

# Synthesis, Characterization, Thermal degradation, X-Ray and DNA Binding Studies on Metal(II) and Mixed Metal Hydrazone Glyoxylate Dihydrates: A Typical One Step Aqueous Condensation Reaction

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Received: 27 February 2017;	Accepted: 27 April 2017;	Published online: 12 June 2017;	AJC-18435
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Glyoxylic acid condenses with hydrazine hydrate in the presence of transition metal(II) ions viz., Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> or Zn<sup>2+</sup> resulting in the formation of metal(II) hydrazoneglyoxylate dihydrates. The compositions of these complexes,  $[M(OOCCH=NNH_2)_2(H_2O)_2]$  were assigned on the basis of hydrazine and metal analyses and further characterized by magnetic susceptibility measurements, UV-visible, infrared, <sup>1</sup>H and <sup>13</sup>C NMR and D<sub>2</sub>O exchange spectra, simultaneous TG-DTA analyses and X-ray powder diffraction techniques. The magnetic moments and UV-visible spectra indicate that these complexes are of high-spin octahedral geometry. The infrared spectra reveal the monodentate coordination of carboxylate ions and coordination of water molecules. The TG-DTA traces are in accordance with the formation of respective metal oxide as the end product after initial dehydration and further pyrolyses of the anhydrous complexes. The Xray powder diffraction patterns indicate the isomorphism among the series of complexes. In these complexes the metal ions are octahedrally surrounded by two bidentate hydrazoneglyoxylate ions and two water molecules. The isomorphism among the series of complexes has been exploited in the preparation of mixed metal complexes. The mixed metal complex when heated to 300 °C in a pre-heated silica crucible undergoes autocatalytic decomposition to yield respective metal cobaltite, MCo<sub>2</sub>O<sub>4</sub> as the final residue. The formation of the mixed metal complexes and metal cobaltites are confirmed by their infrared spectra and X-ray powder diffraction patterns. TG-DTA of the complexes also supports the formation of metal cobaltites. The particle size and SEM analyses of simple oxides and mixed metal oxides were carried out for further application of these metal cobaltites as catalysts. The interaction of Zn(II) complex with calf thymus DNA was investigated by absorption spectra. The DNA binding affinity of Zn(II) complex is  $2.60 \times 10^4 \text{ M}^{-1}$  which reveals the strong binding affinity.

Keywords: Hydrazoneglyoxylate, Transition metal(II) complexes, Metal cobaltites, DNA binding.

## INTRODUCTION

Condensation of aldehydes with simple and higher molecular weight amines conducted in non-aqueous medium to extract hydrazides. Imines and substituted imines type Schiff's base ligands have been revealed to possess stronger coordination ability resulting in an emerging interest. It is well known that imines are not very stable compounds and are easy to hydrolyze. Hence, synthesis of free imine type Schiff's base ligands in the metal free environment with high yield becomes more difficult due to their side polymerization reactions. One effective method to fix this problem involves an '*in situ*' reaction. In other words, the metal ion acts as a templating agent, directing the condensation without polymerization.

Research and review of literature show that the pH values play a vital role in determining the type of complexes formed during the course of the reaction. When the pH is between 5 and 6, the ligand does not ionize and mostly adopts the neutral coordination mode without the participation of the nitrogen atoms from the -C=N- groups. However, if a base is added into the reaction solution, the acidic hydrogen atoms are neutralized, forming -1 charged ligand, which are able to coordinate with transition and rare earth metal ions using the naked nitrogen atom(s). Depending on the reaction conditions employed (acidic or alkaline) complexes were formed with different compositions.

Hydrazine is a versatile and simplest diamine provides access to the syntheses of innumerable organic and inorganic compounds including coordination complexes and coordination polymers. Besides its applications in organic synthesis, hydrazine and its derivatives have been exhaustively exploited in the preparation of number of coordination compounds with several varieties such as mono, *bis-*, *tris*-hydrazine and hydrazinium metal complexes. Among the anions used [1], carboxylate ions are specific in the sense that their complexes undergo complete pyrolyses resulting in the formation of pure metal oxides and mixed metal oxides like chromites, manganites, ferrites and cobaltites [2-5].

The need and role of hydrazine in their complexes are due to the presence of N–N bond which is endothermic and hence undergoes violent exothermic degradation during pyrolyses. This liberates enormous amount of heat energy which in turn utilized naturally to decompose the organic part of the complexes.

In spite of a number of acid hydrazides prepared and utilized as neutral ligands in the preparation of metal complexes, the hydrazone carboxylic acids and their complexes are less in the literature. Among the carboxylic acids, glyoxylic acid is the simplest carboxylic acid possessing an aldehyde group shows interesting chemical behaviour. In the present investigation it is observed that glyoxylic acid has the ability to undergo condensation with hydrazine in aqueous medium at room temperature. In the presence of metal ion the above product, hydrazoneglyoxylate generated *in situ* form insoluble complexes in aqueous solution. These complexes are expected to show interesting structural and thermal properties.

The aqueous condensation reaction and the metal hydrazoneglyoxylates are new to the literature except the cadmium complex for which the crystal structure has been reported [6]. Furthermore, these hydrazonecarboxylate complexes have not been prepared and utilized so far in the preparation of mixed metal oxides though hydrazine complexes were used as precursors for metal oxides and mixed metal oxides such as cobaltites and ferrites [7-10]. The difficulty with hydrazine based mixed metal complexes in the synthesis of metal cobaltites is mainly due to their violent decomposition and explosion when heated. However, the present series of complexes show smooth, self sustaining and autocatalytic degradation behaviour. Hence, in this paper we wish to report the synthesis, spectral, thermal and X-ray diffraction studies on metal and mixed metal hydrazoneglyoxylate hydrates.

#### **EXPERIMENTAL**

Glyoxylic acid monohydrate, hydrazine hydrate (99 %), metal nitrate hydrates and other chemicals used were of AnalaR grade. The solvents were distilled before use and double distilled water was used for the preparation and analyses of the complexes. Calf thymus DNA (CT-DNA) was purchased from Merck and stored at 4 °C. Double distilled water was used throughout the experiment.

The hydrazine contents were determined by volumetric analysis using a 0.025 M KIO<sub>3</sub> solution under Andrew's condition [11]. When concentrated HCl is added to the aqueous suspension of complexes, the complexes decompose to give hydrazine hydrochloride from which the quantity of hydrazine was determined volumetrically. The metal contents in the complexes were determined by EDTA complexometric titrations after completely decomposing a known amount of complexes with concentrated nitric acid for several times to eliminate the organic portion of the molecule to obtain exclusively the respective metal nitrate hydrate [12]. The cobalt and metal ions present in the mixed metal complex and metal cobaltites were determined by separating cobalt as Co(C<sub>10</sub>H<sub>6</sub>ONO)<sub>3</sub> complex using  $\alpha$ -nitroso  $\beta$ -naphthol [13]. The divalent metal ions

contained in the filtrate after the separations were estimated by titration with standard Na<sub>2</sub>H<sub>2</sub>EDTA solution. Room temperature magnetic susceptibility measurements were carried out by Gouy balance using Hg[Co(NCS)<sub>4</sub>] as a calibrant. The diamagnetic corrections were applied by summing up the Pascal's constants for the diamagnetic contributions of various atoms of the molecule. Due to the insoluble nature of the complexes in water and most of the organic solvents, the solid state absorption spectra of the complexes in nujol mull were recorded on a Varian 5000 UV-visible spectrophotometer. The infrared spectra of the complexes were recorded on a Perkin-Elmer 597 spectrophotometer in the range 4000-400 cm<sup>-1</sup> using KBr pellets of the samples. The simultaneous TG-DTA of the samples in air and nitrogen atmosphere were recorded using a SWI TG/DTA 6200 thermal analyzer using about 5 mg of the sample with the heating rate of 10 °C per min and platinum cups as sample holders. The NMR spectra of zinc complex was recorded on a Bruker FT- NMR 500 spectrometer operating at 500.13 MHz for both <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra using DMSO as solvent and tetramethyl silane as internal standard.

The X-ray powder diffraction patterns of the complexes and metal oxides and mixed metal oxides were recorded on a Philips PW 1050/70 employing Cu-K<sub> $\alpha$ </sub> radiation of wavelength  $\lambda = 1.5406$  Å and recorded between the 20 values 80° and 20° at the scan rate of 2° per min. The SEM photographs of the oxides and nickel cobaltite were recorded using a Cambridge Stereoscan model S-150 scanning electron microscope. The particle size distribution and polydipersity index (PDI) measurements of the metal oxides and metal cobaltites were carried out using a Horiba ZS-100-Green laser source (532 nm). All measurements reported were made at a temperature of 25 °C and performed at a scattering angle of 90°. Polydipersity index (PDI) values were calculated from the cumulants analysis [14].

### **DNA binding studies**

Electronic absorption titration: Electronic absorption experiment was performed at room temperature to determine the binding affinity between CT-DNA and Zn(II) complex. Interaction of CT-DNA were carried out in buffer containing 5 mM Tris(hydroxyl-methyl)aminomethane and 50 mM NaCl adjusted to pH 7.2 with hydrochloric acid. A solution of CT-DNA gave a ratio of absorbance at 260 and 280 nm of about 1.8 -1.9, indicating that CT-DNA was sufficiently free protein [15]. The CT-DNA concentration per nucleotide was determined by UV spectrophotometer employing molar absorption coefficient 6000 M<sup>-1</sup> cm<sup>-1</sup> at 260 nm [16]. An appropriate amount of Zn(II) complex is dissolved in a solvent mixture of 1 % DMSO and 99 % Tris-HCl buffer. Absorption titration experiments were performed with fixed concentration of the Zn(II) complex while gradually increasing the concentration of CT-DNA. From the absorption titration data, the binding constant (K<sub>b</sub>) of the complex was determined from eqn. 1, through a plot of [DNA]/ $(\varepsilon_a - \varepsilon_f)$  vs. [DNA].

$$[DNA]/(\varepsilon_a - \varepsilon_f) = [DNA]/(\varepsilon_b - \varepsilon_f) + 1/K_b(\varepsilon_b - \varepsilon_f)$$
(1)

where, [DNA] is the concentration of DNA and  $\varepsilon_a$ ,  $\varepsilon_f$  and  $\varepsilon_b$  the apparent extinction coefficient (A<sub>obs</sub>/[M]), the extinction coefficient for free metal complex (M) and the extinction

coefficient for the free metal complex (M) in the fully bound form, respectively. In plots of  $[DNA]/(\varepsilon_a - \varepsilon_f) vs.$  [DNA], K<sub>b</sub> is given by the ratio of slope to intercept [17].

**Preparation of complexes:** To an aqueous solution (30 mL) respective metal nitrate hydrate (0.01 mol), an aqueous solution (10 mL) of glyoxylic acid monohydrate (1.84 g, 0.02 mol) was added slowly with constant stirring. The resulting clear solution was heated on a water bath in a round bottom flask for about 2 h. To the hot solution, hydrazine monohydrate (1 mL, 0.02 mol) in 10 mL of distilled water was added in drops with constant stirring. The mixture was further heated on a boiling water bath for about 1 h. The resulting solution was allowed to stand at room temperature. The complexes precipitated after 8 to 12 h were filtered and washed with water, then with alcohol and dried in air.

The complexes are stable in air except cobalt complex which undergo decomposition on long standing. They are insoluble in water and organic solvents and decompose in dilute hydrochloric acid. However, the zinc complex is soluble in DMSO. Higher yields of the complexes were obtained when excess hydrazine hydrate (0.03 to 0.04 mol) was used though, in the case of copper, addition of excess hydrazine resulted in the precipitating copper metal.

**Preparation of mixed metal complexes:** The mixed metal complex were prepared by the method described above by using a mixture of cobalt nitrate hexahydrate (0.02 mol) and nickel nitrate hexahydrate (0.01 mol), glyoxylic acid mono-hydrate (0.02 mol) and hydrazine monohydrate (0.02 mol). The complexes formed were homogeneous and stable in air.

**Preparation of metal cobaltites:** Metal cobaltites were prepared by heating the metal-cobalt mixed metal complex in a pre-heated silica crucible at 250 °C. Large amount of gases such as CO<sub>2</sub>, H<sub>2</sub>O, *etc.*, are evolved during decomposition and swelling was observed during the process.

## **RESULTS AND DISCUSSION**

Metal nitrate hydrates in aqueous medium react with glyoxylic acid to yield metal glyoxylate hydrates. When hydrazine hydrate was added to the metal glyoxylate hydrates the free aldehydic groups present undergo condensation with the elimination of water to yield hydrazoneglyoxylate complexes. These complexes are stable in air and insoluble in water and other organic solvents except zinc complex which is partially soluble in DMSO. When dissolved in dilute hydrochloric acid they undergo decomposition to give respective metal chloride along with hydrazine hydrochloride and glyoxylic acid. The qualitative tests confirmed the presence of hydrazine and glyoxylic acid in the above solution.

The mixed metal complexes were prepared in the similar fashion when aqueous mixtures of metal nitrates were used in appropriate ratio. The chemical reactions for the formation of the complexes may be represented as follows:

M(NO <sub>3</sub> ) <sub>2</sub> .xH <sub>2</sub> O	+ 2HOOCCHO.H <sub>2</sub> O → M(OOCCHO) <sub>2</sub> .yH <sub>2</sub> O + (x+2-y)H <sub>2</sub> O	
M(OOCCHO) <sub>2</sub> . Where M = Mn	yH <sub>2</sub> O + 2N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O → M(OOCCH=NNH <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> + (y+2)H <sub>2</sub> O Co, Ni, Cu or Zn	
2/3Co(NO <sub>3</sub> ) <sub>2</sub> .6	H <sub>2</sub> O + 1/3M(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O + 2HOOCCHO.H <sub>2</sub> O → Co <sub>2/3</sub> M <sub>1/3</sub> (OOCC +	HO) <sub>2</sub> .yH <sub>2</sub> O (x+2-y) H <sub>2</sub> O
Co <sub>2/3</sub> M <sub>1/3</sub> (OOC	CHO) <sub>2</sub> .yH <sub>2</sub> O + 2N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	(y+2)H <sub>2</sub> O

The compositions of the metal complexes were assigned on the basis of the metal and hydrazine analyses. The chemical analyses data is summarized in Table-1.

Where M = Mn. Ni or Zn

**Magnetic moments and electronic spectra:** The magnetic moments of the complexes are given in Table-1. These values indicate that the complexes are of high-spin variety. The zinc complex is diamagnetic as expected from its completely filled 3*d* orbital [18]. The electronic spectrum of cobalt complex shows a broad band as a doublet at 20,250 and 19,200 cm<sup>-1</sup> which are assigned to the  ${}^{4}T_{1g(F)} \rightarrow {}^{4}T_{1g(P)}$  transition in which the splitting is attributed to the spin-orbit coupling in the  ${}^{4}T_{1g(P)}$  state. The nickel complex shows two strong bands at 26,600 and 17,400 cm<sup>-1</sup> which are assigned to the  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g(F)}$  and  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g(P)}$  transitions, respectively. The copper complex shows a band at 16,700 cm<sup>-1</sup> due to the  ${}^{2}E_{2g} \rightarrow {}^{2}T_{2g}$  transition. All these observation suggest octahedral geometry around the metal ions [19].

**Infrared spectra:** The infrared spectrum of glyoxylic acid shows two important bands at 1740 and 1628 cm<sup>-1</sup> for the carbonyl stretching of free carboxylic acid and aldehyde groups, respectively. These two bands disappeared in the complexes and a new band appeared at 1643 cm<sup>-1</sup> which is attributed to the -CH=N- stretching which supports the condensation between glyoxylic acid and hydrazine. The monodentate coordination behaviour of carboxylate ions are supported by two bands in the range 1600-1590 cm<sup>-1</sup> and 1370-1360 cm<sup>-1</sup> which are assigned for  $v_{asy}$  and  $v_{sym}$  stretchings of carboxylate ions. A sharp band observed at 3400 cm<sup>-1</sup> revealed the presence of coordinated water molecules in the complexes [20,21]. The infrared spectrum of nickel and cobalt-nickel mixed metal complexes are shown in Figs. 1 and 2, respectively.

TABLE-1 ANALYTICAL DATA OF THE COMPLEXES							
Complex (empirical		Physical	Elementa	Elemental analysis (%): Found (calcd.)			
formula)	111.w.	appearance	М	Со	$N_2H_4$	$(\mu_{eff}, BM)$	
MnX <sub>2</sub> Y <sub>2</sub>	265.08	Colourless	19.81 (20.72)	-	23.67 (24.14)	5.64	
$CoX_2Y_2$	269.07	Pink	21.06 (21.90)	-	24.60 (23.78)	4.76	
$NiX_2Y_2$	268.84	Green	22.54 (21.83)	-	23.19 (23.80)	2.9	
$CuX_2Y_2$	273.69	Blue	22.78 (23.21)	-	22.86 (23.38)	1.8	
$ZnX_2Y_2$	275.54	Colourless	23.34 (23.73)	-	23.92 (23.22)	Diamagnetic	
Mn <sub>1/3</sub> Co <sub>2/3</sub> X <sub>2</sub> Y <sub>2</sub>	267.72	Light pink	6.58 (6.84)	14.20 (14.67)	23.70 (23.90)	-	
Ni <sub>1/3</sub> Co <sub>2/3</sub> X <sub>2</sub> Y <sub>2</sub>	268.97	Greenish pink	7.51 (7.27)	14.05 (14.60)	23.08 (23.79)	-	
Zn <sub>1/3</sub> Co <sub>2/3</sub> X <sub>2</sub> Y <sub>2</sub>	271.21	Red	7.80 (8.04)	14.00 (14.48)	23.20 (23.59)	-	
$X = (OOCCH=NNH_2); Y = (H_2O)$							





<sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum: The <sup>1</sup>H NMR spectrum of the zinc complex was recorded in DMSO. The signal for the azomethine proton was observed at  $\delta$  6.98 ppm. The signals for NH<sub>2</sub> protons and OH<sub>2</sub> protons are observed at  $\delta$  7.04 ppm and  $\delta$  7.30 ppm, respectively. The D<sub>2</sub>O exchange spectrum of the complex clearly shows the disappearance of the signals for NH<sub>2</sub> protons and OH<sub>2</sub> protons. The <sup>1</sup>H NMR spectrum and D<sub>2</sub>O exchange spectrum of the zinc complex are shown in Figs. 3 and 4, respectively. In <sup>13</sup>C NMR two signals are observed for azomethine and carboxylate carbon at  $\delta_C$  166.87 ppm and  $\delta_C$  196.90 ppm, respectively. These peaks are slightly shifted to downfield region (compared with ligand) indicating the azomethine nitrogen and carboxylate oxygen atoms are strongly coordinated with metal(II) ion.

**Thermal degradation studies:** The presence of water molecule and their nature (coordinated of lattice water) could be determined by TG/DTA studies. In the present case, in nitrogen atmosphere all the complexes show a sharp endotherm in the temperature range 145-190 °C which is strong evidence for the presence of coordination water molecules. The TG-weight losses are well in accordance with the elimination of two water molecules. After dehydration, pyrolysis of the organic ligand



Fig. 4. D<sub>2</sub>O exchange spectrum of Zn(OOCCH=NNH<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>

continued to yield respective metal oxide as the final residue. However, manganese and zinc complexes resulted in the formation of respective metal carbonate as the end residue.

In air also the present series of complexes show similar degradation trend, dehydration and ligand pyrolysis resulting in the formation of metal oxides in all the cases. The mixed metal complex was also subjected to thermal degradation in air and the end residue was found to be the respective metal cobaltite. The thermal degradation data for the complexes in nitrogen and air are summarized in Tables 2 and 3, respectively. The simultaneous TG-DTA traces of manganese and cobalt complexes in nitrogen atmosphere are shown in Figs. 5 and 6, respectively. The simultaneous TG-DTA curves for cobalt-nickel mixed metal complex in air are also shown in Fig. 7.

TABLE-2 THERMAL DATA IN NITROGEN ATMOSPHERE						
Commd	DTA peak	TG temp.	TG wei	Destates		
Compa.	temp. (°C)	range (°C)	Found	Calcd.	Residue	
MnV V	147 (+)	110-165	14.00	13.59	$MnX_2$	
$\mathbf{WIII}\mathbf{A}_{2}\mathbf{I}_{2}$	214 (-)	190-400	56.00	56.63	MnCO <sub>3</sub>	
CoV V	161 (+)	125-170	14.00	13.39	CoX <sub>2</sub>	
$\operatorname{COA}_2 \mathbf{I}_2$	239 (-)	200-250	70.00	69.18	$Co_2O_3$	
NIV V	177 (+)	130-190	14.00	13.40	NiX <sub>2</sub>	
$\mathbf{NIA}_{2}\mathbf{I}_{2}$	236 (-)	190-250	73.00	72.21	NiO	
C <sub>w</sub> V V	185 (+)	160-190	13.00	13.16	CuX <sub>2</sub>	
$\operatorname{Cu}_{\mathbf{X}_{2}}\mathbf{I}_{2}$	210 (-)	200-250	69.00	70.93	CuO	
$ZnX_2Y_2$	146 (+)	110-180	14.00	13.08	$ZnX_2$	
	206 (-)	185-400	54.00	54.48	ZnCO <sub>3</sub>	
$X = (OOCCH=NNH_2); Y = (H_2O); (+): endotherm; (-): exotherm$						

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	TABLE-3 THERMAL DATA IN AIR						
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Commd	DTA peak	TG temperature	TG wei	Desther		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Compa.	temperature (°C)	range (°C)	Found	Calcd.	- Residue	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	MnV V	160 (+)	140-200	13.00	13.59	$MnX_2$	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	IVIIIA <sub>2</sub> Y <sub>2</sub>	230 (-)	220-320	70.00	70.22	$Mn_2O_3$	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	CoV V	170 (+)	160-210	12.00	13.39	CoX <sub>2</sub>	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		240 (-)	200-250	62.00	61.64	$Co_2O_3$	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	NIV V	150 (+)	200-240	13.00	13.40	NiX <sub>2</sub>	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		271 (-)	250-320	72.00	72.21	NiO	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	C <sub>W</sub> V V	160 (+)	180-200	13.50	13.16	CuX <sub>2</sub>	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		220 (-)	200-230	70.00	70.93	CuO	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		180 (+)	160-180	12.50	13.08	$ZnX_2$	
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$ZnX_2Y_2$	220 (-)	180-250	55.00	54.48	$ZnCO_3$	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		400 (-)	250-420	71.00	70.45	ZnO	
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$Mn_{1/3}Co_{2/3}X_2Y_2$	170 (+)	160-180	11.90	11.97	Mn <sub>1/3</sub> Co <sub>2/3</sub> X <sub>2</sub>	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		221(-)	180-230	69.80	70.52	MnCo <sub>2</sub> O <sub>4</sub>	
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Ni <sub>1/3</sub> Co <sub>2/3</sub> X <sub>2</sub> Y <sub>2</sub>	190 (+)	180-200	12.50	13.45	Ni <sub>1/3</sub> Co <sub>2/3</sub> X <sub>2</sub>	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		230 (-)	200-240	69.00	70.19	NiCo <sub>2</sub> O <sub>4</sub>	
$\frac{231_{1/3} CO_{2/3} A_2 I_2}{250 (-)} \qquad 200-260 \qquad 69.00 \qquad 69.62 \qquad ZnCo_2O_4$	$Zn_{1/3}Co_{2/3}X_2Y_2$	180 (+)	170-200	11.30	11.82	Zn <sub>1/3</sub> Co <sub>2/3</sub> X <sub>2</sub>	
		250 (-)	200-260	69.00	69.62	ZnCo <sub>2</sub> O <sub>4</sub>	

 $X = (OOCCH=NNH_2); Y = (H_2O); (+): endotherm; (-): exotherm.$ 



Fig. 5. Simultaneous TG-DTA of Mn(OOCCH=NNH<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> in nitrogen



Fig. 6. Simultaneous TG-DTA of Co(OOCCH=NNH<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> in nitrogen

**XRD:** The present set of complexes shows almost super imposable powder pattern which reveal the isomorphism among the complexes. The mixed metal complex also shows a similar pattern with sharp lines indicating the formation of solid solutions. X-ray powder diffraction patterns of Co, Ni and Ni-Co complexes are shown in Fig. 8.







Fig. 8. X-ray powder diffraction patterns of (a) Co(OOCCH=NNH<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> (b) Ni(OOCCH=NNH<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and (c) Ni<sub>1/3</sub>Co<sub>2/3</sub>(OOCCH=NNH<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>

## **DNA binding studies**

**Electronic absorption titration:** The electronic absorption spectroscopy is most common and useful technique to

determine interaction of complexes with DNA [22]. The Zn(II) complex in DMSO-buffer mixture exhibit intense band at 261 nm and also show hyperchromic effect with blue shift (about 1 nm) indicate that complex bind to DNA by external contact possibly via electrostatic binding [23,24]. The absorption intensities of Zn(II) complex increased (hyperchromism) upon increasing the concentration of CT-DNA preferably binding to the DNA helix via groove binding interaction [25]. Thus the conformation changes of CT-DNA occur due to damage or unwinding of the double helix structure. The binding constant  $K_b$  for Zn(II) complex is determined from plot of [DNA]/( $\epsilon_a$ - $\epsilon_f$ ) vs. [DNA] and found to be  $2.60 \times 10^4$  M<sup>-1</sup> indicating strong binding affinity. The absorption spectral trace of Zn(II) complex is shown in Fig. 9.

Characterization of metal cobaltites: The infrared spectrum of nickel cobaltite shows two bands at 660 and 555 cm<sup>-1</sup>



which were assigned to the M-O stretching of tetrahedral and octahedral sites, respectively (Table-4). The X-ray powder pattern of NiCo<sub>2</sub>O<sub>4</sub> is in agreement with the standard pattern [26]. The SEM photograph of the nickel cobaltite shows lot of voids and cracks indicating the large quantity of gases evolved during the decomposition. The SEM photograph of NiCo<sub>2</sub>O<sub>4</sub> is shown in Fig. 10. The SEM image shows irregularly shaped agglomerated particles of sub micron size.



Fig. 10. SEM photograph of NiCo<sub>2</sub>O<sub>4</sub>

Particle size distribution: The particle size distribution values of the metal oxides were obtained from the light scattering measurements. The polydispersity index (PDI) values were calculated from cumulant operation. The particle size distribution and polydispersity index (PDI) of oxides are summarized in Table-5. The mean intensity diameter of cobalt and nickel oxides are shown in Fig. 11.



TABLE-4 ANALYTICAL AND SPECTRAL DATA OF METAL COBALTITES								
Ovida	Coba	lt (%)	Meta	1 (%)	Co/M ratio	IR spect	$ra(cm^{-1})$	
Oxide	Found	Calcd.	Found	Calcd.	Found	$\mathbf{v}_1$	$v_2$	AKD (A)
MnCo <sub>2</sub> O <sub>4</sub>	50.00	49.78	23.00	23.20	2.01	658	562	8.193
NiCo <sub>2</sub> O <sub>4</sub>	49.30	49.00	24.00	24.40	1.99	663	560	8.132
ZnCo <sub>2</sub> O <sub>4</sub>	47.00	47.67	26.00	26.45	1.98	660	558	8.154

	TABLE-5 PARTICLE SIZE ANALYS	SIS
Metal oxides	Particle size by intensity (nm)	Polydipersity index (PDI)
$MnO_2$	214.66	2.562
$Co_2O_3$	218.60	2.743
NiO	246.90	3.800
CuO	255.24	3.844
ZnO	261.40	3.891
CdO	268.28	3.924
NiCo <sub>2</sub> O <sub>3</sub>	279.44	3.968
MnCo <sub>2</sub> O <sub>4</sub>	356.21	4.292
$ZnCo_2O_4$	230.56	3.214

#### **ACKNOWLEDGEMENTS**

The authors sincerely acknowledge University Grants Commission-SERO, Hyderabad, India for the financial assistance in the form of minor research project (Ref. No. F MRP-4964/ 14 (SERO/UGC). One of the authors, R. Pradeep is highly thankful to University Grants Commission, New Delhi, India for RGNFD fellowship (Ref. No. F/2014-15/RGNF-2014-15D-OBC-TAM-84300).

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