

Preparation, characterization and thermal analysis of metal hydrazinocarboxylate derivatives

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Abstract. The reaction of hydrazinocarboxylic acid, N_2H_3COOH , with metal ions in the presence of hydrazine hydrate yields metal hydrazinocarboxylate derivatives like: $M(N_2H_3COO)_2 \cdot nH_2O$, $M = Mg, Ca$ and Mn ; $M(N_2H_3COO)_2(N_2H_4)_2$, $M = Mn, Fe, Co, Ni$ and Zn ; $N_2H_3M(N_2H_3COO)_3 \cdot H_2O$, $M = Fe, Co, Ni, Zn$; and $N_2H_3Mg(N_2H_3COO)_3$. Reaction conditions to obtain a desired product have been standardised and a probable reaction mechanism for the formation of different products proposed. Thermal analysis of the compounds has been investigated using simultaneous TG-DTG-DTA. Metal hydrazinocarboxylate derivatives decompose in air at low temperatures to the respective metal oxides.

Keywords. Metal hydrazinocarboxylates; infrared spectra; thermal analysis.

1. Introduction

Transition metal ions are known to react with hydrazine hydrate saturated with carbon dioxide to yield metal hydrazinocarboxylate derivatives like $M(N_2H_3COO)_2$, $M(N_2H_3COO)_2 \cdot nH_2O$, $M(N_2H_3COO)_2(N_2H_4)_2$ or $N_2H_3M(N_2H_3COO)_3 \cdot H_2O$. Hydrazinocarboxylic acid, N_2H_3COOH formed metathetically by the reaction of CO_2 with N_2H_4 appears to react with the metal ions to form these complexes. Ferrari *et al* (1965) and Braibanti *et al* (1966, 1967a, b, 1968, 1971) have reported the preparation, IR spectra and crystal structures of a number of these complexes. They have shown that the hydrazinocarboxylate anion, $N_2H_3COO^-$ acts as a bidentate group coordinating to the metal through both N and O atoms. Thermal decomposition of some metal hydrazinocarboxylate complexes has been studied and reported to yield finely divided metals or metal oxides (Macek *et al* 1976).

During the course of our studies on hydrazine derivatives we have reported the preparation and thermal properties of some metal hydrazinocarboxylate derivatives (Patil *et al* 1979a, b, 1983). They were prepared both by homogeneous and heterogeneous reactions. However, the exact reaction conditions to obtain a desired product do not appear to have been standardised. Present study is, therefore, aimed at standardising the reaction conditions to obtain any desired product and suggesting a possible reaction mechanism. Metal hydrazinocarboxylate derivatives are of interest as precursors to metal and metal oxides.

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2. Experimental

Hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) 99–100%, BDH, was used in all the reactions.

2.1 Preparation of hydrazinocarboxylic acid, $\text{N}_2\text{H}_3\text{COOH}$

(a) Hydrazine hydrate was saturated with carbon dioxide at room temperature until a white precipitate separated. The precipitate was dried and stored over P_2O_5 in a vacuum desiccator.

(b) Dissolution of 25 g of ammonium carbonate in 50 ml of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ gave a viscous liquid ($\text{N}_2\text{H}_5\text{COON}_2\text{H}_3$). Passing $\text{CO}_2(g)$ through this resulted in the formation of a white solid which was dried and stored over P_2O_5 in a vacuum desiccator.

The chemical analysis and IR spectrum of the white solid correspond to that of $\text{N}_2\text{H}_3\text{COOH}$. A 5% solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was used in the preparation of metal hydrazinocarboxylate hydrates and hydrazinates. In the case of hydrazinium derivatives a 15% solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was employed.

2.2 Preparation of metal hydrazinocarboxylate hydrates and hydrazinates

An aqueous solution containing metal ions like Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} or Zn^{2+} (25 ml, 0.4 M) was treated with a 5% solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ until the precipitate formed initially just dissolved. The clear solution thus obtained was kept open to the atmosphere. Crystalline solids separated from the solution within a couple of days. The composition of the crystals was fixed by chemical analysis to be $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$, $\text{M} = \text{Mg, Ca and Mn}$; and $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 (\text{N}_2\text{H}_4)_2$, $\text{M} = \text{Mn, Fe, Co, Ni and Zn}$ (table 1). Manganese hydrazinocarboxylate hydrazinate, $\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$ was obtained by treating a fine powder of $\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

2.3 Preparation of hydrazinium metal hydrazinocarboxylate derivatives

An aqueous solution containing metal ions like Fe^{2+} , Co^{2+} , Ni^{2+} or Zn^{2+} (25 ml, 0.4 M) was treated with a 15% solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ until the precipitate formed initially just dissolved. The resulting clear solution was left open to atmosphere. Beautiful crystals separated from the solution in 3–4 days. The composition of the crystals was fixed by chemical analysis to be $\text{N}_2\text{H}_5\text{M}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$, $\text{M} = \text{Fe, Co, Ni and Zn}$ (table 1).

Hydrazinium magnesium hydrazinocarboxylate, $\text{N}_2\text{H}_5\text{Mg}(\text{N}_2\text{H}_3\text{COO})_3$ was obtained by dissolving magnesium powder in the 15% solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. The complex was precipitated by the addition of alcohol.

2.4 Analysis

The metal content in the complexes were determined by EDTA complexometric titration. Hydrazine content was estimated volumetrically using 0.025 M KIO_3 solution under Andrews' conditions (Vogel 1961).

2.5 Physicochemical studies

Infrared spectra of the complexes were recorded as nujol mulls using a Perkin Elmer 781 Spectrophotometer. Simultaneous TG-DTG-DTA of the samples were recorded using a

Table 1. Chemical analysis of metal hydrazinocarboxylate derivatives.

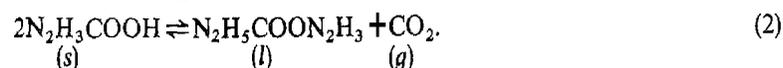
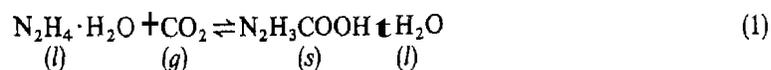
Compound	% of Metal		% of Hydrazine	
	Observed	Required	Observed	Required
Mg(N ₂ H ₃ COO) ₂ (H ₂ O) ₂	11.44	11.55	30.24	30.43
Ca(N ₂ H ₃ COO) ₂ H ₂ O	19.12	19.26	30.64	30.75
Mn(N ₂ H ₃ COO) ₂ (H ₂ O) ₂	22.75	22.80	26.46	26.56
Mn(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	20.22	20.42	47.32	47.59
Fe(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	20.70	20.69	47.50	47.47
Co(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	21.60	21.58	46.40	46.89
Ni(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	21.48	21.52	46.23	46.93
Zn(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	23.23	23.39	45.38	45.81
N ₂ H ₅ Mg(N ₂ H ₃ COO) ₃	7.99	8.01	43.00	42.62
N ₂ H ₅ Fe(N ₂ H ₃ COO) ₃ · H ₂ O	16.32	16.82	38.64	38.57
N ₂ H ₅ Co(N ₂ H ₃ COO) ₃ · H ₂ O	17.48	17.59	38.11	38.21
N ₂ H ₅ Ni(N ₂ H ₃ COO) ₃ · H ₂ O	17.50	17.58	38.20	38.28
N ₂ H ₅ Zn(N ₂ H ₃ COO) ₃ · H ₂ O	19.08	19.14	37.56	37.49

TGD-5000 RH. thermobalance of ULVAC-RIKO, Japan. All the experiments were carried out using 4-5 mg samples under ambient conditions. The heating rate employed was 20°C/min. The decomposition/combustion residues of the complexes were characterized by x-ray powder diffraction patterns recorded on a Philips PW 1050/70 diffractometer using CuK α and CoK α radiation.

3. Results and discussion

3.1 Hydrazinocarboxylic acid, N₂H₃COOH

Stolle and Hoffman (1904) have reported the formation of hydrazinocarboxylic acid, N₂H₃COOH by passing a current of CO₂ through a well cooled solution of hydrazine. The acid, N₂H₃COOH, was reported to decompose partially with the evolution of CO, when heated (~ 90°C) to give a viscous liquid whose composition was not exactly known. Presently, we were able to prepare N₂H₃COOH not only by passing a current of CO₂ through N₂H₄ · H₂O at room temperature but also by the reaction of CO, with N₂H₅COON₂H₃ prepared by dissolving ammonium carbonate in N₂H₄ · H₂O (Patil *et al* 1979b). Thus the following equilibrium appears to exist in the N₂H₄ · H₂O-CO₂ reaction.



Hydrazinocarboxylic acid (carbamic acid) is highly hygroscopic and should be stored over P₂O₅ or H₂SO₄ in a vacuum desiccator. It dissolves in water with dissociation as shown in (1). The acid was characterized by chemical analysis (% N₂H₄-observed 44.55, required 44.74) and infrared spectra (figure 1). Characteristic infrared absorption bands of N₂H₃COO⁻ group are seen at 3220, 1650, 1545, 1255, 1110, 995, 820, 770 and

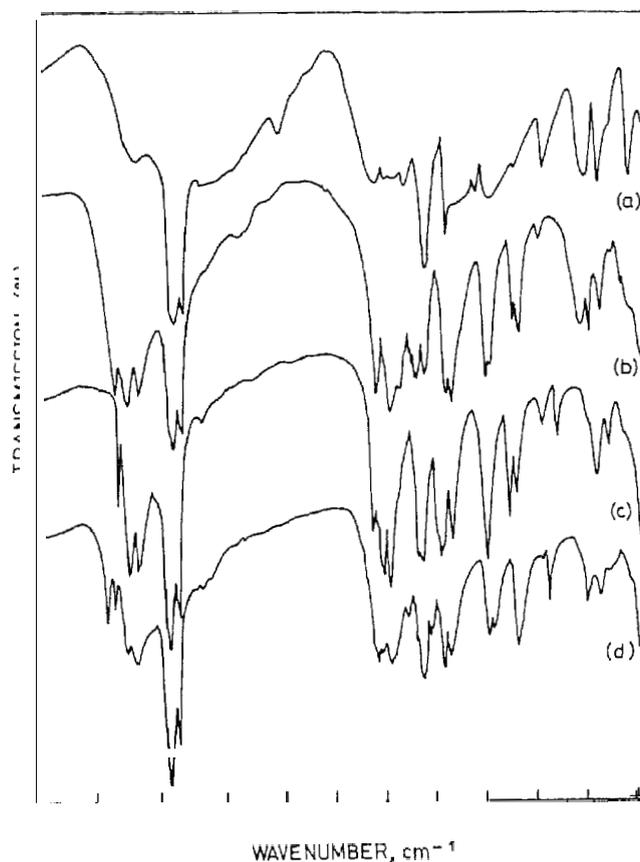


Figure 1. Infrared absorption spectra of (a) $\text{N}_2\text{H}_3\text{COOH}$, (b) $\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2(\text{H}_2\text{O})_2$, (c) $\text{Co}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$, (d) $\text{N}_2\text{H}_5\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$.

640 cm^{-1} . The TG-DTG-DTA curve of $\text{N}_2\text{H}_3\text{COOH}$ (figure 2) shows a two-step decomposition. The first step with a weight loss of 15% could be attributed to the partial decomposition of $\text{N}_2\text{H}_3\text{COOH}$ to $\text{N}_2\text{H}_5\text{COON}_2\text{H}_3$ with the evolution of CO_2 as in (2). The corresponding reaction in DTA is seen as a broad endotherm at 107°C probably due to the combination of melting and decomposition. In the second step (100% weight loss) the resulting viscous liquid $\text{N}_2\text{H}_5\text{COON}_2\text{H}_3$ volatilizes with decomposition.

3.2 Mechanism

The reaction of metal ions with $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ gave $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$, $\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$ and/or $\text{N}_2\text{H}_5\text{M}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ type complexes. It is interesting to note that dilute solutions of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ gave either hydrates or hydrazinates and concentrated solutions (15%) gave hydrazinium complexes. Since the solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ essentially contains N_2H_5^+ , $\text{N}_2\text{H}_3\text{COO}^-$, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and H^+ species, one can write the following stoichiometric reactions for the various complexes formed.

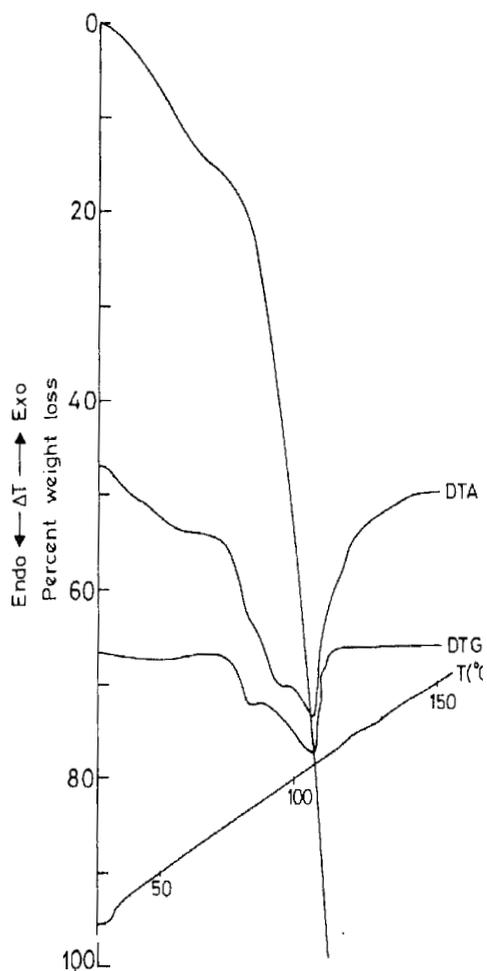
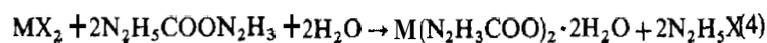
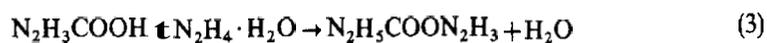
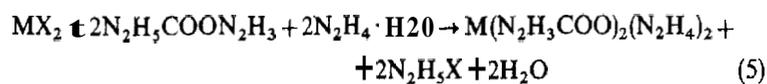


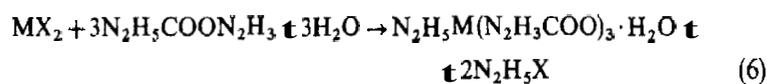
Figure 2. Simultaneous TG-DTG-DTA of N_2H_3COOH .



M = Mg, Ca and Mn.

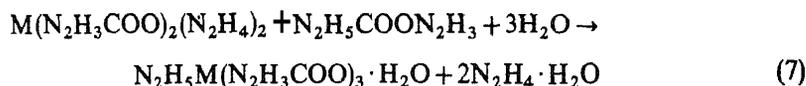


M = Fe, Co, Ni and Zn.



M = Fe, Co, Ni and Zn.

Thus, metal ions react with a dilute solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ to yield either $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ or $\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$. Only transition metal ions appear to form both hydrazinate and hydrazinium complexes. Hydrazinate complexes initially formed appear to react with excess of ligand (in concentrated solutions) to yield the corresponding hydrazinium salts as shown below:



This fact was confirmed by treating hydrazinate complexes with the ligand. However, manganese does not form $\text{N}_2\text{H}_5\text{Mn}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$. The calcium salt appears to be unique in that it forms only monohydrate, $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ whereas magnesium forms $\text{N}_2\text{H}_5\text{Mg}(\text{N}_2\text{H}_3\text{COO})_3$ by the dissolution of the metal.

3.3 Infrared spectra

Infrared spectra of metal hydrazinocarboxylates have been studied and important IR absorption frequencies assigned (Patil *et al* 1983; Braibanti *et al* 1968). Typical IR spectra of $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$ and $\text{N}_2\text{H}_5\text{M}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ are shown in figure 1. As mentioned earlier, the $\text{N}_2\text{H}_3\text{COO}^-$ group acts as a bidentate ligand and coordinates to the metal through both the N and the O atoms forming a 5-membered ring. The characteristic N–N stretching frequency of bidentate $\text{N}_2\text{H}_3\text{COO}^-$ is seen in the region $990\text{--}1015\text{ cm}^{-1}$ in all the complexes. The metal ions in all these complexes have octahedral coordination. The octahedra is completed by the two water molecules in $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$; and by the two monodentate N_2H_4 groups in $\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$. Infrared spectra of the hydrazinates clearly show $\nu_{\text{N-N}}$ of monodentate $\text{N}_2\text{H}_4 \sim 925\text{ cm}^{-1}$ in addition to $\nu_{\text{N-N}}$ of $\text{N}_2\text{H}_3\text{COO}^- \sim 1000\text{ cm}^{-1}$. In the case of hydrazinium complexes, $\text{N}_2\text{H}_5\text{M}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ the octahedra around the metal atom involve 3 bidentate $\text{N}_2\text{H}_3\text{COO}^-$ groups, neither N_2H_5^+ nor H_2O is coordinated to the metal. The characteristic IR frequency of ionic N_2H_5^+ is seen $\sim 965\text{ cm}^{-1}$ in all these complexes.

3.4 Thermal analysis

The results of TG-DTG-DTA of $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$, $\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$ and $\text{N}_2\text{H}_5\text{M}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ are summarized in tables 2, 3 and 4 respectively. Some representative thermograms are shown in figure 3–5.

3.4a Metal hydrazinocarboxylate hydrates: All the metal hydrazinocarboxylate hydrates [$\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$, $\text{M} = \text{Mg, Ca and Mn}$] lose the water of hydration initially to yield the corresponding metal hydrazinocarboxylates. The dehydration takes place at fairly high temperature ($100\text{--}200^\circ\text{C}$) indicating the presence of coordinated water molecules. The anhydrous metal hydrazinocarboxylates decompose exothermically to yield the corresponding metal oxides. The decomposition of the calcium salt shows 4 distinct steps corresponding to the formation of $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2$, CaC_2O_4 , CaCO_3 and CaO respectively. Based on this observation and our early study (Patil *et al* 1979b) the intermediates in the decomposition of both $\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2$ and $\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2$ could be the corresponding metal oxalates. The composition of

Table 2 Thermal analysis of metal hydrazinocarboxylate hydrate.

Compound	DTA peak temperature (°C)	Step no.	Temperature range (°C)	Thermogravimetry		Products
				Total weight loss (%)		
				Observed	Required	
$\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2(\text{H}_2\text{O})_2$	170 (endo)	1	150–180	18.00	17.11	$\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2$
	325 (exo) } 380 (exo) }	2	180–485	81.00	80.83	MgO
$\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2\text{H}_2\text{O}$	135 (endo)	1	115–152	8.60	8.65	$\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2$
	281 (exo) } 308 (exo) }	2	152–310	38.20	38.44	CaC_2O_4
	345 (exo) } 420 (exo) }	3	310–700	51.80	51.90	CaCO_3
	720 (endo)	4	700–930	73.00	73.04	CaO
$\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2(\text{H}_2\text{O})_2$	130 (endo)	1	110–170	15.80	14.94	$\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2$
	170 (exo) 180 (exo)	2	170–205	29.50	27.39	$\text{MnC}_2\text{O}_4 \cdot \text{N}_2\text{H}_4$
	200 (exo)	3	205–300	69.90	70.55	MnO

Table 3. Thermal data of metal hydrazinocarboxylate hydrazinates.

Compound	DTA peak temperature (°C)	Step no.	Temperature range (°C)	Thermogravimetry		Products
				Total weight loss (%)		
				Observed	Required	
Mn(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	175 (exo) 195 (exo)	1	130-290	72.80	73.68	MnO
Fe(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	135 (exo) 175 (exo)	1	130-205	70.10	70.41	Fe ₂ O ₃
Co(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	190 (exo) 200 (exo)	1	210-269	70.00	70.59	Co ₃ O ₄
Ni(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	195 (exo) 228 (exo)	1	187-200	72.00	72.60	NiO
Zn(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	200 (exo) 310 (exo)	1 2	155-250 250-325	32.00 71.90	33.64 70.87	ZnC ₂ O ₄ ·N ₂ H ₄ ZnO

Table 4. Thermal analysis of hydrazinium metal hydrazinocarboxylates.

Compound	DTA peak temperature (°C)	Step No.	Thermogravimetry			
			Temperature range (°C)	Total weight loss (%)		Products
				Observed	Required	
$N_2H_5Fe(N_2H_3COO)_3 \cdot H_2O$	165 (exo) } 180 (exo) }	1	145–220	76.00	75.93	Fe_2O_3
$N_2H_5Co(N_2H_3COO)_3 \cdot H_2O$	175 (exo) 245 (exo)	1 2	170–245 245–280	36.50 76.10	37.61 76.03	$CoC_2O_4 \cdot 2N_2H_4$ CO_3O_4
$N_2H_5Ni(N_2H_3COO)_3 \cdot H_2O$	182 (exo) 193 (exo) } 220 (exo) }	1 2	170–210 210–385	48.00 76.00	46.60 77.67	$NiC_2O_4 \cdot N_2H_4$ NiO
$N_2H_5Zn(N_2H_3COO)_3 \cdot H_2O$	145 (endo) 195 (exo) 240 (exo)	1 2 3	70–165 165–215 215–390	18.00 53.00 76.00	18.16 55.07 76.17	$Zn(N_2H_3COO)_2(N_2H_4)_2$ ZnC_2O_4 ZnO
$N_2H_5Mg(N_2H_3COO)_3$	120 (endo) 320 (exo) 390 (endo)	1 2 3	50–135 135–343 343–418	36.00 72.20 86.00	37.52 701.3 85.72	$MgC_2O_4 \cdot 2N_2H_4$ $MgCO_3$ MgO

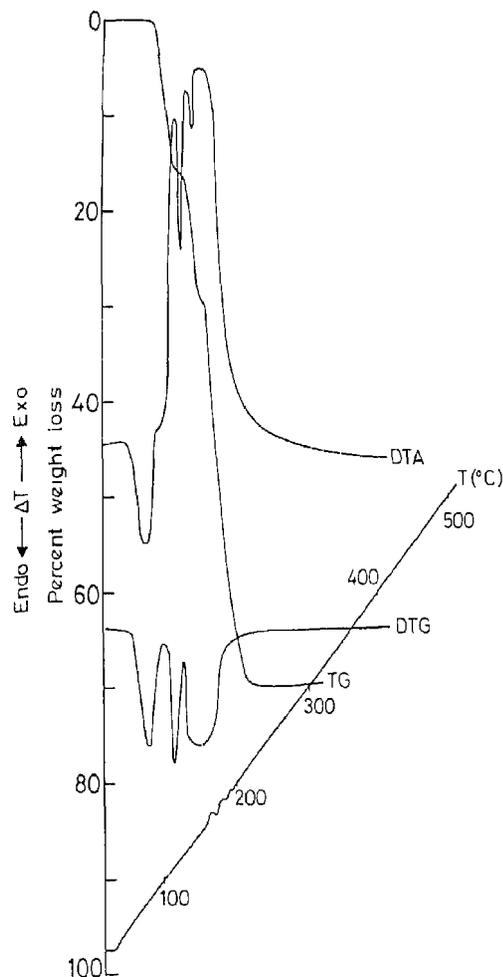


Figure 3. Simultaneous TG-DTG-DTA of $\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2(\text{H}_2\text{O})_2$.

the final metal oxides was fixed by the observed weight loss in TG and their characteristic x-ray powder diffraction patterns.

3.4b Metal hydrazinocarboxylate hydrazinates: All the hydrazinate complexes $[\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2]$, $\text{M} = \text{Mn, Fe, Co, Ni}$ and Zn except zinc show single step decomposition in TG-DTG. However, DTA shows two exotherms probably corresponding to the decomposition of coordinated hydrazine followed by the decomposition of metal hydrazinocarboxylates to the respective metal oxides. The zinc complex appears to decompose through $\text{ZnC}_2\text{O}_4 \cdot \text{N}_2\text{H}_4$. The decomposition products (metal oxides) were identified by their x-ray powder diffraction patterns.

3.4c Hydrazinium metal hydrazinocarboxylate derivatives: Thermal decomposition of these complexes $[\text{N}_2\text{H}_5\text{M}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}]$, $\text{M} = \text{Fe, Co, Ni}$ and Zn , and $[\text{N}_2\text{H}_5\text{Mg}(\text{N}_2\text{H}_3\text{COO})_3]$ show one to three steps. The iron complex shows a single step in TG-DTG and two exotherms in DTA. Both cobalt and nickel complexes show 2-step

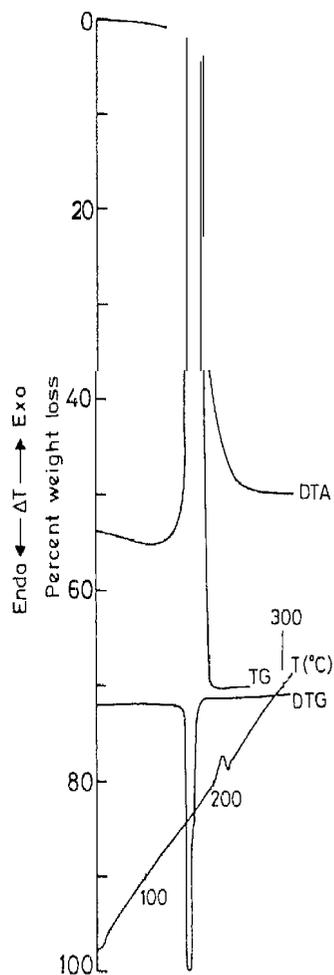


Figure 4. Simultaneous TG-DTG-DTA of $\text{Co}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$.

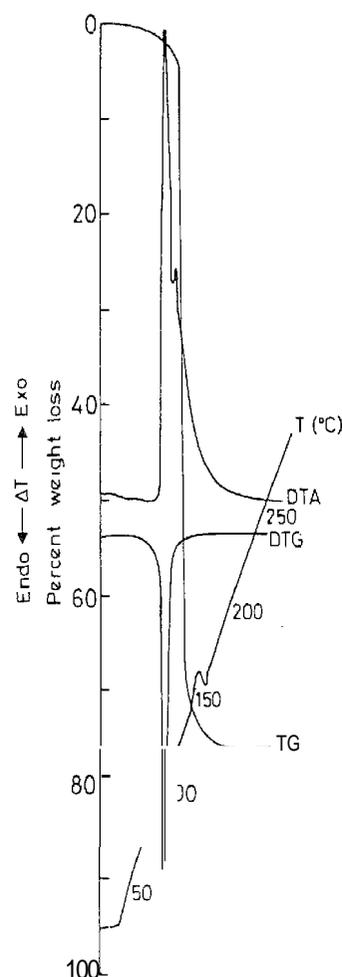


Figure 5. Simultaneous TG-DTG-DTA of $\text{N}_2\text{H}_5\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$.

decomposition in TG-DTG and two exotherms in DTA. The observed weight loss after the first step corresponds to the formation corresponding to the metal oxalate hydrazinate, $\text{MC}_2\text{O}_4 \cdot \text{N}_2\text{H}_4$ intermediate. The decomposition of zinc and magnesium complexes involve 3-steps each. Possible intermediates could be $\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$, $\text{MC}_2\text{O}_4 \cdot \text{N}_2\text{H}_4$, MC_2O_4 , etc. Final residues of decomposition corresponds to the respective metal oxides as confirmed by x-ray powder diffraction patterns.

4. Conclusions

Metal hydrazinocarboxylate derivatives like $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$, $\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$ or $\text{N}_2\text{H}_5\text{M}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ are formed by the reaction of metal ions with $\text{N}_2\text{H}_3\text{COOH}$ in the presence of hydrazine hydrate. The following general observations emerge from the present study.

- (i) None of the metal ions studied form all the three types of hydrazinocarboxylate derivatives.
- (ii) Transition metal ions form hydrazinate $[M(N_2H_3COO)_2(N_2H_4)_2]$ and hydrazinium $[N_2H_5M(N_2H_3COO)_3 \cdot H_2O]$ complexes. Though manganese forms the hydrazinate it does not form the hydrazinium complex.
- (iii) Magnesium, calcium and manganese hydrazinocarboxylates form hydrated complexes. Only $Mn(N_2H_3COO)_2 \cdot 2H_2O$ when treated with $N_2H_4 \cdot H_2O$ yields the corresponding hydrazinate, $Mn(N_2H_3COO)_2(N_2H_4)_2$. Magnesium, however, gave anhydrous hydrazinium hydrazinocarboxylate, $N_2H_5Mg(N_2H_3COO)_3$.
- (iv) Transition metal hydrazinocarboxylate derivatives decompose in air at low temperature (100–200°C) to the respective metal oxides.

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