Spectral, thermal and X-ray studies on some new bis-hydrazine metal glyoxylates and bis-hydrazine mixed metal glyoxylates

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Abstract

Bis-hydrazine complexes of metal glyoxylates and mixed metal glyoxylates of 3d-metal ions of the formula $M(OOCCHO)_2(N_2H_4)_2$, where $M = Mg$, Mn, Co, Ni, Cu, Zn or Cd and $M_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$, where $M = Mg$, Mn, Ni, Zn or Cd, respectively, have been prepared and studied. The compositions of the complexes have been determined by chemical analyses. The magnetic moments and electronic spectra suggest a high-spin octahedral geometry for the metal complexes. Infrared spectral data indicate the bidentate bridging by hydrazine molecules and monodentate coordination by glyoxylate ions in both the metal and mixed metal compounds. Thermogravimetry and differential thermal analyses in air have been used to study the thermal behaviour of the complexes. The simultaneous TG-DTA traces of all the complexes show multi-step degradation and the final products are found to be the respective metal oxides in the case of metal complexes and metal cobaltites in the case of mixed metal complexes. The final residues were identified by their X-ray powder diffraction patterns. X-ray powder diffraction patterns of the complexes including mixed metal complexes are almost superimposable with in each of the series indicating isomorphism. The metal cobaltites MCo_2O_4, where $M = Mg$, Mn, Ni, Zn or Cd were also prepared by decomposing the respective mixed metal complex in a pre-heated silica crucible at about 300 °C, and their identities were confirmed by chemical analyses, infrared spectra and X-ray powder diffraction.
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1. Introduction

Hydrazine complexes of the first row transition metal ions with a variety of carboxylic acids have been reported in the literature [1]. These include simple aliphatic mono-carboxylic acids [2–5], aliphatic dicarboxylic acids [6–10], aromatic mono- and dicarboxylic acids [11,12], aliphatic and aromatic hydroxy acids [13,14], halo acids [15], amino acids [16–18] and heterocylic carboxylic acids [19]. Among these a few carboxylic acids are capable of forming tris-hydrazine complexes besides the bis-hydrazine complexes [17]. While the hydrazinium metal carboxylates and their hydrates are crystalline solids and many of them are water soluble, the bis- and tris-hydrazine complexes are either microcrystalline or amorphous powders and are insoluble in water.

Though hydrazinium complexes are gaining attention due to their interesting structures and scarcity, the bis-hydrazine complexes are widely used in the preparation of metal powders, metal oxides and mixed metal oxides [5,7,20–22] due to their thermal instability. Inspite of many bis-hydrazine and hydrazinium metal carboxylates and mixed metal carboxylates being known and used as precursors for metal oxides and mixed metal oxides such as ferrites, cobaltites, manganites, chromites, etc., only a few complexes like hydrazinium and bis-hydrazine metal and mixed metal hydrazine carboxylates are known to undergo auto catalytic decomposition once ignited [23,24]. Such precursors result in the formation of voluminous, foamy and fine particle oxide materials with high surface area which are the essential characteristics of a metal oxide to be an effective catalyst.

In continuation of our earlier work on hydrazine metal carboxylates, in this paper we wish to report several, hitherto unknown bis-hydrazine metal glyoxylates and similar mixed metal complexes, which show self-sustaining auto decomposition behaviour. This paper describes the preparation, characterization, thermal and X-ray powder studies on the above mentioned complexes and also the preparation and characterization of metal cobaltites.

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2. Experimental

The solvents were distilled prior to use and double distilled water was used for the preparation and chemical analyses. All the chemicals used were of AR grade received from SD Fine Chemicals. The hydrazine hydrate, 99–100% was used as such as received.

2.1. Preparation of M(OOCCHO)$_2$(N$_2$H$_4$)$_2$

An aqueous solution (30 ml) containing a mixture of glyoxylic acid monohydrate (1.84 g, 0.02 mol) and hydrazine hydrate (2 ml, 0.04 mol) was added slowly with constant stirring to an aqueous solution (30 ml) of the respective metal nitrate hydrate (0.01 mol). The resulting clear solution was filtered through a Whatman filter paper and left aside at room temperature. After 24 h the complex settling as crystalline powder was filtered under suction in a vacuum pump, washed several times first with water and then with alcohol and finally dried in air.

The above procedure was also repeated with 0.02 mol of hydrazine hydrate instead of 0.04 mol. This method also resulted in the formation of the same complexes. However, with the other carboxylic acids reported so far this method did not yield the complexes.

The above glyoxylate complexes were also prepared by adding excess hydrazine hydrate (2 ml, 0.04 mol) in 10 ml of water to an aqueous solution of the respective metal glyoxylates.

In the latter method, the respective metal nitrate hydrate (0.01 mol) and glyoxylic acid monohydrate (1.84 g, 0.02 mol) were separately dissolved in 25 ml of water each and the solutions were mixed. The resulting solution after filtration was slowly evaporated on a water bath to about 20 ml. To this hot solution hydrazine hydrate (2 ml, 0.04 mol) in 10 ml water was added with constant stirring. The clear viscous liquid was allowed to stand at room temperature. The crystalline complexes settling down after 30–45 min were filtered, washed several times with water and then with alcohol and dried in air.

2.2. Preparation of M$_{1/3}$Co$_{2/3}$(OOCCHO)$_2$(N$_2$H$_4$)$_2$

Among the above three methods described for the preparation of bis-hydrazine metal glyoxylates the third method was followed for the preparation of mixed metal complexes. Though in all the three methods the complexes got precipitated from the clear solutions, the last method was preferred due to the high yield of the complexes.

Initially all the metal nitrate hydrate solutions were prepared separately in standard flasks. The concentrations of metal ions were determined by complexometric titrations and gravimetric analysis [25].

The mixed metal solutions were prepared by mixing respective metal nitrate (0.01 mol) and cobalt nitrate hexahydrate (5.94 g, 0.02 mol) by pipetting out the required volumes of the standard metal nitrate solutions. To the resulting solution glyoxylic acid monohydrate (5.52 g, 0.06 mol) in 20 ml of water was added. This solution after filtration was evaporated on a water bath to about 20 ml. To this hot concentrated solution hydrazine hydrate (6 ml, 0.12 mol) in 10 ml of water was added with stirring. After the addition, the clear solution was allowed to stand at room temperature. Highly crystalline mixed metal complexes formed slowly after 30 min was filtered using a vacuum pump after 1 h, washed twice with water and then with alcohol and finally dried inside a vacuum desiccator. With Co–Cu mixture a dirty brown complex was obtained with indefinite composition.

2.3. Preparation of metal cobaltites

The mixed metal complexes were heated at 300 °C in a preheated silica crucible for about 5 min to yield the respective metal cobaltites.

Alternatively the mixed metal complexes were ignited and allowed to undergo autocatalytic decomposition. This decomposition was complete within 2 min. The resulting residue, metal cobaltites were collected.

2.4. Physico-chemical techniques

The metal contents in the complexes were determined by EDTA titration [25] after decomposing a known weight of the complex with nitric acid for atleast three times to destroy the organic matter. In the case of mixed metal complexes after decomposing a known amount of the complex with nitric acid, the residue was dissolved in water and the cobalt content in the solution was determined by separating cobalt as Co(C$_{10}$H$_6$ONO)$_3$ complex using α-nitroso β-napthol [26]. The divalent metal ion contained in the filtrate of this separation was estimated by titration with standard EDTA solution. The hydrazine content in the complex was determined volumetrically using a standard KIO$_3$ solution (0.025 mol dm^{-3}) under Andrew's conditions [25]. The cobalt and metal contents present in the metal cobaltites also were determined by the above method after dissolving the respective cobaltites in a minimum amount of nitric acid.

The room temperature magnetic moment measurements were carried out in a Gouy's balance using Hg[Co(SCN)$_4$] as the calibrant. Diamagnetic corrections were applied using Pascal's constants. The solid-state absorption spectra of the complexes in nujol mull were recorded on a Shimadzu UV–visible 240 A spectrophotometer. The infrared spectra of the complexes were recorded on a Perkin-Elmer 597 spectrophotometer in the range 4000–400 cm^{-1} using KBr discs of the samples. The simultaneous TG-DTA of the samples in air were recorded using a Netzsch STA 1500 simultaneous thermal analysis system, version V4.30, PL thermal sciences Division, UK using 2.5 mg of the samples with platinum cups as sample holders. The heating rate was 10 °C/min. The X-ray powder diffraction patterns of the complexes were recorded using a Philips X-ray diffractometer model PW 1050/70 employing Cu Kα radiation of wavelength λ = 1.5406 Å and recorded between the 80° and 10°, 2Θ values at a scan rate of 2° min^{-1}. The X-ray patterns of the cobaltites were recorded with the Co KαC radiation of wavelength 1.7902 Å using Philips X-ray diffractometer (model PW 1050/70).
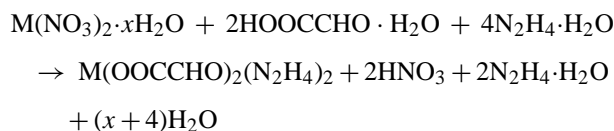
3. Results and discussion

Hydrazine hydrate in aqueous solution is expected to undergo neutralization reaction with glyoxylic acid to give hydrazinium glyoxylate, $OHCCOON_2H_5$. However, our attempt to isolate this ligand in solid state was not successful and only a dark brown viscous liquid was obtained.

Hence an aqueous mixture of glyoxylic acid and hydrazine hydrate in appropriate ratio was used as the ligand in the preparation of complexes. The thermal instability of bis-hydrazine complexes have been exploited in the preparation of metal oxides and metal cobaltites at low temperatures (250–300 °C) using bis-hydrazine metal glyoxylates and bis-hydrazine mixed metal glyoxylates, respectively as precursors. Similar hydrazinium complexes are expected to undergo degradation at higher temperatures.
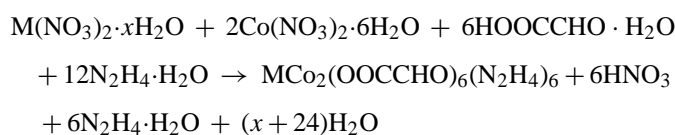
Bis-hydrazine metal glyoxylates and mixed metal complexes were prepared by the aqueous reaction of the respective metal nitrates or mixture of metal nitrates, glyoxylic acid and hydrazine hydrate in an appropriate ratio. The hydrazine hydrate was used in excess to maintain the solution at pH 9–10. The bis-hydrazine adducts separated form the basic solution as crystalline powder.

It has been reported in literature that these types of complexes may be prepared by the heterogeneous reaction between the respective solid metal carboxylates and hydrazine hydrate. However, the purities of the compounds obtained were low. Hence, we have prepared the present set of complexes by adding hydrazine hydrate to a concentrated solution containing metal nitrate hydrate (or mixture of metal nitrate hydrates) and glyoxylic acid in a proper ratio. A clear solution was first obtained from which the complexes slowly got precipitated. The yields were found to be high.

Though in many cases the aqueous reaction of the metal nitrate hydrate, the respective mono-carboxylic acid and hydrazine hydrate in 1:2:2 ratio did not yield the complex, due to the solution being almost neutral and the adducts being precipitated only from the basic solution, we were able to isolate the bis-hydrazine metal glyoxylates with the above ratio of the reagents. However, the yields were found to be very low. The chemical reaction may be represented as follows:

$$M(NO_3)_2 \cdot xH_2O + 2HOOCCHO \cdot H_2O + 4N_2H_4 \cdot H_2O$$
$$\rightarrow M(OOCCHO)_2(N_2H_4)_2 + 2HNO_3 + 2N_2H_4 \cdot H_2O$$
$$+ (x+4)H_2O$$

where M = Mg, Mn, Co, Ni, Cu, Zn, or Cd.

$$M(NO_3)_2 \cdot xH_2O + 2Co(NO_3)_2 \cdot 6H_2O + 6HOOCCHO \cdot H_2O$$
$$+ 12N_2H_4 \cdot H_2O \rightarrow MCo_2(OOCCHO)_6(N_2H_4)_6 + 6HNO_3$$
$$+ 6N_2H_4 \cdot H_2O + (x+24)H_2O$$

where M = Mg, Mn, Ni, Zn or Cd.

In the present case, we were able to isolate copper complex also. However, on long standing it underwent decomposition. With most of the carboxylic acids in the presence of excess hydrazine, copper undergoes reduction. Hence copper complexes could not be prepared. Due to the formation of hydroxide in basic condition our attempt to prepare iron complex was also not successful.

The compositions of the complexes were assigned on the basis of the hydrazine and metal contents (Tables 1 and 2). All the complexes were insoluble in water, alcohol and other organic solvents.

Table 1
Analytical data of the complexes

Compound	Color	Yield (%)	Hydrazine (%)		Metal (%)		μ_{eff} (BM)
			Found	Calculated	Found	Calculated	
$Mg(OOCCHO)_2(N_2H_4)_2$	Colorless	95	26.60	27.34	10.00	10.37	–
$Mn(OOCCHO)_2(N_2H_4)_2$	Colorless	90	25.20	24.18	20.00	20.72	5.75
$Co(OOCCHO)_2(N_2H_4)_2$	Rosy red	95	24.00	23.82	21.10	21.90	4.82
$Ni(OOCCHO)_2(N_2H_4)_2$	Green	95	24.50	23.84	20.80	21.83	3.38
$Cu(OOCCHO)_2(N_2H_4)_2$	Light blue	80	23.00	23.42	22.50	23.22	1.78
$Zn(OOCCHO)_2(N_2H_4)_2$	Colorless	90	23.60	23.26	23.80	23.73	–
$Cd(OOCCHO)_2(N_2H_4)_2$	Colorless	90	20.00	19.87	34.00	34.85	–

Table 2
Analytical data of the mixed metal complexes

Compound	Color	Yield (%)	Hydrazine		Cobalt (%)		Metal (%)		Co/M ratio Found
			Found	Calculated	Found	Calculated	Found	Calculated	
$Mg_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$	Rose	90	24.10	24.89	14.60	15.26	2.95	3.15	2.04
$Mn_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$	Rosy red	90	23.20	23.94	13.90	14.67	6.60	6.84	1.96
$Ni_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$	Greenish red	95	24.70	23.83	14.10	14.61	6.90	7.27	2.03
$Zn_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$	Red	90	23.00	23.63	13.90	14.49	7.70	8.04	2.00
$Cd_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$	Red	90	22.00	22.34	13.00	13.69	12.60	13.06	1.97

3.1. Magnetic moments

The magnetic moments of the bis-hydrazine metal glyoxylates (Table 1) are in accordance with the high-spin octahedral nature of the complexes [27]. As expected the magnesium, zinc and cadmium complexes are diamagnetic.

3.2. Electronic spectra

The electronic spectrum of cobalt complex shows strong bands at 20,300 and 19,250 cm^{-1} which are assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition which usually splits due to spin-orbit coupling in the $^4T_{1g}(P)$ state.

The bis-hydrazine nickel glyoxylate shows two bands at 26,700 and 17,300 cm^{-1} which are attributed to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively. The copper complex shows a band at 16,500 cm^{-1}, which is assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition. These electronic transitions are comparable with the spectra of the respective octahedral metal(II) complexes as reported earlier [28].

3.3. Infrared spectra

Both the bis-hydrazine metal glyoxylates and bis-hydrazine mixed metal glyoxylate complexes show almost superimposable IR spectra. The infrared spectra of $Ni(OOCCHO)_2(N_2H_4)_2$ and $Ni_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$ are shown in Figs. 1 and 2 respectively as representative examples. All the complexes show two sharp and strong band in the regions 3390–3400 and 3140–3150 cm^{-1} which are due to the N–H stretching of hydrazine molecules. A sharp band at 1670 cm^{-1} in all the cases is attributed to the carbonyl stretching of aldehyde group. The presence of aldehydic group was also confirmed by heating the complexes with dilute silver nitrate solutions, which gave silver mirror. There is no shift in this band in the complexes when compared to the glyoxylic acid which indicates that there is no interaction between metal ion and aldehydic oxygen. The ν_{asy} and ν_{sym} stretching of carboxylate ions are observed at 1580–1590 and 1350–1360 cm^{-1} with the $\Delta \nu$ separation of about 220–240 cm^{-1} which indicates the monodentate coordination of carboxylate ion [29]. The N–N stretching in
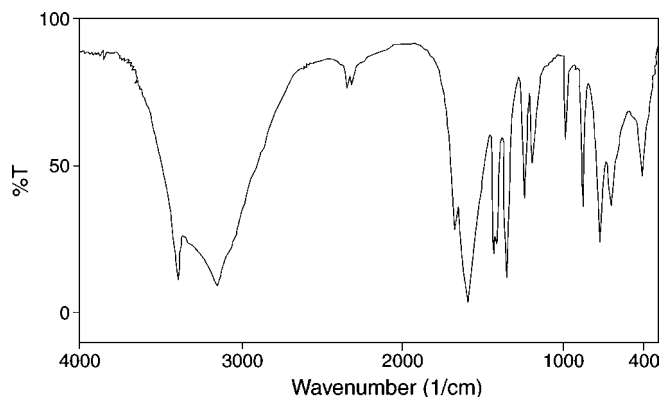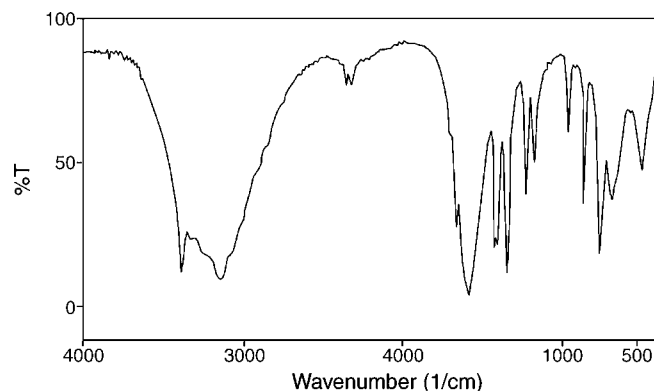

Fig. 1. IR spectrum of $Ni(OHCCOO)_2(N_2H_4)_2$.

Fig. 2. IR spectrum of $Ni_{1/3}Co_{2/3}(OHCCOO)_2(N_2H_4)_2$.

all the complexes are seen at 985–990 cm^{-1}. This shows the bridged bidentate nature of hydrazine moieties. Though it is below 990 cm^{-1} a bit higher frequency (5–10 cm^{-1}) than the bands observed normally for various bis-hydrazine complexes [30] may be due to the strong interaction between metal ion and nitrogen.

3.4. Thermal decomposition

3.4.1. Bis-hydrazine metal glyoxylates

The magnesium complex after endothermic dehydrazination undergoes sharp exothermic decomposition to give magnesium carbonate which further decomposed in the broad temperature range (280–570 °C) to give MgO. Cobalt, nickel and cadmium complexes show similar decomposition behaviour. The TG and DTA traces are almost the same except for the temperature range. In the first stage one molecule of hydrazine is eliminated to give the respective mono-hydrazine metal glyoxylate as the intermediate. This process is endothermic in all the cases. The intermediate then undergoes sharp and highly exothermic degradation to give the respective metal oxide as the final product. The hydrazine molecule is eliminated in the temperature range of 125–220 °C. Further decomposition completes before 330 °C. The mass losses observed in TG are well in accordance with the theoretical values.

The manganese and zinc complexes show similar decomposition trend. In both the complexes after endothermic dehydrazination, the intermediates namely mono-hydrazine derivatives undergo decomposition at a broad temperature range of 180–450 °C to give MnO_2 and ZnO respectively as the end residue. The DTA of manganese complex shows only one sharp exotherm for the second stage whereas zinc complex shows two exotherms at 220 and 430 °C for the second stage.

The copper complex undergoes one-step decomposition in the temperature range of 180–220 °C to give the copper oxide. The DTA shows an exotherm as doublet at 195 and 215 °C. The cadmium complex after dehydrazination undergoes explosive degradation at 330 °C to give CdO.

The final products in all the cases were identified by the TG mass loss and X-ray powder diffraction patterns.

3.4.2. Bis-hydrazine mixed metal glyoxylates

All these complexes undergo similar type of decomposition and the decomposition behaviour is almost similar to the degradation of cobalt complex. Since these mixed metal complexes have cobalt metal as the major component, their properties are expected to be the same as that of simple cobalt complex. All the mixed metal complexes show autocatalytic behaviour. As expected these complexes show two-step degradations to give the respective metal cobaltites as the final products and respective mono-hydrazine derivative as the intermediate. The first stage is endothermic and the second stage is exothermic. The intermediates decompose in a narrow temperature range of 185–285 °C. Due to their continuous decomposition we were not able to isolate the intermediates.

The simultaneous TG-DTA of magnesium, manganese, cobalt and zinc complexes are shown in Figs. 3–6 respectively.
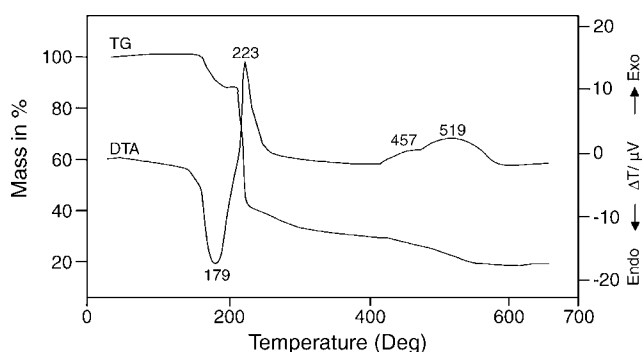
Fig. 3. Simultaneous TG-DTA of $Mg(OHCCOO)_2(N_2H_4)_2$.
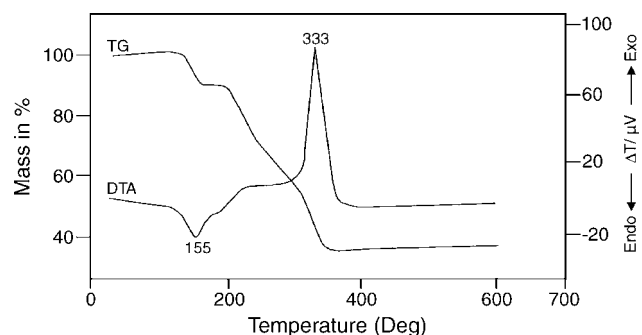
Fig. 4. Simultaneous TG-DTA of $Mn(OHCCOO)_2(N_2H_4)_2$.
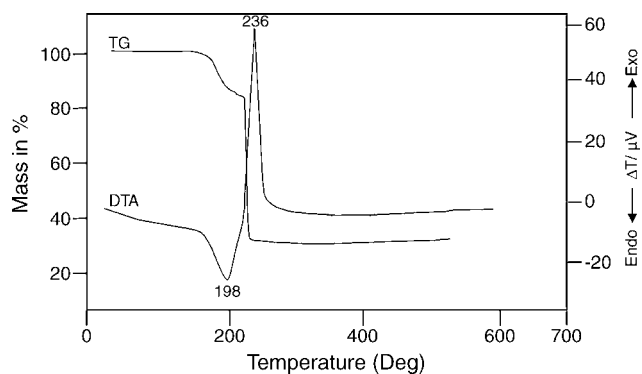
Fig. 5. Simultaneous TG-DTA of $Co(OHCCOO)_2(N_2H_4)_2$.
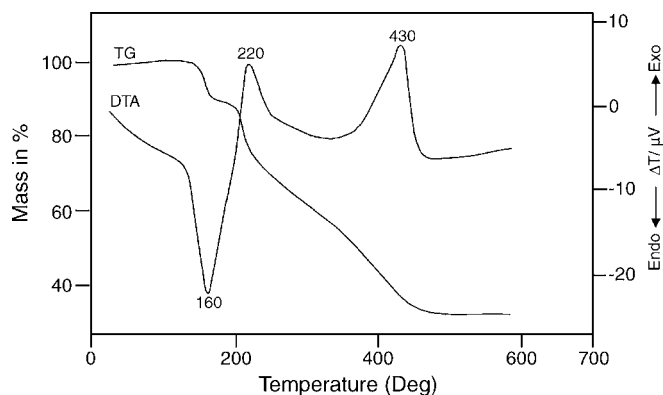
Fig. 6. Simultaneous TG-DTA of $Zn(OHCCOO)_2(N_2H_4)_2$.

The simultaneous TG-DTA of $Ni_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$ is given in Fig. 7 as typical example. The thermal data of all the complexes are summarized in Table 3.

3.5. X-ray diffraction

The X-ray powder diffraction patterns of the complexes were recorded to support the similarity in the structures of these compounds. The powder patterns are almost superimposable indicating the isomorphism among the series of compounds.

The X-ray powder diffraction data of the mixed metal complexes also have been recorded and are found to be similar to the corresponding simple bis-hydrazine metal complexes and the peaks observed are almost superimposable and sharp indicating the solid solution formation

The *d*-spacings and relative intensities of the complexes are given in Table 4. The X-ray patterns of bis-hydrazine cadmium glyoxylate and cobalt–cadmium precursor are given in Figs. 8 and 9 respectively.

3.6. Metal cobaltites

The mixed metal complexes on heating to about 300 °C in a silica crucible or ignited once and allowed to decompose autocatalytically yield the respective metal cobaltites, MCo_2O_4, where M = Mg, Mn, Ni, Zn or Cd. While heating in a silica crucible the complexes should be added in small portions to avoid sudden decomposition and explosions.

Fig. 7. Simultaneous TG-DTA of $Ni_{1/3}Co_{2/3}(OHCCOO)_2(N_2H_4)_2$.

Table 3
Thermal decomposition data

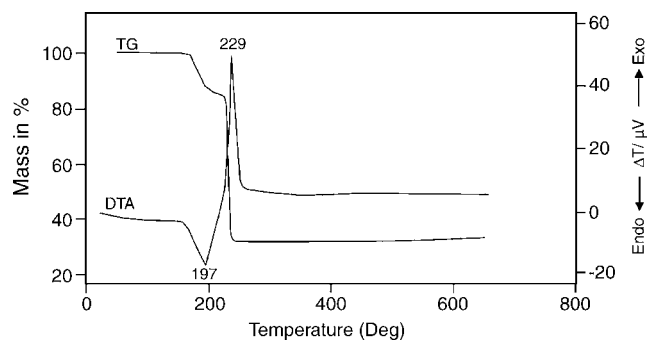| Compound	DTA peak temperature (°C)	TG temperature range (°C)	TG mass loss (%)		Residue
			Found	Calculated	
$Mg(OOCCHO)_2(N_2H_4)_2$	179(+)	153–210	12.50	13.67	$Mg(OOCCHO)_2(N_2H_4)$
	223(−, s)	210–280	65.00	64.04	$MgCO_3$
	457(−), 519(−)	280–570	82.60	82.81	MgO
$Mn(OOCCHO)_2(N_2H_4)_2$	155(+)	125–198	11.00	12.09	$Mn(OOCCHO)_2(N_2H_4)$
	333(−, s)	198–355	66.00	67.18	MnO_2
$Co(OOCCHO)_2(N_2H_4)_2$	198(+)	158–203	13.00	11.91	$Co(OOCCHO)_2(N_2H_4)$
	236(−, s)	203–239	69.20	69.18	Co_2O_3
$Ni(OOCCHO)_2(N_2H_4)_2$	212(+)	180–218	13.40	11.92	$Ni(OOCCHO)_2(N_2H_4)$
	252(−, s)	218–329	71.50	72.22	NiO
$Cu(OOCCHO)_2(N_2H_4)_2$	195(−, s)				
	215(−, s)/d	180–220	69.50	70.94	CuO
$Zn(OOCCHO)_2(N_2H_4)_2$	160(+)	133–193	11.00	11.63	$Zn(OOCCHO)_2(N_2H_4)$
	220(−, s)	193–444	69.00	70.46	ZnO
	430(−, s)				
$Cd(OOCCHO)_2(N_2H_4)_2$	174(+)	150–185	10.00	9.94	$Cd(OOCCHO)_2(N_2H_4)$
	320(−, s)	285–330	62.00	60.19	CdO
$Mg_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$	206(+)	160–210	11.50	12.44	$Mg_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)$
	234(−, s)	210–255	72.00	73.32	$MgCo_2O_4$
$Mn_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$	192(+)	160–195	12.00	11.97	$Mn_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)$
	216(−, s)	195–225	69.50	70.52	$MnCo_2O_4$
$Ni_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$	197(+)	155–204	14.00	11.91	$Ni_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)$
	229(−, s)	204–242	68.00	70.19	$NiCo_2O_4$
$Zn_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$	175(+)	140–185	11.50	11.82	$Zn_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)$
	252(−, s)	185–280	71.00	69.62	$ZnCo_2O_4$
$Cd_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$	182(+)	140–190	11.00	11.17	$Cd_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)$
	260(−, s)	90–285	67.00	65.81	$CdCo_2O_4$

(+): Endotherm; (−): exotherm; d: doublet; s: sharp.

It was observed that during heating, the manganese, cobalt, nickel and copper complexes undergo autocatalytic decomposition, i.e. if ignited they undergo self sustained degradation. However, magnesium, zinc and cadmium complexes did not show this behaviour. Further, the nickel complex decomposes with spurting while cadmium complex undergoes sudden and explosive decomposition.

The metal and cobalt contents in these cobaltites determined by chemical analyses, shows a cobalt to metal ratio of 1.97–2.02. The formation of cobaltites was con-

Table 4
X-ray powder diffraction data (*d*-values in Å)

Mg	Mn	Co	Ni	Cu	Zn	Cd	Co–Mg	Co–Ni	Co–Cd
7.80	7.76	7.38	7.43	7.69	7.76	7.80	7.76	7.56	7.50
5.75	5.88	5.72	5.83	7.64	5.83	5.88	5.72	5.83	5.83
5.34	5.31	5.33	5.30	5.41	5.38	5.38	5.31	5.33	5.34
4.46	4.46	4.43	4.42	4.42	4.51	4.50	4.43	4.43	4.42
4.27	4.38	4.25	4.39	4.33	4.42	4.44	4.33	4.38	4.38
3.90	3.88	3.88	3.90	3.86	3.86	3.88	3.88	3.90	3.88
3.21	3.19	–	3.18	3.19	3.19	3.19	–	3.18	–
3.12	3.13	3.12	3.16	3.15	3.13	3.16	3.13	3.13	3.15
3.03	–	3.02	3.01	3.02	3.01	–	3.01	3.02	3.03
2.95	2.94	2.94	2.95	2.96	2.97	2.97	2.96	2.96	2.97
2.59	2.59	2.59	2.58	2.59	2.58	2.58	2.59	2.59	2.58
2.40	2.40	2.40	2.38	2.38	2.38	2.38	2.40	2.38	2.40
2.24	2.23	2.24	2.24	2.24	2.24	2.24	2.24	2.23	2.24
2.13	2.13	2.13	2.13	2.13	2.13	2.13	2.13	2.13	2.13
1.70	1.70	1.70	1.70	1.70	1.70	1.70	1.70	1.70	1.70

Table 5
Analytical and spectral data of metal cobaltites

Oxide	Cobalt (%)		Metal (%)		Co/M ratio Found	IR spectra (cm^{-1})		XRD (Å)
	Found	Calculated	Found	Calculated		ν_1	ν_2	
$MgCo_2O_4$	56.80	57.17	11.60	11.79	2.02	660	555	8.211
$MnCo_2O_4$	49.40	49.78	23.40	23.20	1.97	660	560	8.191
$NiCo_2O_4$	48.60	49.00	24.10	24.40	2.01	665	560	8.123
$ZnCo_2O_4$	47.30	47.67	26.15	26.45	2.01	660	555	8.165
$CdCo_2O_4$	39.20	40.08	37.60	38.22	1.99	665	560	8.105
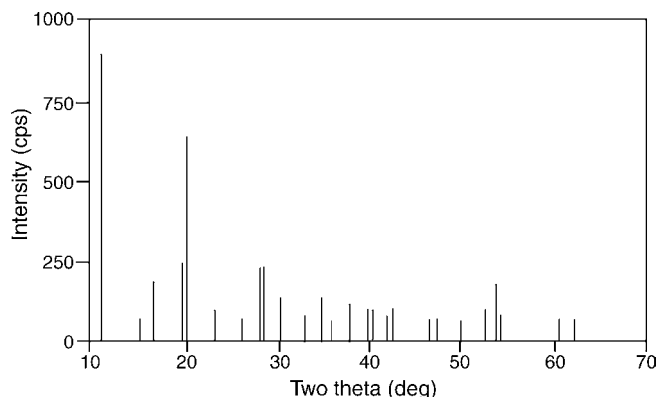
Fig. 8. X-ray powder pattern of $Cd(OHCCOO)_2(N_2H_4)$.

Fig. 10. X-ray powder pattern of $NiCo_2O_4$.

firmed by the infrared spectra and XRD patterns of the residues.

The infrared spectra of the residues show two bands at 660–665 and 555–560 cm^{-1} which correspond to the metal oxygen stretching from tetrahedral and octahedral sites, respectively, which are characteristics of cobaltites. The X-ray powder diffraction patterns of the residues are in good agreement with those reported in the literature [31]. The line broadening indicates the fine particle nature of these oxides. The analytical and spectral data and the cell parameters, '*a*' for the cobaltites with cubic symmetry calculated from XRD data are given in Table 5. The X-ray powder pattern of $NiCo_2O_4$ is given in Fig. 10.
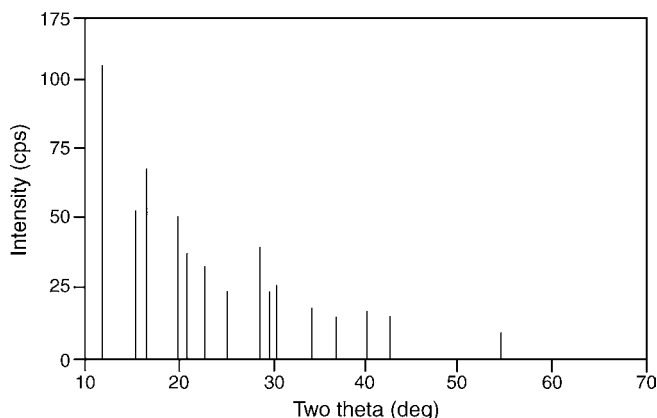
4. Conclusions

Transition metal ions such as Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} react with glyoxylic acid in the presence of excess hydrazine hydrate to yield bis-hydrazine metal glyoxylates.

These complexes were found to be isomorphous and also these were obtained as crystalline solids from a homogeneous solution. Hence the above method was exploited for the preparation of bis-hydrazine mixed metal glyoxylates.

The magnetic moment and electronic spectra suggest the high-spin octahedral nature of the complexes. Infrared spectra indicate the monodentate nature of carboxylate ions and bidentate bridged nature of hydrazine moities.

During the thermal degradation all the complexes underwent two-step decomposition to give the respective metal oxides through mono-hydrazine intermediates. Many complexes showed autocatalytic behaviour. The mixed metal complexes gave the respective metal cobaltites below 290 °C.

The X-ray powder patterns of the complexes were superimposable and the *d*-values suggested isomorphism among the complexes. The metal cobalites formed as the residues during the decomposition of mixed metal complexes were confirmed by their IR spectra and XRD patterns.

Fig. 9. X-ray powder pattern of $Co_{2/3}Cd_{1/3}(OHCCOO)_2(N_2H_4)_2$.

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