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COBALT(II), NICKEL(II) AND ZINC(II) DICARBOXYLATE COMPLEXES WITH HYDRAZINE AS BRIDGED LIGAND

Characterization and thermal degradation

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Cobalt, nickel and zinc dicarboxylate complexes containing neutral hydrazine as bridged bidentate ligand of the type $MX(N_2H_4)_n$ where n=1 for X=$OOCCH_2COO$ and n=2 for X=$OOCCH_2COO$, $OOCCH_2CH_2COO$ and $OOCC(CH_2)CH_2COO$ have been prepared by aqueous reactions. These complexes have been characterized by analytical, spectral and thermal studies. The electronic spectra coupled with magnetic moments of cobalt and nickel complexes suggest these complexes are of high-spin variety with octahedral geometry. Infrared spectra indicate the bridging bidentate nature of hydrazine moieties present in both *mono*-hydrazine and *bis*-hydrazine complexes and the dicarboxylate ions coordinate to the metal as bidentate ligand through the monodentate coordination of each carboxylate ion. However, in the *mono*-hydrazine metal malonates both carboxylate ions act as bridged ligands.

Simultaneous TG-DTA curves of all the complexes in air resulted in the formation of respective metal oxide as final residue at low temperatures (300–400°C). These complexes decompose either in single step or decompose through respective metal carboxylate intermediates. In most of the cases the decompositions are exothermic while in some cases they are violently exothermic. The thermal degradation of these complexes in nitrogen atmosphere also gives the respective metal oxide as the final residue.

Keywords: *hydrazine metal carboxylates, metal oxides, thermal decomposition*

Introduction

Hydrazine complexes with carboxylate and dicarboxylate anions, besides their interesting structure, provide access to the preparation of metal oxides at low temperatures. Neutral hydrazine coordinates to the metal ions in various fashions as either monodentate or bidentate bridging ligand. In the presence of mono- and dicarboxylic acids, hydrazine may exist as hydrazinium cation, $N_2H_5^+$ which is also capable of coordination with metal ions. The concentration of hydrazine, pH of the reaction mixture and property of the metal ion decide the nature of complex formed. Though *mono*-protonated hydrazine, hydrazinium complexes are structurally interesting thermally they are less effective than neutral hydrazine complexes.

Further, the dicarboxylate ion like malonate dianion, although simple, exhibit a rather flexible stereochemistry and variable mode of binding with metal ions in the crystalline state. It can act as chelating as well as bridging ligand at the same time. In many complexes the malonate ion coordinates to the metal ion as bidentate ligand through COO^- coordination without involving COO^- chelation. The versatility [1] of malonate ion binding of metal ions in the solid state is shown in Fig. 1.

Succinate and methylene succinate (itaconate) ions are known to coordinate with metal ions in a bridged bidentate fashion. Hence, metal succinate and metal methylene succinate complexes containing hydrazine are expected to have three dimensional bridged structure and hence result in the polymeric complexes.

As a part of our research work we have reported several *bis*-hydrazine, *tris*-hydrazine and hydrazinium metal carboxylates and hydrazinium metal sulphites [2–10]. Though, the *bis*-hydrazine metal malonates and succinates have been studied and their thermal decompositions are mentioned, detailed thermal behavior and their kinetics have not been reported. Further, *mono*-hydrazine complexes are scarce [11] due to the precipitation of *bis*-hydrazine complexes in basic medium which are highly stable. Though in many cases the *mono*-hydrazine complexes were reported as the intermediates during the thermal degradation of *bis*-hydrazine complexes, their instability at that temperature and their continuous decomposition make them very difficult to isolate though in the case of *bis*-hydrazine nickel glycinate the corresponding *mono*-hydrazine complex has been removed during thermal degradation and studied further [12]. Also *bis*-hydrazine metal itaconates which may have similar structure and thermal behavior to that of *bis*-hydrazine metal succinate complexes have not been reported so far.

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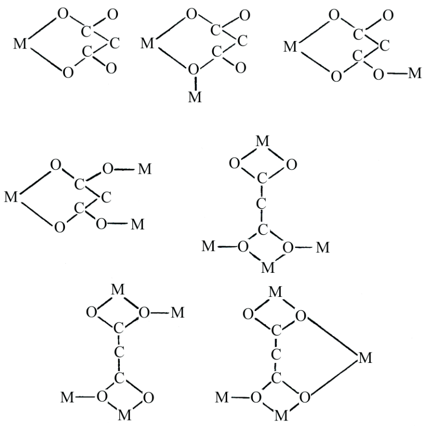

Fig. 1 Malonate ion bonding with metal ions

We have thoroughly investigated the structural and thermal behavior of *mono*-hydrazine metal malonates and *bis*-hydrazine metal malonates, succinates and methylene succinates and studied the thermal kinetics of the above complexes. The results of the above investigations are presented in this paper.

Experimental

All the chemicals used were of analar grade and 99–100% hydrazine hydrate was used in all the reactions. The solvents were distilled before use. *Bis*-hydrazine metal malonates and succinates were prepared by the methods reported earlier [5].

Preparation of mono-hydrazine metal malonates $M(OOCCH_2COO)(N_2H_4)$ where M=Co, Ni or Zn

An aqueous solution (50 mL) containing a mixture of malonic acid (1.04 g, 0.01 mol) and hydrazine hydrate (1.5 mL, 0.03 mol) was added slowly with constant stirring to an aqueous solution (50 mL) of respective metal nitrate hydrates (0.01 mol). The resultant solution was filtered and kept aside at room temperature. The crystalline complexes settled was collected after 24 h, washed with water and alcohol and then dried in air.

Preparation of bis-hydrazine cobalt and nickel itaconates $M(OOCC(CH_2)CH_2COO)(N_2H_4)_2$ where M=Co and Ni

The above complexes were prepared by adding an aqueous solution (25 mL) containing itaconic acid (1.3 g, 0.01 mol) and hydrazine hydrate (2 mL, 0.04 mol) to an aqueous solution (25 mL) of cobalt nitrate hexahydrate or nickel nitrate hexahydrate (2.91 g, 0.01 mol). The complexes precipitated immediately in the form of powders were allowed to settle down then filtered, washed with water and alcohol and dried in air.

Preparation of bis-hydrazine zinc itaconates dihydrate $Zn(OOCC(CH_2)CH_2COO)(N_2H_4)_2(H_2O)_2$

To an aqueous solution (25 mL) containing zinc nitrate hexahydrate (2.97 g, 0.01 mol), an aqueous solution of itaconic acid (1.3 g, 0.01 mol) in 25 mL of deionised water was added, the resultant solution was filtered and the clear solution was evaporated on a water bath to about 20 mL. To this hot concentrated solution, hydrazine hydrate was added in excess (2 mL, 0.04 mol). The crystalline precipitate formed was filtered, washed first with water then with alcohol and dried in air.

Methods

The composition of all the complexes were determined by hydrazine and metal analyses. The hydrazine content in the complexes were determined by titrating against 0.025 mol potassium iodate solution under Andrew's condition [13]. The metal contents were determined volumetrically using standard disodium ethylenediaminetetraacetic acid after converting a known amount of the complex into the metal nitrate hydrate by decomposing the complex with concentrated nitric acid and evaporating the resultant solution. This process was repeated for three times for the complete decomposition so as to destroy the organic part of the complex.

The magnetic studies of the complex at room temperature were determined by Gouy's method using $Hg[Co(CNS)_4]$ as calibrant. The solid state electronic absorption spectra of the complexes in nujol mull were recorded on a Shimadzu 160A UV-visible spectrophotometer in the range 200–800 nm. The infrared spectra of the complexes were recorded on a Perkin-Elmer 597 spectrophotometer using KBr discs in the range 200–4000 cm^{-1}. Simultaneous TG-DTA of the complexes were recorded in static air/nitrogen using a General V2-2A DuPont 9900 thermal analyzer using platinum cups as sample holders. About 5–10 mg of the samples were used for the thermal studies and the heating rate employed was 10°C min^{-1}. The X-ray powder diffraction patterns of the thermal residues were recorded with a Philips pw 1050/70 diffractometer using CuK_{α} and CoK_{α} radiations.

Results and discussion

Mono-hydrazine and *bis*-hydrazine metal dicarboxylates were prepared in basic conditions by the reaction of respective metal nitrate hydrates with the aqueous mixture containing hydrazine hydrate and the respective dicarboxylic acid in appropriate ratio. The chemical reaction may be represented by the following general equation.

$$M(NO_3)_2\cdot 6H_2O+H_2X+yN_2H_4\cdot H_2O\rightarrow$$
$$MX(N_2H_4)_n+2HNO_3+(y-n)N_2H_4+(y+6)H_2O$$

where M=Co, Ni or Zn, y=3 or 4 for X=$OOCCH_2COO$ and y=4 for X=$OOC(CH_2)_2COO$ or $OOCC(CH_2)CH_2COO$.

Our attempt to prepare *bis*-hydrazine zinc itaconate by the above method resulted in the formation of zinc itaconate. Hence, though in most of the cases aqueous mixture containing hydrazine hydrate and respective acid was used as ligands the *bis*-hydrazine zinc itaconate dihydrate was prepared by adding hydrazine hydrate to a hot concentrated solution containing a mixture of zinc nitrate hexahydrate and itaconic acid in 1:1 ratio.

We were also interested in *mono*-hydrazine complexes of Co(II), Ni(II) and Zn(II) ions with succinate and itaconate dianions. However, in these cases when 0.03 mol of hydrazine hydrate was used similar to the malonic acid always deposited the *bis*-hydrazine complexes and incomplete conversion of metal ions to the complexes was observed. Hence the formation of *mono*-hydrazine metal carboxylates and dicarboxylates are rare except very few cases [14].

The composition of the complexes were determined by hydrazine and metal analyses and the results of these analyses are summarized in Table 1.

Magnetic moments and electronic spectra

The magnetic moments of all the cobalt complexes are in the range 4.5–4.6 BM and for the nickel complexes the magnetic moments are in the range 3.2–3.3 BM indicate the spin-free octahedral geometry. The electronic spectrum of cobalt complexes show bands in the region 20950–20980 cm^{-1} which are assigned to the $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ transition which usually split due to spin orbit coupling in the $^4T_{1g}(P)$ state. All the nickel complexes show two bands at 26300–27700 and 17240–17500 cm^{-1} which are attributed to $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ transitions, respectively. These transitions are characteristic of octahedral metal(II) complexes [15].

Infrared spectra

The infrared spectra of the complexes show two or three bands in the region 3200–3400 cm^{-1} which are ascribable for the N–H stretching frequencies. The N–N stretching frequency in both *mono*- and *bis*-hydrazine complexes are observed in the region 960–970 cm^{-1} which are typical for bidentate bridging nature of neutral hydrazine molecules [16]. All the *bis*-hydrazine complexes show two bands in

Table 1 Analytical data

Complex	Colour	Yield/%	Hydrazine/%		Metal/%	
			found	calculated	found	calculated
$Co(mal)(N_2H_4)$ $[C_3H_6O_4N_2Co]$	rosy red	90	16.50	16.60	30.20	30.53
$Ni(mal)(N_2H_4)$ $[C_3H_6O_4N_2Ni]$	light blue	95	16.50	16.62	30.00	30.45
$Zn(mal)(N_2H_4)$ $[C_3H_6O_4N_2Zn]$	colourless	85	16.00	16.07	32.00	32.77
$Co(mal)(N_2H_4)_2$ $[C_3H_{10}O_4N_4Co]$	rosy red	90	28.00	28.48	25.80	26.18
$Ni(mal)(N_2H_4)_2$ $[C_3H_{10}O_4N_4Ni]$	violet	90	28.20	28.51	25.60	26.12
$Zn(mal)(N_2H_4)_2$ $[C_3H_{10}O_4N_4Zn]$	colourless	80	27.90	27.69	27.80	28.24
$Co(suc)(N_2H_4)_2$ $[C_4H_{12}O_4N_4Co]$	rosy red	95	26.50	26.81	24.00	24.65
$Ni(suc)(N_2H_4)_2$ $[C_4H_{12}O_4N_4Ni]$	violet	95	26.40	26.83	24.10	24.58
$Zn(suc)(N_2H_4)_2$ $[C_4H_{12}O_4N_4Zn]$	colourless	90	26.30	26.11	26.20	26.62
$Co(ita)(N_2H_4)_2$ $[C_5H_{12}O_4N_4Co]$	rosy red	85	25.50	25.53	22.60	23.47
$Ni(ita)(N_2H_4)_2$ $[C_5H_{12}O_4N_4Ni]$	violet	90	25.50	25.55	23.80	23.40
$Zn(ita)(N_2H_4)_2(H_2O)_2$ $[C_5H_{16}O_6N_4Zn]$	colourless	75	22.00	21.83	22.00	22.27

mal – malonate , suc – succinate and ita – itaconate the region 1610–1620 and 1380–1410 cm^{-1} for ν_{asy} and ν_{sym} stretching of carboxylate ions, respectively, with $\Delta\nu$ separation of 210–240 cm^{-1} indicating the monodentate coordination of both carboxylate groups in the dicarboxylate ion [17]. However, in the *mono*-hydrazine complexes these bands are observed at higher frequencies and splitting is observed in both the bands. This may be due to the bridging of both carbonyl oxygen with other metal ions. These observations along with electronic spectra of *mono*-hydrazine complexes suggest the octahedral structure of these complexes with both bridged hydrazine and bridged carboxylate ions. In addition *bis*-hydrazine zinc complexes shows a band at 3400 cm^{-1} due to the presence of O–H stretching of water molecules.

The magnetic, electronic and infrared spectral data of the complexes are summarized in Table 2. Based on the analytical, magnetic and spectral studies the following structures have been assigned for the *mono*-hydrazine metal malonate (Fig. 2), *bis*-hydrazine metal malonate (Fig. 3) and *bis*-hydrazine metal succinate/itaconate (Fig. 4) complexes.

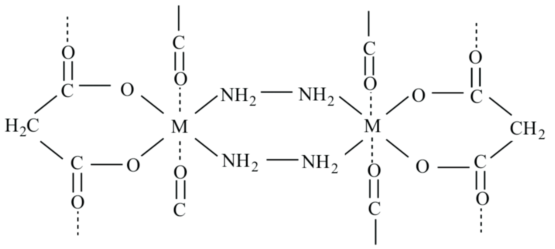

Fig. 2 Suggested structure of *mono*-hydrazine metal malonates

Thermal degradation studies

These complexes decompose in different fashion to give respective metal oxides as end residues. In most of the cases the intermediate formed undergo continuous degradation and hence the intermediates could not be isolated for further studies. However, the final products have been analysed for their metal contents

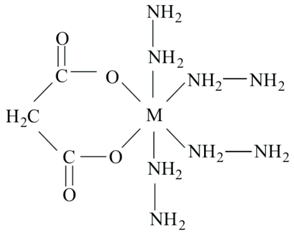

Fig. 3 Suggested structure of *bis*-hydrazine metal malonates

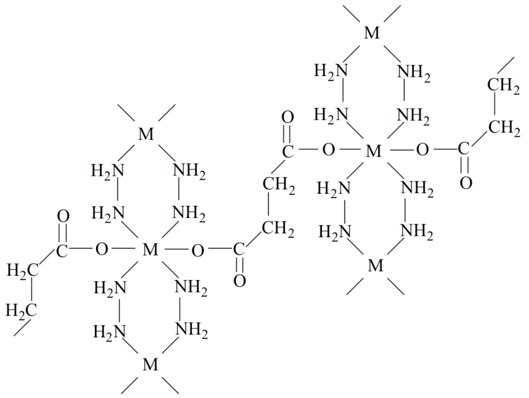

Fig. 4 Suggested structure of *bis*-hydrazine metal succinates/itaconates

Table 2 Magnetic, electronic and infrared spectral data

Complex	μ_{eff}/BM	Electronic spectra/cm^{-1}	Absorption maxima/cm^{-1}	Assigned transitions	Infrared spectral data			
					$\nu_{asy(COO)}$	$\nu_{sym(COO)}$	$\Delta\nu$	$\nu_{N–N}$
Co(mal)(N_2H_4)	4.65	21050	19100	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$	1640	1400	240	960
Ni(mal)(N_2H_4)	3.15	26300 17300		$^3A_{2g}\rightarrow{}^3T_{1g}(F)$ $^3A_{2g}\rightarrow{}^3T_{1g}(P)$	1640	1400	240	960
Zn(mal)(N_2H_4)	diamagnetic	–		–	1640	1400	240	960
Co(mal)(N_2H_4)$_2$	4.60	20960	19230	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$	1600	1380	220	960
Ni(mal)(N_2H_4)$_2$	3.25	26950 17240		$^3A_{2g}\rightarrow{}^3T_{1g}(F)$ $^3A_{2g}\rightarrow{}^3T_{1g}(P)$	1600	1380	220	960
Zn(mal)(N_2H_4)$_2$	diamagnetic	–		–	1600	1380	220	970
Co(suc)(N_2H_4)$_2$	4.60	20880	19610	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$	1610	1380	230	970
Ni(suc)(N_2H_4)$_2$	3.35	27700 17240		$^3A_{2g}\rightarrow{}^3T_{1g}(F)$ $^3A_{2g}\rightarrow{}^3T_{1g}(P)$	1600	1380	220	970
Zn(suc)(N_2H_4)$_2$	diamagnetic	–		–	1610	1410	200	980
Co(ita)(N_2H_4)$_2$	4.80	20500		$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$	1610	1400	210	970
Ni(ita)(N_2H_4)$_2$	3.30	26680 17500		$^3A_{2g}\rightarrow{}^3T_{1g}(F)$ $^3A_{2g}\rightarrow{}^3T_{1g}(P)$	1620	1390	230	980
Zn(ita)(N_2H_4)$_2$(H_2O)$_2$	diamagnetic	–		–	1620	1410	210	975

to confirm their composition. The intermediates have been assigned on the basis of TG mass loss and earlier studies on hydrazine metal carboxylates [18–20].

Mono-hydrazine cobalt malonate

This complex undergoes two-step decomposition in air and gives cobaltic oxide as end product. The first stage in TG curve corresponds to the loss of one hydrazine molecule in the temperature range 240–280°C to give cobalt malonate as intermediate which further decomposes at higher temperatures.

Mono-hydrazine nickel malonate

This complex decomposes in three stages to give nickel oxide The first stage is endothermic as shown by DTA curve and TG shows the loss of hydrazine molecule corresponding to this stage. The nickel malonate further decomposes to give nickel oxalate as another intermediate which finally gives nickel oxide. These two stages are exothermic. DTA shows one endotherm at 220°C and two exotherms at 285 and 340°C. The total mass loss in TG is 60% which is in accordance with the calculated loss of 61.25%.

Mono-hydrazine zinc malonate

Unlike cobalt and nickel complexes, the zinc complex shows two distinct endotherms at 190 and 245°C showing the loss of one hydrazine molecule in two stages. In the first stage $1/2N_2H_4$ is lost followed by another $1/2N_2H_4$ molecule to give zinc malonate. Zinc malonate decomposes in the broad temperature range (250–450°C) to give zinc oxide. The DTA corresponding to this stage is also broad with a doublet at the narrow temperature range (410–430°C). However, TG shows only a continuous decomposition without any break. The formation of intermediate, $Zn(OOCCH_2COO)(N_2H_4)_{1/2}$ is not surprising because hydrazine complexes with $1/2N_2H_4$ have been prepared and characterised with many metals [21]. The thermal degradation data of the above three complexes are summarized in Table 3.

Bis-hydrazine cobalt malonate

One step decomposition of this complex in air in the temperature range 180–280°C results in the formation of Co_2O_3 as the final residue (Fig. 5). DTA shows an exotherm at 220°C corresponding to this step.

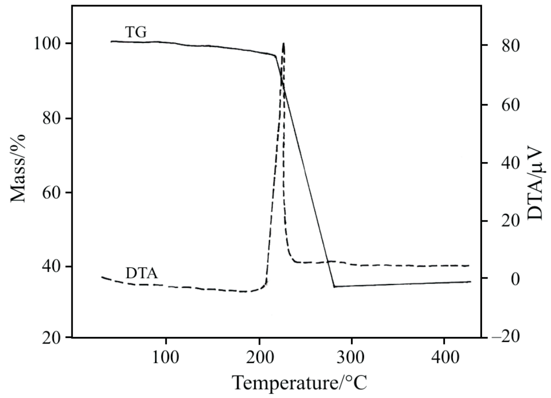

Fig. 5 TG and DTA curves of $Co(C_3H_2O_4)(N_2H_4)_2$

Bis-hydrazine nickel malonate

This complex decomposes in three stages (Fig. 6). The first stage is endothermic with the peak temperature at 90°C and in this step $1/2N_2H_4$ is lost in the temperature range 50–130°C. The intermediate undergoes exothermic degradation to give nickel oxalate, which further decomposes exothermically at higher temperatures (310–350°C) to give nickel oxide. It is interesting to note that both *mono*- and *bis*-hydrazine metal malonate complexes decompose via nickel oxalate intermediate and the temperature range corresponding to this stage in these two cases are almost similar.

Bis-hydrazine zinc malonate

Zinc complex is found to decompose in two stages, both exothermic with the DTA peak temperatures 210 and 280°C. These two exotherms are very sharp. The first step corresponds to the loss of one hydrazine molecule to give *mono*-hydrazine zinc malonate intermediate which further decomposes in the temperature range 260–300°C to give zinc oxide (Fig. 7).

Table 3 Thermal degradation data of $M(mal)(N_2H_4)$ in air

M	Stage	DTA peak temperature/°C	TG temperature range/°C	TG mass loss/%		Residue
				found	calcd	
Co	I	265(+)	240–280	15.00	16.60	Co(mal)
	II	320(–)	280–340	56.00	57.04	Co_2O_3
Ni	I	220(+)	180–280	17.00	16.62	Ni(mal)
	II	285(–)	280–290	23.00	23.90	Ni(oxa)
	III	340(–)	290–360	60.00	61.25	NiO
Zn	I	190(+)	180–200	8.00	8.03	$Zn(mal)(N_2H_4)_{1/2}$
	II	245(+)	200–250	16.00	16.07	Zn(mal)
	III	410(–)	250–440	58.00	59.21	ZnO

(+) – endotherm and (–) – exotherm, mal – malonate ($C_3H_2O_4$) and oxa – oxalate (C_2O_4)

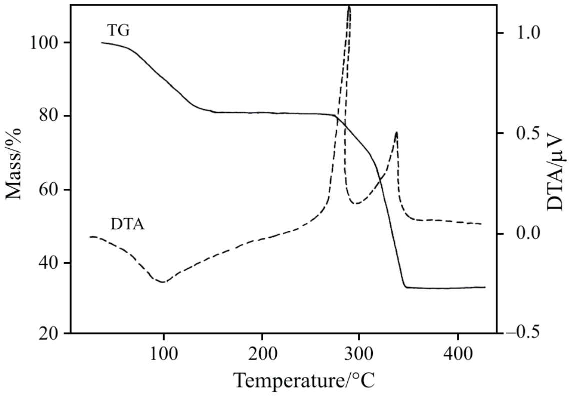

Fig. 6 TG and DTA curves of $Ni(C_3H_2O_4)(N_2H_4)_2$

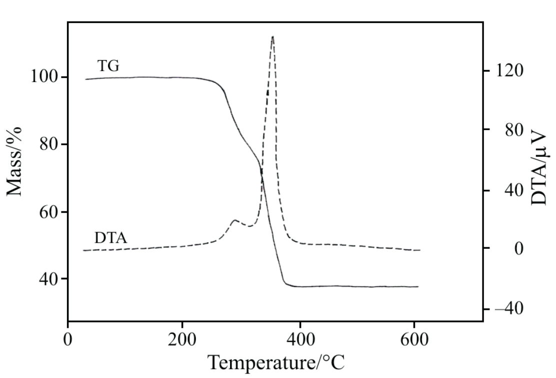

Fig. 8 TG and DTA curves of $Co(C_5H_4O_4)(N_2H_4)_2$

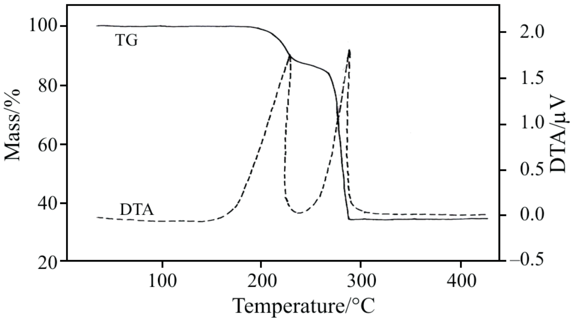

Fig. 7 TG and DTA curves of $Zn(C_3H_2O_4)(N_2H_4)_2$

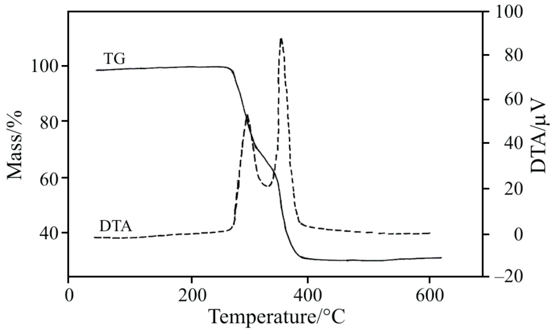

Fig. 9 TG and DTA curves of $Ni(C_5H_4O_4)(N_2H_4)_2$

Though in the case of *mono*-hydrazine zinc malonate the decomposition is multi-step, in the present case, since the first step is exothermic the heat generated in that step decomposes the intermediate in one step. The observed mass losses are well coincident with the calculated values.

Bis-hydrazine cobalt succinate

Single step decomposition of this complex resulted in the formation of cobalt oxide. DTA shows an exotherm at 330°C. The TG mass loss is observed in the temperature range 275–390°C. The observed mass loss is very well in agreement with the calculated value.

Bis-hydrazine nickel succinate

Nickel complex also decompose in single stage in the temperature range 190–310°C with an exotherm at 290°C in DTA.

Bis-hydrazine zinc succinate

In the first stage this complex liberates one molecule of hydrazine to give *mono*-hydrazine derivative. This stage is very sharp and the degradation takes place between 290–295°C with an exotherm at 292°C in DTA. The intermediate further decomposes at higher temperature (295–370°C) to give zinc oxide.

Bis-hydrazine cobalt itaconate

Thermal traces for this complex shows two-step decomposition (Fig. 8). In the first stage one hydrazine molecule is lost to give *mono*-hydrazine intermediate which in the temperature range 332–365°C decomposes to give Co_2O_3 as the final residue. Both the stages are exothermic.

Bis-hydrazine nickel itaconate

The thermal degradation of this complex is almost similar to that of cobalt complex showing two-step decomposition to give nickel oxide as the final residue (Fig. 9). Both the stages are exothermic with the peak temperatures 303 and 360°C, respectively, for the first and second stages.

Bis-hydrazine zinc itaconate dihydrate

The formation of hydrates are not common in the case of aliphatic mono- and dicarboxylic acids though it is observed with aromatic carboxylic acids [21, 22] and hydrazine uranyl carboxylates [23]. However, in the present case there are clear evidences for the presence of water molecules. This complex shows an endotherm at 251°C with the TG mass loss of 14% clearly indicates the dehydration. The anhydrous complex further decomposes exothermically in two stages sim-

Table 4 Thermal degradation data of M(mal)$(N_2H_4)_2$ in air

M	Stage	DTA peak temperature/°C	TG temperature range/°C	TG mass loss/%		Residue
				found	calcd	
Co	I	220(–)	180–280	64.00	63.11	Co_2O_3
Ni	I	90(+)	50–130	21.41	20.00	Ni(mal)$(N_2H_4)_{1/2}$
	II	280(–)	265–315	34.75	33.00	Ni(oxa)
	III	330(–)	310–350	68.00	66.78	NiO
Zn	I	210(–)	180–230	14.00	13.87	Zn(mal)(N_2H_4)
	II	280(–)	260–300	65.00	64.85	ZnO

(+) – endotherm and (–) – exotherm, mal – malonate $(C_3H_2O_4)$ and oxa – oxalate (C_2O_4)

Table 5 Thermal degradation data of M(suc)$(N_2H_4)_2$ in air

M	Stage	DTA peak temperature/°C	TG temperature range/°C	TG mass loss/%		Residue
				found	calcd	
Co	I	330(–)	275–390	70.00	68.73	CoO
Ni	I	290(–)	190–310	70.00	68.73	NiO
Zn	I	292(+)	290–295	14.00	13.05	Zn(suc)(N_2H_4)
	II	360(–)	295–370	66.00	66.86	ZnO

(+) – endotherm and (–) – exotherm, suc – succinate $(C_4H_4O_4)$

Table 6 Thermal degradation data of *bis*-hydrazine metal itaconates and *bis*-hydrazine zinc itaconate dehydrate in air

M	Stage	DTA peak temperature/°C	TG temperature range/°C	TG mass loss/%		Residue
				found	calcd	
Co	I	290(–)	250–332	24.00	25.43	Co(ita)
	II	361(–)	332–365	64.00	65.79	Co_2O_3
Ni	I	303(–)	270–342	27.00	25.53	Ni(ita)
	II	360(–)	342–372	70.00	70.34	NiO
Zn	I	251(+)	183–262	14.00	12.23	Zn(ita)$(N_2H_4)_2$
	II	306(–)	262–433	32.00	33.99	Zn(ita)
	III	470(–)	433–513	57.00	57.45	$ZnCO_3$

(+) – endotherm and (–) – exotherm, ita – itaconate $(C_5H_4O_4)$

ilar to the cobalt and nickel complexes to give zinc carbonate as the final residue and zinc itaconate being the intermediate.

The intermediates formed during the thermal degradation of the complexes were isolated by subjecting the samples to controlled heating and removing the different intermediates expected from the thermal analyses at the particular temperatures as shown by the TG-DTA traces (Fig. 10). The metal and hydrazine contents were determined for the intermediates containing hydrazine are in good agreement with the expected values. In the case of simple metal carboxylate intermediates viz., metal malonates, metal succinates and metal itaconates, their metal contents were determined which are in accordance with the theoretical values. Further, the infrared spectra of these intermediates, the metal carboxylates are also found to be superimposable to that of the authentic samples. The final degradation residues were also identified by X-ray powder diffraction patterns.

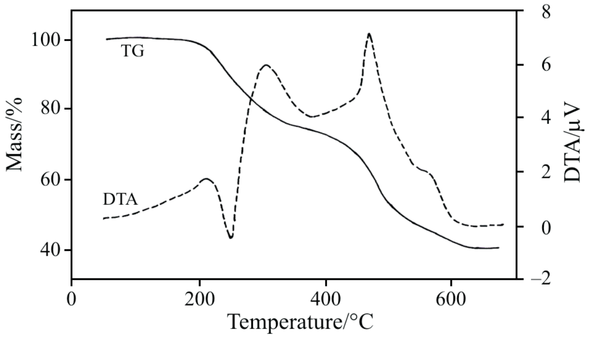

Fig. 10 TG and DTA curves of $Zn(C_5H_4O_4)(N_2H_4)_2$

Thermal degradation data of *bis*-hydrazine metal malonates, *bis*-hydrazine metal succinates and *bis*-hydrazine metal itaconates are summarized in Tables 4–6, respectively.

The X-ray powder diffraction patterns of NiO obtained as a TG residue with malonate, succinate and itaconate complexes are shown in Fig. 11 as the representative example.

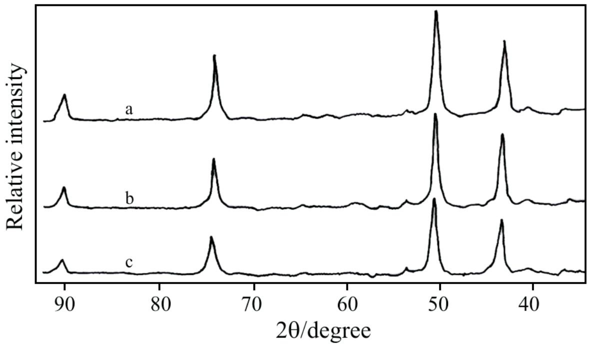

Fig. 11 X-ray powder diffraction pattern of NiO obtained from a – $Ni(mal)(N_2H_4)_2$, b – $Ni(suc)(N_2H_4)_2$ and c – $Ni(ita)(N_2H_4)_2$

Conclusions

Mono- and *bis*-hydrazine complexes have been prepared in basic conditions using excess hydrazine hydrate.

The magnetic moments and electronic spectral data indicate the high-spin octahedral nature of the metal ions.

Infrared spectra show that each carboxylate group bound to metal ion in a bidentate fashion and hydrazine present as bidentate bridged ligand.

Thermal degradation clearly shows that, generally these complexes decompose in single step or multi-step to give the respective metal oxide as the final residue and respective *mono*-hydrazine complex or metal carboxylate as intermediate.

The thermal degradation of these complexes in nitrogen atmosphere also gives the respective metal oxide as the final residue.

Based on the analytical, spectral and thermal studies the structures given in Figs 2–4 have been tentatively assigned for the *mono*-hydrazine metal malonates, *bis*-hydrazine metal malonates and *bis*-hydrazine metal succinates/itaconates, respectively.

However, in the case of *bis*-hydrazine zinc itaconate dihydrate though thermal degradation suggest the coordination of water molecules, spectral studies are not in accordance with this. Hence, at this stage it is not possible to give convincing structure for this complex.

Further, the succinic acid forms solid solution with fumeric acid, they are expected to have similar structure [24]. Hence succinate ion is expected to coordinate as a trans dianion bridge. The similar structure is also assigned for itaconate complexes. Based on these facts the three dimensional polymeric structure (Fig. 4) has been proposed for these complexes.

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