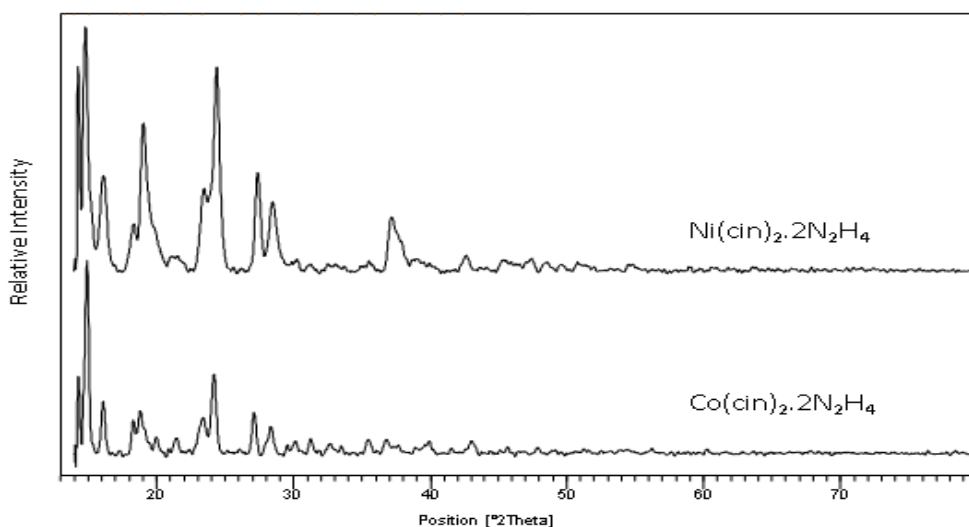


Fig 9. X – ray pattern of $\text{Co(cin)}_2\text{.(N}_2\text{H}_4)_2$ and $\text{Ni(cin)}_2\text{.(N}_2\text{H}_4)_2$

CONCLUSIONS

Coordination Geometry

The analytical and physicochemical studies suggest that, in these complexes hydrazine molecule is present as a bridging bidentate ligand. In monohydrazinate complexes, cinnamate and crotonate ions are seen to present as chelating bidentate ligand and in dihydrazinate complexes these are present as monodentate ligand.

The complexes are isolated only as polycrystalline powders. Hence, without crystal structure, it is very difficult to predict the environment of the metal in the complexes. Therefore six - coordination has been tentatively proposed for all the complexes with octahedral stereochemistry (fig 10 and 11). The insoluble nature of these complexes confirms the polymeric structure.

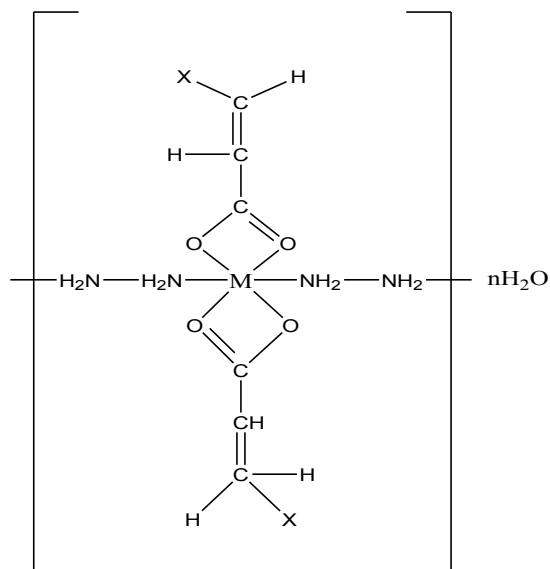


Fig 10. Polymeric structure $M(X-CH=CH-COO)_2.N_2H_4.nH_2O$
 Where $M = Co$ (or) Zn when $X = C_6H_5$ and $n = 0$
 $M = Ni$, when $X = CH_3$ and $n = 1$

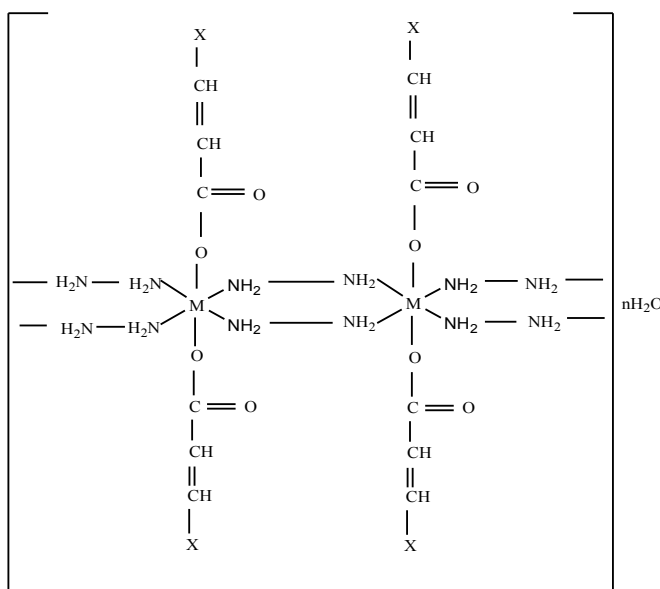


Fig 11. Polymeric structure of $M(X-CH=CH-COO)_2.2N_2H_4.nH_2O$
 Where $M = Co, Ni, Zn$ or Cd , when $X = C_6H_5$ and $n = 0$
 $M = Co, Ni$ when $X = CH_3$ and $n = 0$
 $M = Cd$ when $X = CH_3$ and $n = 1$

Further scope

Transition metal oxides are well established class of materials having diverse applications due to their useful properties like magnetic, electrical and catalytic applications. TG – DTA pattern of our prepared complexes confirm the formation of respective metal oxide as the final product. Further separation and characterization of these oxide may confirm they are formed in different nano scale, based on the various environment around the central metal ion.

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