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ACETATE AND MALONATE COMPLEXES OF COBALT(II), NICKEL(II) AND ZINC(II) WITH HYDRAZINIUM CATION
Preparation, spectral and thermal studies

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Abstract

The hydrazinium(1+) metal acetates and malonate dihydrates of the molecular formula $[(N_2H_5)_2M(CH_3COO)_4]$ and $(N_2H_5)_2[M(OOCCH_2COO)_2(H_2O)_2]$ respectively, where M=Co, Ni or Zn, have been prepared and characterized by chemical analyses, conductance, magnetic, spectral, thermal and X-ray powder diffraction studies. The magnetic moments and electronic spectra indicate that these complexes are of high-spin octahedral variety. The infrared spectra show that the hydrazinium ions are coordinated in the case of acetate complexes, whereas in the malonate complexes the hydrazinium ions are out side the coordination sphere. These complexes undergo exothermic decomposition in the temperature range 150–450°C to give the respective metal oxide as the final residue. The X-ray powder diffraction patterns of the malonate complexes indicate isomorphism among them.

Keywords: complexes, metal oxides, thermal analysis, XRD

Introduction

Metal complexes containing positively charged ligand are rare in contrast with those containing negatively charged and neutral ligands. Hydrazinium(1+) cation, $N_2H_5^+$, is one such positively charged ligand which is capable of coordinating with metal ions due to the presence of lone pair. The increasing interest in the metal complexes containing $N_2H_5^+$ ion are due to their structure and thermal reactivity, since the $N_2H_5^+$ moiety may either coordinate to the metal ion or be outside the coordination sphere as counter ion.

Despite a large number of hydrazinium metal complexes are known with a variety of anions such as fluoride [1, 2], chloride [3–5], thiocyanate [6], sulfate [7, 8] and hydrazidocarboxylate [9, 10], similar complexes with aliphatic carboxylates as anions are rare, except a few [11–16]. In most of the cases the bis- or tris-hydrazine metal carboxylates are precipitated instead of hydrazinium complexes. Hence, specific reaction conditions are to be maintained for the preparation of the hydrazinium complexes. In the carboxylic acid system the only known hydrazinium complexes

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are the hydrates of hydrazinium metal formate [15], oxalate [11–13] and ethylenediaminetetraacetate [14]. Though the preparation, structure and thermal properties of bis-hydrazine transition metal formates [17], acetates [18] and malonates [19] and tris-hydrazine metal glycinates and glycolates [20] have been reported, the corresponding hydrazinium derivatives are not known. In this paper, we wish to report the preparation, spectral and thermal properties of some new hydrazinium metal acetates and malonate dihydrates.

Experimental

All the chemicals used were of Analar grade; hydrazine hydrate (99–100%) and glacial acetic acid (99%) were used as received. The solvents were distilled prior to use. Hydrazinium cobalt hydrazidocarboxylate monohydrate, $N_2H_5[Co(N_2H_3COO)_3]\cdot H_2O$ was obtained by the reported method [9].

Preparation of the complexes

Hydrazinium metal acetates

Hydrazinium metal acetate complexes were prepared by adding an aqueous solution (20 mL) of hydrazinium acetate (1.84 g, 0.02 mol) to an aqueous solution (20 mL) of respective metal nitrate hexahydrate (0.01 mol). The resulting solution was acidified by adding an aqueous solution (20 mL) of acetic acid (1.2 mL, 0.02 mol) and refluxed on a water bath for about 8 h. The final solution was concentrated on a water bath to about 20 mL and kept in a vacuum desiccator for crystallization. The compound separated from the solution after 2–3 days was removed, washed with alcohol and then dried over P_2O_5. The complexes are water soluble and insoluble in alcohol and most of the organic solvents. The compounds are hygroscopic and hence stored in vacuum desiccator over P_2O_5.

The cobalt complex was also prepared by adding a fine powder of hydrazinium cobalt hydrazidocarboxylate monohydrate, $N_2H_5[Co(N_2H_3COO)_3]\cdot H_2O$, to a dilute aqueous solution of acetic acid. During the addition, the complex decomposed in acetic acid with the evolution of carbon dioxide. The addition was continued till the solution became neutral. Then the resulting solution of *pH* 7 was allowed to stand at room temperature and the red compound separated after 2–3 days was removed, washed with alcohol and dried in vacuum desiccator over P_2O_5. Our attempts to prepare the corresponding nickel and zinc complexes by this method were unsuccessful and always resulted in the bis-hydrazine metal acetates, $M(CH_3COO)_3(N_2H_4)_2$ where M=Ni or Zn.

Preparation of hydrazinium metal malonate dihydrates

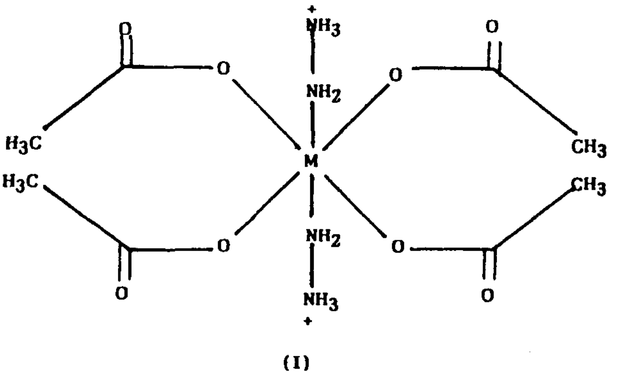
An aqueous solution (25 mL) of metal nitrate hexahydrate (0.01 mol) was added slowly with constant stirring to an aqueous solution (25 mL) of a mixture of malonic acid (4.08 g, 0.04 mol) and hydrazine hydrate (4 mL, 0.08 mol). The resulting clear solution ($pH \approx 6$–7) was allowed to crystallize at room temperature. The crystals separated after two to three days were filtered, washed with water and then with alcohol and dried in air. These complexes are insoluble in water and most of the organic solvents.

Physico-chemical techniques

The composition of the complexes was determined by chemical analyses. The metal content was determined by EDTA complexometric titration after decomposing a known weight of the sample with concentrated nitric acid [21]. The hydrazine content was determined volumetrically using 0.025 *M* KIO_3 solution under Andrews' conditions [21]. The conductance measurements were carried out at room temperature in water using a century digital conductivity meter model CC 601 and dip-type cell with a smooth platinum electrode. Room temperature magnetic moments were carried out by Gouy's method using $Hg[Co(SCN)_4]$ as the calibrant. Diamagnetic corrections were applied using Pascal's constants. Electronic spectra of the acetate complexes were recorded on a Hitachi Perkin Elmer 20/200 recording spectrophotometer using water as a solvent. The solid state absorption spectra of the malonate complexes in nujol mull were recorded on Shimadzu UV-visible 240A spectrophotometer. Infrared spectra were recorded on a Perkin Elmer spectrophotometer model 597 using KBr disc in the range 4000–400 cm^{-1}. Simultaneous TG–DTA of the acetate complexes were carried out using a Natzsch Thermal Analyser STA-409. For the malonate complexes the simultaneous TG-DTA experiments were recorded using a STA-1500 version V_4·30 Thermal Analyser. The thermal analyses were carried out in static air with the heating rate of 10°C min^{-1} using aluminium crucible as sample holder and Al_2O_3 as reference material. About 10–15 mg of the samples were used to carry out the thermal experiments. The X-ray powder diffraction of the malonate complexes were recorded using a Philips X-ray diffractometer model PW 1050/70 using CuK_α radiation.

Results and discussion

The hydrazinium metal acetates were prepared by the reaction of corresponding metal nitrate hexahydrate with an aqueous solution of hydrazinium acetate in 1:2 ratio, in the presence of acetic acid. The reaction may be represented as follows:



(I)

Structure of I $[(N_2H_5)_2M(CH_3COO)_4]$

$$M(NO_3)_2{\cdot}6H_2O + 2CH_3COON_2H_5 + 2CH_3COOH \rightarrow [(N_2H_5)_2M(CH_3COO)_4] + 2HNO_3 + 6H_2O$$

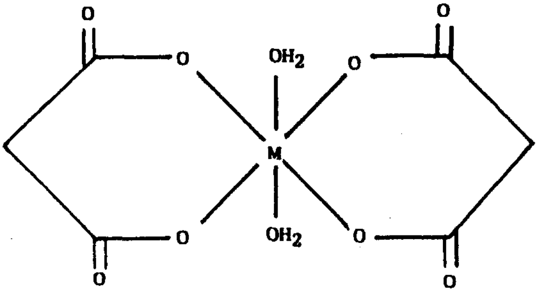
where M=Co, Ni or Zn.

The cobalt compound was also prepared by the reaction of hydrazinium cobalt hydrazidocarboxylate monohydrate and dilute acetic acid. The reaction can be written as follows:

$$N_2H_5[Co(N_2H_3COO)_3]{\cdot}H_2O + 4CH_3COOH \rightarrow [(N_2H_5)_2Co(CH_3COO)_4] + 2N_2H_4 + 3CO_2 + H_2O$$

The reaction of malonic acid and hydrazine hydrate in 1:1 ratio resulted in hydrazinium hydrogenmalonate. Our attempt to prepare the dihydrazinium malonate by reacting one part of malonic acid with two parts of hydrazinium hydrate was not successful and resulted in the hydrazinium hydrogenmalonate salt. When this salt was used as a ligand in the preparation of complexes, only the metal malonates were formed and hence, though the dihydrazinium malonate has not been isolated in solid state, the aqueous solution containing a 1:2 mixture of malonic acids and hydrazine hydrate was used as the ligand.

The hydrazinium metal malonate dihydrates have been prepared by the reaction of metal nitrate hexa hydrates with the ligand solution in 1:4 ratio. The reaction may be represented as follows:



(II)

Structure of II $[M(OOCCH_2COO)_2(H_2O)_2]^{2-}$

$$M(NO_3)_2{\cdot}6H_2O + 4CH_2(COOH)_2 + 8N_2H_4{\cdot}H_2O \rightarrow (N_2H_5)_2[M(OOCCH_2COO)_2(H_2O)_2] + 2CH_2(COON_2H_5)_2 + 2N_2H_5NO_3 + 12H_2O$$

where M=Co, Ni or Zn.

The chemical analyses of the complexes (Table 1) conform to the desired composition. The molar conductance values (Table 1) obtained for the acetate complexes in water lie in the range 15–20 mho cm^2 mol^{-1} indicating their non-electrolytic nature. Hence, in these complexes both hydrazinium and acetate moieties may be coordinated to the metal ion. Due to the insoluble nature of the malonate complexes both in water and common organic solvents their conductances could not be measured.

Magnetic moments and electronic spectra

The magnetic moments and electronic spectra (Table 2) indicate that the complexes are of high-spin octahedral variety [22, 23]. As expected the zinc and cadmium complexes are diamagnetic and show only the charge transfer transition.

Infrared spectra

All the complexes show two or three bands in the region 3200–3250 cm^{-1} due to the N–H stretching frequency of hydrazinium ions. In addition, the malonate complexes show bands in the region 3300–3350 cm^{-1} which is ascribable to the O–H stretching of coordinated water molecules. The asymmetric and symmetric stretching frequencies of the carboxylate groups, for the acetate complexes, are observed at 1640 and 1380 cm^{-1}, respectively, while the malonate complexes show these bands at 1650 and 1400 cm^{-1}. The νN–N observed for the acetate complexes at 1000 cm^{-1} indicates the coordination of $N_2H_5^+$ ions in these complexes. However, the malonate complexes show the N–N stretching frequency at 960 cm^{-1} indicating the non-involvement of the hydrazinium cations in coordination [24].

Thermal studies

Hydrazinium metal acetates

The hydrazinium cobalt acetate undergoes a two step decomposition (Fig. 1a) in the temperature range 260–325°C to give Co_3O_4. The DTA shows two exotherms at 280 and 320°C.

In TG there are no distinct steps corresponding to these two exotherms, though the final weight loss is in good agreement with the calculated value.

The nickel complex undergoes three step degradation (Fig. 1b). The TG curve shows about 25% mass loss in the temperature range 275–300°C which coincides with the calculated mass loss for the formation of $N_2H_5Ni(CH_3COO)_3$ as an intermediate. This intermediate further decomposes in the temperature range 275–325°C to give nickel carbonate which decomposes between 340–400°C to give NiO. The DTA shows three exotherm corresponding to the above three stages at 290, 310 and 365°C, respectively.

The TG–DTA traces of the zinc complex are given in Fig. 1c. The DTA curve reveals three peaks corresponding to three step decomposition of the complex as shown by TG. The first endothermic peak at 265°C is assigned to the loss of a molecule of acetic acid. The second step corresponds to the decomposition of the intermediate, $N_2H_5Zn(CH_3COO)_3{\cdot}N_2H_4$ to yield $ZnCO_3$ which is observed as an exotherm at 290°C, in DTA. The $ZnCO_3$ further decomposes exothermically at 465°C in the final step to form ZnO as the end product.

Table 1 Analytical data

Compound	Colour	Yield/%	Metal/%		Hydrazine/%		Molar conductance/ mho cm^2 mol^{-1}
			found	calcd.	found	calcd.	
$[(N_2H_5)_2Co(CH_3COO)_4]$	red	80(70)*	17.50	17.75	16.00	16.31	16
$[(N_2H_5)_2Ni(CH_3COO)_4]$	blue	85	18.00	17.76	15.80	16.26	20
$[(N_2H_5)_2Zn(CH_3COO)_4]$	colourless	80	18.00	17.43	17.20	17.78	18
$(N_2H_5)_2[Co(OOCCH_2COO)_2(H_2O)_2]$	pink	90	16.00	16.14	17.70	17.55	–
$(N_2H_5)_2[Ni(OOCCH_2COO)_2(H_2O)_2]$	blue	80	15.80	16.09	17.30	17.56	–
$(N_2H_5)_2[Zn(OOCCH_2COO)_2(H_2O)_2]$	colourless	85	17.30	17.59	17.50	17.25	–

*Complex prepared by decomposing $[N_2H_5Co(N_2H_3COO)_3]\cdot H_2O$

Table 2 Magnetic moments and electronic spectral data

Compound	Absorption maxima/		Assignments	Magnetic moment
	nm	cm^{-1}		μ_{eff} (BM)
$[(N_2H_5)_2Co(CH_3COO)_4]$	505	19800	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.80
	495	20200		
	300	33300	charge transfer	
$[(N_2H_5)_2Ni(CH_3COO)_4]$	630	15870	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	3.20
	381	26230	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	
	301	33200	charge transfer	
$[(N_2H_5)_2Zn(CH_3COO)_4]$	301	33200	charge transfer	diamagnetic
$(N_2H_5)_2[Co(OOCCH_2COO)_2(H_2O)_2]$	524	19100	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.90
	475	21050		
	300	33300	charge transfer	
$(N_2H_5)_2[Ni(OOCCH_2COO)_2(H_2O)_2]$	578	17300	$^3A_{2g} \rightarrow {}^4T_{1g}(F)$	3.20
	380	26300	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	
	301	33200	charge transfer	
$(N_2H_5)_2[Zn(OOCCH_2COO)_2(H_2O)_2]$	300	33300	charge transfer	diamagnetic

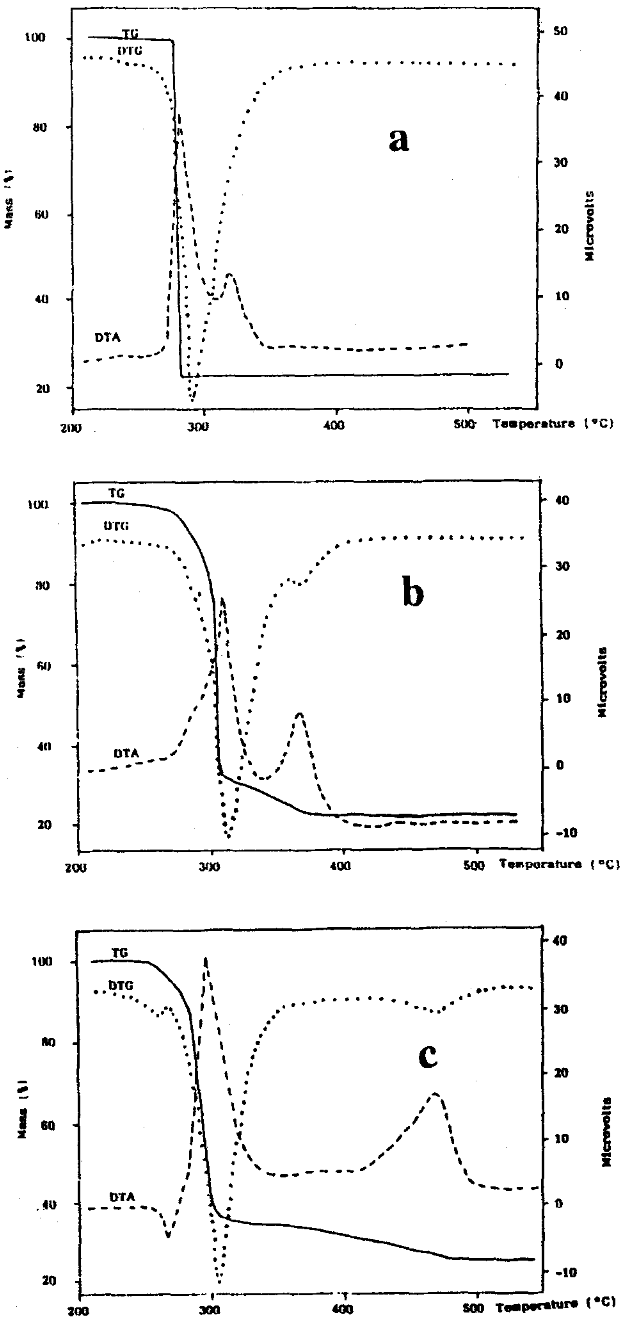


Fig. 1 Simultaneous TG–DTA–DTG of a) $[(N_2H_5)_2Co(CH_3COO)_4]$; b) $[(N_2H_5)_2Ni(CH_3COO)_4]$; c) $[(N_2H_5)_2Zn(CH_3COO)_4]$

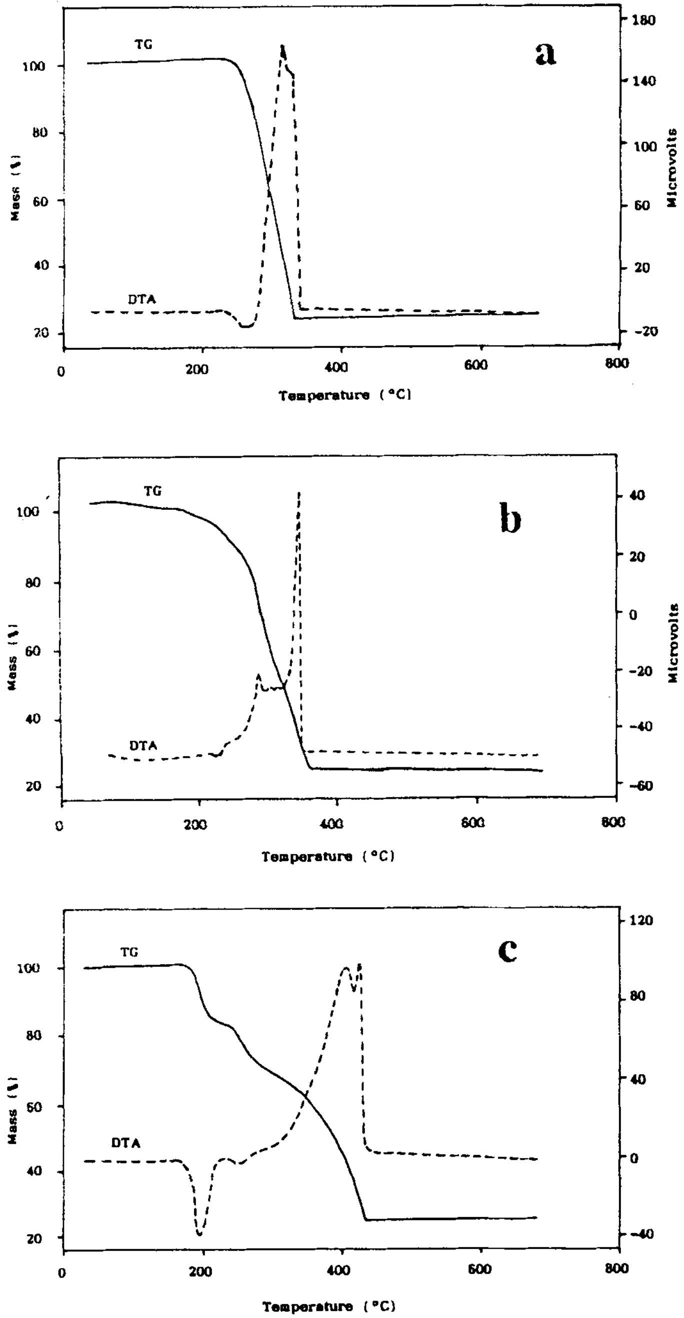


Fig. 2 Simultaneous TG–DTA of a) $(N_2H_5)_2[Co(OOCCH_2COO)_2(H_2O)_2]$; b) $(N_2H_5)_2[Ni(OOCCH_2COO)_2(H_2O)_2]$; c) $(N_2H_5)_2[Zn(OOCCH_2COO)_2(H_2O)_2]$

Table 3 Thermal data

Compound	DTA-peak temp./°C	TG-temp. range/°C	Mass loss/%		Final residue
			found	calcd.	
$[(N_2H_5)_2Co(CH_3COO)_4]$	280(exo)				
	320(exo)	260–325	76.00	77.78	Co_3O_4
$[(N_2H_5)_2Ni(CH_3COO)_4]$	290(exo)	275–300	25.00	25.52	$N_2H_5Ni(CH_3COO)_3$
	310(exo)	300–340	68.00	67.11	$NiCO_3$
	365(exo)	340–400	78.00	79.31	NiO
$[(N_2H_5)_2Zn(CH_3COO)_4]$	265(endo)	250–275	16.00	16.33	$N_2H_5Zn(CH_3COO)_3{\cdot}N_2H_4$
	290(exo)	275–325	66.00	65.90	$ZnCO_3$
	465(exo)	350–500	76.00	77.87	ZnO
$(N_2H_5)_2[Co(OOCCH_2COO)_2(H_2O)_2]$	260(endo)	240–280	10.00	9.87	$(N_2H_5)_2Co(OOCCH_2COO)_2$
	305(exo)	280–330	76.00	78.02	Co_3O_4
$(N_2H_5)_2[Ni(OOCCH_2COO)_2(H_2O)_2]$	220(endo)	180–250	10.00	9.87	$(N_2H_5)_2Ni(OOCCH_2COO)_2$
	270(exo)	250–290	38.00	38.39	$Ni(OOCCH_2COO){\cdot}2N_2H_4$
	300(exo)	290–310	48.00	47.17	$Ni(OOCCH_2COO){\cdot}N_2H_4$
	340(exo)	310–340	77.00	79.53	NiO
$(N_2H_5)_2[Zn(OOCCH_2COO)_2(H_2O)_2]$	195(endo)	170–220	11.00	9.70	$(N_2H_5)_2Zn(OOCCH_2COO)_2$
	250(endo)	220–300	36.00	34.30	$N_2H_5Zn(OOCCH_2COO)_{1.5}$
	400(exo)	300–405	59.00	58.73	ZnC_2O_4
	420(exo)	405–440	76.00	78.10	ZnO

exo: exotherm; endo: endotherm

Hydrazinium metal malonate dihydrates

The DTA traces for the cobalt complex (Fig. 2a) show an endotherm at 260°C corresponding to dehydration followed by an overall sharp exotherm with a dip around 320°C in the temperature range 280–330°C owing to the decomposition of the anhydrous compound to Co_3O_4. The TG data are in overall agreement with the DTA data, though the changes are not sufficiently resolved in TG.

In the case of nickel complex (Fig. 2b) the endothermic dehydration takes place as the first stage of decomposition in the temperature range 180–250°C to give the anhydrous compound. The hydrazinium nickel malonate decomposes between 250–290°C to give nickel malonate dihydrazinate with the removal of one molecule of malonic acid. The bis-hydrazine adduct further undergoes dehydrazination to give mono-hydrazinate adduct,which then decomposes to give nickel oxide. The DTA shows an endotherm at 220°C corresponding to the dehydration and three exotherms at 270, 300 and 340°C for the decomposition of the anhydrous com-

Table 4 X-ray powder data of $(N_2H_5)_2[M(OOCCH_2COO)_2(H_2O)_2]$ *d*-spacing in Å and relative intensity (in parentheses)

Co	Ni	Zn
6.81(48)	6.92(100)	6.42(67)
5.99(27)	6.15(54)	5.69(17)
4.93(100)	4.87(42)	4.96(100)
4.25(3)	4.27(4)	4.31(8)
3.85(22)	3.87(21)	3.88(16)
3.41(31)	3.43(63)	3.80(8)
3.10(24)	3.35(21)	3.56(29)
2.80(7)	3.28(8)	3.43(4)
2.55(36)	3.11(8)	3.10(38)
2.45(24)	2.83(20)	2.75(37)
2.40(12)	2.54(8)	2.55(17)
2.37(24)	2.44(25)	2.46(29)
2.21(17)	2.40(8)	2.42(25)
2.15(14)	2.36(12)	2.34(3)
2.09(9)	2.28(17)	2.21(8)
2.00(7)	2.20(8)	2.15(8)
1.82(13)	2.15(8)	2.08(13)
1.79(8)	2.00(6)	1.99(6)
1.74(6)	1.87(8)	1.87(4)
1.72(4)	1.82(4)	1.82(11)
	1.79(3)	1.79(3)
	1.74(8)	1.75(4)
	1.72(4)	1.72(8)

pound, dihydrazinate and mono-hydrazinate adducts, respectively. The decomposition of the bis-hydrazine nickel malonate intermediate is similar to that observed for the chemically prepared compound [19].

The DTA curves of the zinc complex shows two endotherms (195 and 250°C) followed by an overall exotherm in the range 300–440°C, with doublet at 400 and 420°C (Fig. 3c). The TG first step corresponds to the loss of two water molecules and the second to the decomposition of the anhydrous compound to $N_2H_5Zn(OOCCH_2COO)_{1.5}$. The third and fourth stages correspond to the decomposition of the above intermediate to ZnO via zinc oxalate.

The actual weight losses reported in the Table 3 for the decomposition processes of the metal complexes compare favourably with the calculated losses.

In all the compounds the dehydration takes place relatively at higher temperatures, (170–260°C), indicating the presence of coordinated water molecules. The TG–DTA data of these complexes are summarized in Table 3.

X-ray powder diffraction

The X-ray powder diffraction data of the hydrazinium metal acetates could not be recorded due to their hygroscopic nature. However, based on the physico-chemical studies the octahedral structure (I) has been assigned for these complexes.

The X-ray powder diffraction data of the hydrazinium metal malonate dihydrates indicate that they are isomorphous. The X-ray powder diffraction data of these complexes are summarized in Table 4. Based on the physicochemical studies, the structure (II) has been assigned for the malonate complexes.

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