Preparation of transition metal 2-hydroxy-1-naphthoate complexes with hydrazine, their thermal characterization and use as precursors of nano metal oxides

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ABSTRACT

Reaction of aqueous metal (Ni(II), Co(II), Cd(II), Zn(II), Cu(II) and Mn(II)) nitrate/ acetate solution with an aqueous solution mixture of hydrazine and 2-hydroxy - 1- naphthoic acid yielded the complexes with formula, $(N_2H_5)_2[M\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$ where M(II) = Ni, Co, Cd, Zn, Cu and Mn in the pH range of 4-7 and $[M(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$ where M(II) = Ni, Co, Cd and Zn at the pH 9. They were characterized by the spectroscopic methods, IR, UV- visible and ESR, magnetic measurements, simultaneous TG–DTA methods and XRD. Hydrazinium metal naphthoate complexes undergo endothermic dehydration from 105°C to 200°C and a strong exothermic decomposition between 336°C and 465°C, forming the respective metal oxides via unstable intermediate $[M\{C_{10}H_6(COO)(O)\}]$, while neutral hydrazine complexes lose water and hydrazine exothermally in the range 192-230°C, and then undergo strong exothermic decomposition above 230°C upto 451 °C to form metal oxides with no stable intermediates. Incineration of all the complexes at their decomposition temperatures gives metal oxides with the particle size in the range of 25 - 50 nm. The electronic spectra of the Ni, Co and Cu complexes reveal their probable geometry distorted octahedral with CN 6 which was further substantiated by magnetic susceptibility measurement and ESR study. The kinetic parameters for their decomposition have been evaluated by using integrated Coats-Redfern equation from TG data.   © 2009 Trade Science Inc. - INDIA

INTRODUCTION

Complexes between naphthalene derivatives and different metal ions have been studied since the early 1960s. In these studies, different methods, such as voltammetry[1], spectrophotometry and flame atomic-absorption spectroscopy[2,3] have been used to examine these complexes. In general, 2-hydroxy -1-naphthoic acid is a well known naphthalene derivative, because of its excellent co-ordination capability due to –OH group together with the carboxylic group on adjacent carbons (Figure 1). As examples, several references on studies of complexes of lanthanides[4] and uranium[5] with 2-hydroxy-1-naphthoic acid have been found. It is also noted that a ternary complex between 2H1NA and

nitrilotriacetic acid with Cu(II), Ni(II) and Zn(II) has been reported by Pradyot Kumar Datta et al[6]. These molecules are used as fluorescent indicators and in the manufacture of dyestuffs.
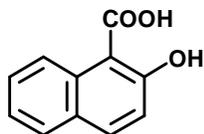
Figure 1 : 2-hydroxy-1-naphthoic acid

Hydrazine, a versatile ligand acting in different fashions, monodentate (Figure 2a), bidentate (Figure 2b) and monodentate cation (Figure 2c) leading to the formation of polymeric complexes[7,8] can also act as a charge compensating species like $N_2H_5^+$ ammonium cation[9]. Thermal decomposition of hydrazinium metal carboxylates is interesting due to their easier combustibility. Simultaneous DTA-TG-DTG study of metal hydrazine formate[10], succinate[11] and hydroxybenzoate[12] indicate that these complexes undergo decomposition at lower temperature than their non-carboxylate counterparts. This behaviour has been used for the preparation of fine particles of ferrites[13] and cobaltites[14] at the low temperatures. In this work, preparation of mixed ligand complexes using 2 hydroxy- 1- naphthoic acid and hydrazine as ligands and their thermal decomposition have been studied.
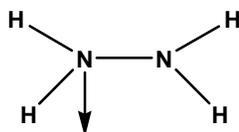
Figure 2a : Monodentate hydrazine
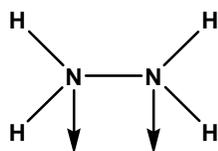
Figure 2b : Bidentate hydrazine
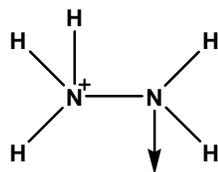
Figure 2c : Monodentate hydrazinium cation

EXPERIMENTAL

Preparation of complexes

$(N_2H_5)_2[M\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$ where M(II) = Ni, Co, Cd and Zn

These complexes were prepared by adding 60 mL of the hot ligand solution at 60° C containing an aqueous solution mixture of 2-hydroxy-1-naphthoic acid (0.188g ; 1mmol) and hydrazine hydrate (0.1mL; 2mmol) to 20 mL of an aqueous solution of the respective metal nitrate (for example, 0.291g of $Co(NO_3)_2.6H_2O$; 1mmol in 20mL of distilled water) at pH 6. The same procedure was adopted for the preparation of cadmium complex at pH 7, manganous complex at pH 6 and copper complex at pH 4, by taking the ratio, metal :acid : hydrazine, 1:1:4, 1:2:4 and 1:2:4, respectively.

Manganous complex was prepared by taking manganous acetate tetrahydrate as starting material. Copper complex was prepared by using 1:1 water-alcohol solution of the ligand at the room temperature.

The above solution mixtures which appeared cloudy at first, turned out to be a micro crystalline solid on digestion when kept over a hot water bath at 90ºC for 20 minutes. It was cooled, filtered and washed with distilled water, ethanol and then with ether. The crystals were dried in a desiccator over anhydrous $CaCl_2$.
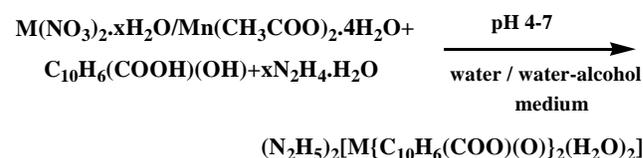
$$M(NO_3)_2.xH_2O/Mn(CH_3COO)_2.4H_2O+ \atop C_{10}H_6(COOH)(OH)+xN_2H_4.H_2O \xrightarrow[\text{water / water-alcohol medium}]{\text{pH 4-7}}$$

$$(N_2H_5)_2[M\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$$

$[M(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$ where M(II) = Ni, Co, Cd and Zn

These complexes were prepared by adding 60mL of the hot ligand solution at 60° C containing an aqueous solution mixture of 2-hydroxy-1-naphthoic acid (0.188g ; 1m mol) and hydrazine hydrate (0.5mL ;10mmol) to 20 mL of an aqueous solution of the respective metal nitrate pH 9.

$$M(NO_3)_2.xH_2O+ \atop C_{10}H_6(COOH)(OH)+10N_2H_4.H_2O \xrightarrow[\text{water medium}]{\text{pH 9}}$$

$$[M(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$$
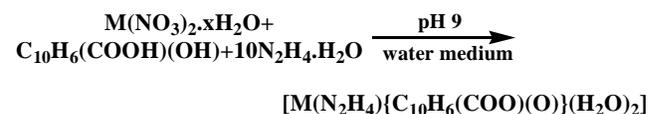
All the complexes obtained are microcrystalline solids, which are stable in air and insensitive to light.

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They are insoluble in water and in common organic solvents like ethanol, acetone and chloroform. The analytical data of the complexes are compatible with the proposed composition for the complexes (TABLE 1).

TABLE 1 : Analytical and IR data of the complexes

Molecular Formula of Complexes	Colour	Yield %	D.pt/ °C	Analytical data (%)					IR data							
				Carbon Fd. (calcd.)	Hydrogen Fd. (calcd.)	Nitrogen Fd. (calcd.)	Hyrazine Fd. (calcd.)	Metal Fd. (calcd.)	$\upsilon_{O\text{-}H}$ (H$_2$O) cm^{-1}	ρ_r (H$_2$O) cm^{-1}	$\upsilon_{C=O}$ asym cm^{-1}	$\upsilon_{C=O}$ sym cm^{-1}	υ_{asy}-υ_{sy} cm^{-1}	$\upsilon_{M\text{-}O}$ cm^{-1}	$\upsilon_{N\text{-}N}$ cm^{-1}	υ_{NH} cm^{-1}
(N$_2$H$_5$)$_2$[Ni{C$_{10}$H$_6$(COO)(O)}$_2$(H$_2$O)$_2$]	Light violet	85	170	49.5 (49.6)	4.9 (4.9)	10.4 (10.5)	12.1 (12.0)	10.9 (11.0)	3438 (b)	829 (s)	1623 (s)	1411 (m)	212	418 (s)	974 (s)	3309 (s)
(N$_2$H$_5$)$_2$[Co{C$_{10}$H$_6$(COO)(O)}$_2$(H$_2$O)$_2$]	Pink	85	190	49.4 (49.5)	4.8 (4.9)	10.4 (10.5)	12.1 (12.0)	11.0 (11.1)	3442 (b)	829 (s)	1623 (s)	1409 (m)	214	418 (s)	973 (s)	3309 (s)
(N$_2$H$_5$)$_2$[Cd{C$_{10}$H$_6$(COO)(O)}$_2$ (H$_2$O)$_2$]	White	95	175	45.1 (45.0)	4.3 (4.4)	9.4 (9.5)	10.8 (10.9)	19.2 (19.2)	3440 (b)	827 (s)	1623 (s)	1411 (m)	212	432 (b)	972 (s)	3305 (m)
(N$_2$H$_5$)$_2$[Zn{C$_{10}$H$_6$(COO)(O)}$_2$(H$_2$O)$_2$]	Dull brown	90	180	48.8 (48.9)	4.7 (4.8)	10.3 (10.4)	11.8 (11.9)	12.3 (12.1)	3404 (b)	829 (s)	1618 (s)	1411 (m)	207	418 (s)	975 (s)	3307 (s)
(N$_2$H$_5$)$_2$[Mn{C$_{10}$H$_6$(COO)(O)}$_2$(H$_2$O)$_2$]	Light brown	80	170	50.1 (49.9)	4.8 (4.9)	10.7 (10.6)	12.1 (12.1)	10.3 (10.4)	3438 (b)	829 (s)	1616 (s)	1409 (s)	207	416 (s)	977 (s)	3309 (s)
(N$_2$H$_5$)$_2$[Cu{C$_{10}$H$_6$(COO)(O)}$_2$(H$_2$O)$_2$]	Grass green	75	100	49.2 (49.1)	4.7 (4.8)	10.3 (10.4)	11.8 (11.9)	11.6 (11.8)	3404 (b)	827 (s)	1623 (s)	1411 (m)	212	437 (s)	975 (s)	3236 (s)
[Ni(N$_2$H$_4$){C$_{10}$H$_6$(COO)(O)}(H$_2$O)$_2$]	Light green	85	220	42.0 (42.2)	4.5 (4.5)	8.7 (8.9)	10.0 (10.2)	18.6 (18.8)	3404 (b)	829 (s)	1631 (m)	1411 (s)	220	437 (s)	943 (s)	3309 (s)
[Co(N$_2$H$_4$){C$_{10}$H$_6$(COO)(O)}(H$_2$O)$_2$]	Light pink	80	220	42.1 (42.2)	4.4 (4.5)	8.8 (8.9)	10.1 (10.2)	18.7 (18.8)	3406 (b)	829 (s)	1623 (s)	1409 (s)	214	416 (s)	943 (s)	3309 (s)
[Cd(N$_2$H$_4$){C$_{10}$H$_6$(COO)(O)}(H$_2$O)$_2$]	White	95	210	36.2 (36.0)	3.7 (3.8)	7.5 (7.6)	8.8 (8.7)	30.6 (30.7)	3404 (b)	827 (s)	1623 (s)	1411 (s)	212	412 (m)	958 (s)	3284 (s)
[Zn(N$_2$H$_4$){C$_{10}$H$_6$(COO)(O)}(H$_2$O)$_2$]	White	85	180	41.3 (41.3)	4.3 (4.4)	8.7 (8.8)	10.2 (10.0)	20.5 (20.5)	3404 (b)	829 (s)	1618 (b)	1411 (s)	207	418 (m)	943 (s)	3307 (s)

b = broad; s = sharp; m = medium

Physicochemical techniques

The compositions of the complexes were fixed by chemical analysis and confirmed by micro elemental analysis. Hydrazine content was determined by titrating against standard KIO$_3$ (0.025 mol L^{-1}) under Andrew's conditions. Metal Contents were determined by titrating with EDTA (0.01 mol L^{-1}) after decomposing the complexes with 1:1 nitric acid[15].

IR spectra of the complexes in the region 4000-400 cm^{-1} were recorded as KBr pellets using a Perkin Elmer 597 spectrophotometer. Electronic reflectance spectra for the solid state complexes were obtained using a Varian, Cary 5000 recording spectrophotometer. The magnetic susceptibility of the complexes was measured using a vibrating sample magnetometer, VSM EG&G Model 155 at room temperature and the data were corrected for diamagnetism.

The X-ray powder patterns of the complexes were recorded using a Philips X-ray diffractometer (model PW 1050/70) employing Cu-Kα radiation with a nickel filter. The simultaneous TG-DTA experiments were carried out using SDT Q600 V8.3 instrument and Stanton 781 simultaneous thermal analyzer. Thermal analyses were carried out in air at the heating rate of 10 °C min^{-1} using 5 to 10 mg of the samples. Platinum cups were employed as sample holders and alumina as reference. The temperature range was ambient to 700 °C. The SEM images of the residual oxides were recorded using a Cambridge Scanning Electron Microscope with EDAX attachment (CF).

RESULTS AND DISCUSSION

Electronic spectra, magnetic susceptibility and ESR spectra

The cobalt complexes of hydrazinium transition metal complexes register a band in the regions of 18170 and 20000 cm^{-1} due to transitions $^3T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F) and $^3T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$ (P) of typical six co-ordinated Co(II) complexes. The corresponding nickel complexes show bands in the regions 16130, 18180 and 26320 cm^{-1} which are ascribable to transition $^3A_{2g} \rightarrow$ $^3T_{1g}$ (F) and the copper complex shows bands in the regions 13,540 and 18,670 cm^{-1} assigned to $^2B_{1g} \rightarrow$ $^2A_{2g}$ and $^2B_{1g} \rightarrow$ $^2B_{2g}$ transitions, respectively, evidence the octahedral geometry of the complexes[16]. The magnetic moment values obtained for the nickel, cobalt and copper complexes, 3.25, 4.95 and 1.8 BM respectively, confirm the high spin octahedral structures.

The axial ESR spectrum for copper complex shown in Figure 3 has features at $g_{\parallel} = 2.1$ and $g_{\perp} = 1.9$ which clearly indicate that the copper(II) ion geometry is that of a distorted octahedron.
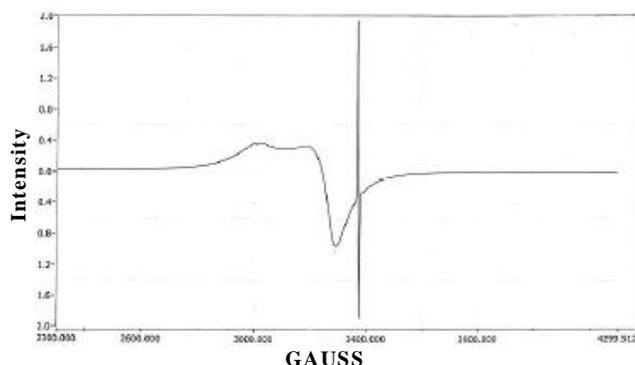
Figure 3 : ESR spectrum of $(N_2H_5)_2[Cu\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$

A band appears in the region 23584, 22030 and 19685 cm^{-1} and is assigned to the $^4T_{1g}$ (P) $\rightarrow$ $^4T_{1g}$ (F) transition for Co (II) complex. The corresponding nickel complexes show bands in the region 25316, 23696 and 22270 cm^{-1} which are assigned to $^3A_{2g}$ $\rightarrow$ $^3T_{1g}$ transition, substantiating the octahedral environment of Ni(II). The effective magnetic moment values, 3.20 and 5.09 BM of Nickel and Cobalt complexes respectively, also support the geometry.

IR spectra of complexes

The IR spectral data of the complexes are summarized in TABLE 1.

All the hydrated complexes display a medium broad

peak centered around 3440 cm^{-1}, indicating the O-H stretch of water molecules. An additional sharp peak in the region 827-829 cm^{-1} is observed which may be due to the presence of coordinated water molecules. The sharp bands in the range of 3309-3236 cm^{-1} which were not seen in the spectrum of free acid, are due to υ_{NH} of $N_2H_5^+$ ion and hydrazine. In all the complexes the asymmetric and symmetric stretching frequencies of the carboxylate ion are seen in the range 1616-1631 cm^{-1} and 1409-1411 cm^{-1}, respectively, with an average separation of ($\Delta\upsilon = \upsilon_{asy} - \upsilon_{sy}$) 220 cm^{-1} indicating the monodentate coordination of carboxylate oxygen to metal[17]. The N-N stretching frequencies for the hydrazinium complexes observed in the range of 972-977 cm^{-1} is an ample evidence for the presence of noncoordinated $N_2H_5^+$ ion in the complexes. In the case of neutral hydrazine complexes, N-N stretching frequency is observed in the range of 943-958 cm^{-1} which is the evidence for neutral, bridging hydrazine[18].

Thermal studies

The thermal data of the complexes are summarized in TABLE 2. The compositions of the intermediates and the final products are those which best fit with the observed mass losses in the TG studies. Thermogravimetric results are in good agreement with the DTA data.

TABLE 2 : Thermal analysis of the complexes.

Molecular Formula of Complexes	DTA peak Temp (° C)	TG			Decomposition products
		Temp. Range(°C)	Weight loss%		
			obsd.	calcd.	
$(N_2H_5)_2[Ni\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	173 (+)	150 -195	6.6	6.8	$(N_2H_5)_2Ni\{C_{10}H_6(COO)(O)\}_2$
	240 (-)	195 -290	53.8	53.7	$Ni\{C_{10}H_6(COO)(O)\}$
	360 (-) 392 (-)	290 - 700	85.8	85.9	NiO
$(N_2H_5)_2[Co\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	200 (+)	180 -220	6.7	6.8	$(N_2H_5)_2Co\{C_{10}H_6(COO)(O)\}_2$
	252 (-)	220 - 334	54.1	54.0	$Co\{C_{10}H_6(COO)(O)\}$
	364 (-)	334 -700	84.8	84.9	Co_3O_4
$(N_2H_5)_2[Cd\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	180 (+)	170 -190	6.2	6.1	$(N_2H_5)_2Cd\{C_{10}H_6(COO)(O)\}_2$
	235 (-)	190 - 272	48.9	48.8	$Cd\{C_{10}H_6(COO)(O)\}$
	354 (-) 416(-)	272 - 700	78.0	78.1	CdO
$(N_2H_5)_2[Zn\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	186 (+)	176 - 220	6.6	6.7	$(N_2H_5)_2Zn\{C_{10}H_6(COO)(O)\}_2$
	257 (-)	220 - 317	53.2	53	$Zn\{C_{10}H_6(COO)(O)\}$
	366 (-) 412 (-) 465 (-)	317 - 700	84.8	84.9	ZnO

Continued

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Molecular Formula of Complexes	DTA peak Temp (° C)	TG			Decomposition products
		Temp. Range(°C)	Weight loss%		
			obsd.	calcd.	
$(N_2H_5)_2[Mn\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	175 (+)	170 - 181	6.6	6.8	$(N_2H_5)_2Mn\{C_{10}H_6(COO)(O)\}_2$
	213 (-)	181 - 295	54.3	54.1	$Mn\{C_{10}H_6(COO)(O)\}$
	374 (-)	295 -700	83.4	83.6	MnO_2
$(N_2H_5)_2[Cu\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	105 (+)	98 -125	6.6	6.7	$(N_2H_5)_2Cu\{C_{10}H_6(COO)(O)\}_2$
	166 (-)	125 -260	53.5	53.2	$Cu\{C_{10}H_6(COO)(O)\}$
	336 (-)	260 -700	85.0	85.2	CuO
$[Ni(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$	226(-)	174 - 255	37.7	37.7	$[Ni\{C_6H_4(COO)(O)\}]$
	357 (-)	255-700	76.2	76.1	NiO
$[Co(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$	230 (-)	171 - 246	37.5	37.7	$[Co\{C_6H_4(COO)(O)\}]$
	337 (-)	246 - 700	74.2	74.4	Co_3O_4
$[Cd(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$	212 (-)	170 -233	32.3	32.2	$[Cd\{C_6H_4(COO)(O)\}]$
	352 (-) 405 (-)	233 -700	64.9	65.0	CdO
$[Zn(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$	192 (-)	175 - 232	37.0	36.9	$[Zn\{C_6H_4(COO)(O)\}]$
	451 (-)	232 - 700	74.7	74.5	ZnO

(+) = endotherm; (-) = exotherm

$(N_2H_5)_2[M\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$ where M=Ni, Co, Cd, Zn, Mn and Cu

The TG curves reveal three step decomposition of the complexes. Dehydration takes place in the first step, exhibiting endotherms in the range of 105-200°C (Figure 4a), followed by a decomposition in the second step forming an unstable intermediate, probably $[M\{C_{10}H_6(COO)(O)\}]$, with a display of an exothermic peak in the range of 166-257°C in DTA. During the last step of decomposition of the complexes, the intermediate degrades to the respective metal oxide showing a strong exothermic peak in the range of 336-465°C.

The sequence of reactions proposed for the decompositions are:

$$(N_2H_5)_2[M\{(C_{10}H_6(COO)(O)\}_2(H_2O)_2] \xrightarrow{105\text{-}200°C}$$
$$(N_2H_5)_2[M\{C_{10}H_6(COO)(O)\}_2]+2H_2O$$

$$(N_2H_5)_2[M\{C_{10}H_6(COO)(O)\}_2]+11\tfrac{1}{2}O_2 \xrightarrow{166\text{-}257°C}$$
$$[M\{C_{10}H_6(COO)(O)\}]+2N_2H_4+11CO_2+4H_2O$$

$$[M\{C_{10}H_6(COO)(O)\}]+O_2 \xrightarrow{336\text{-}465°C}$$
$$MO/M_3O_4/MO_2+CO_2+H_2O$$
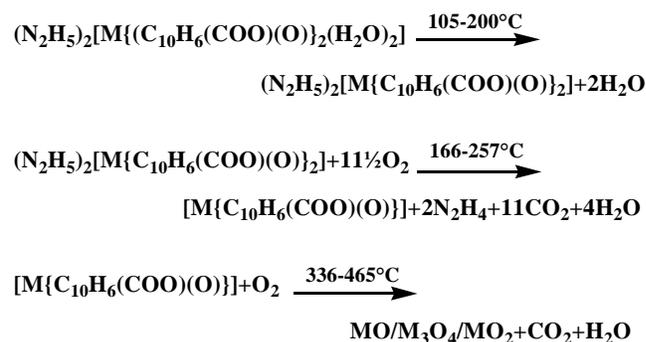
The metal oxides formed after the incineration of the complexes at their decomposition points found from DTA, followed by sintering at the same temperature for

Figure 4a : TG-DTA of $(N_2H_5)_2[Zn\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$
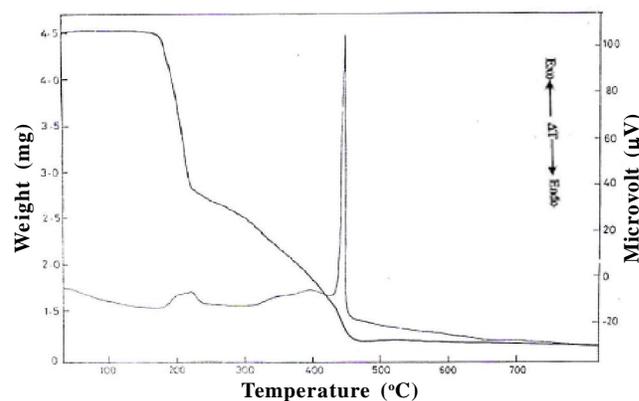
Figure 4b : TG-DTA of $[Zn(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$

about 3 -4 hours were found to be pure and uniform in nano scale (25-50 nm) as noted from XRD using Scherer's formula[19]. The oxides obtained in this way are expected to be chemically more homogeneous, free of contamination by impurities and highly reactive. As a representative example, image of MnO_2 from SEM is shown in Figure 5.

$[(N_2H_4)M\{C_{10}H_6(COO)(O)\}(H_2O)_2]$ where M(II) = Ni, Co, Cd and Zn

The simultaneous TG-DTA results of all the com-

plexes are similar and all of them undergo two stages of weight loss upon heating (Figure 4b). The first stage, which occurs in the range 170-255 °C, is attributed to the loss of two water molecules and one hydrazine molecule. In DTA, this loss of water is observed as an exotherm in the range, 192-230°C. Though intermediates work out to be the respective metal phthalates, they are found to be highly unstable. Finally, they undergo a strong exothermic decomposition in the range 337-451°C, resulting in the formation of corresponding metal oxides as final product.
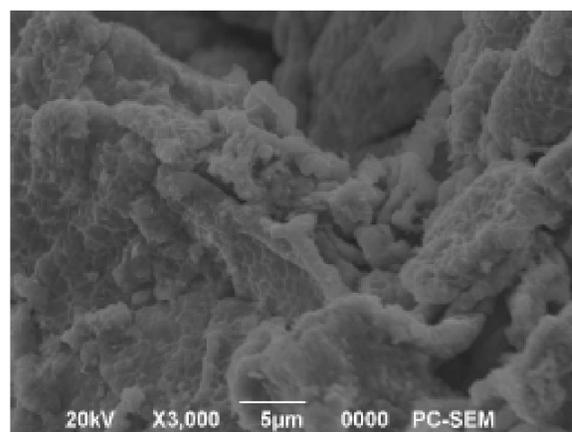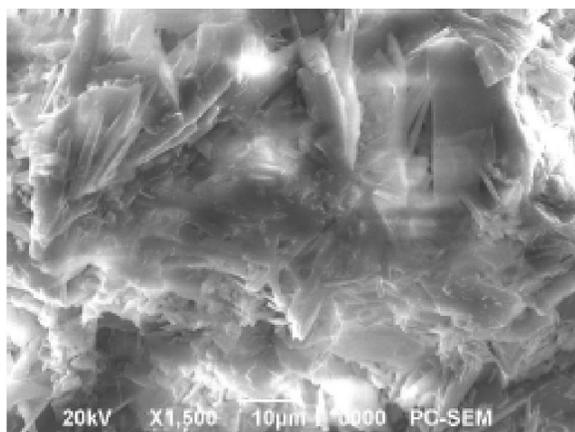
Figure 5 : SEM image of MnO_2

X-ray diffraction

X -ray powder diffraction of the complexes is shown in Figure 6a & Figure 6b. XRD data of the complexes reveal the isomorphism among the com-

plexes $(N_2H_5)_2[M\{C_{10}H_6(COO)(O)_2\}(H_2O)_2]$ where M= Ni, Co, Cd, Zn, Mn and Cu and $[(N_2H_4)M\{C_{10}H_6(COO)(O)\}(H_2O)_2]$ where M(II) = Ni, Co, Cd and Zn.
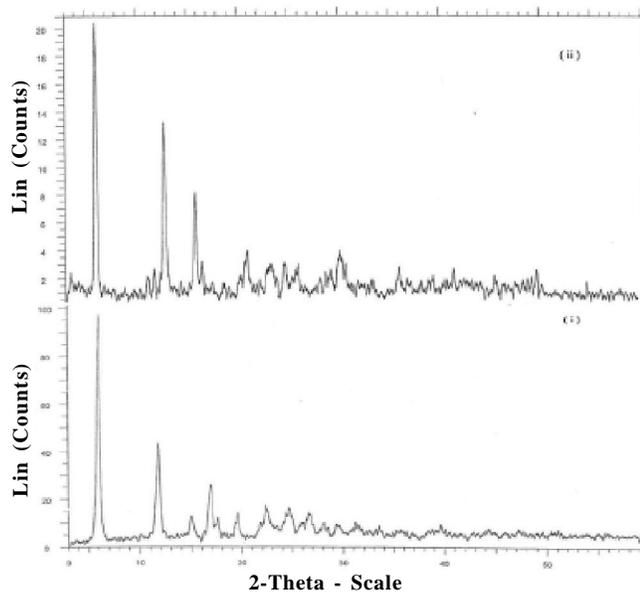
Figure 6a : XRD of (i) $(N_2H_5)_2[Ni\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$ and (ii) $(N_2H_5)_2[Cd\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$
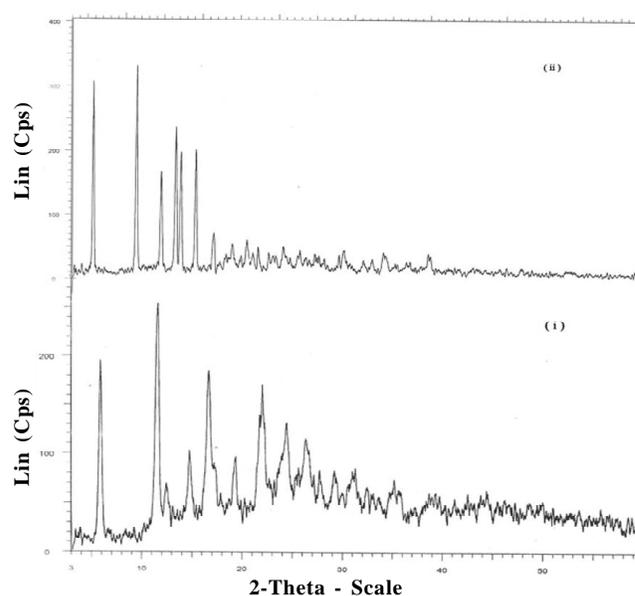
Figure 6b : XRD of (i) $[Ni(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$ and (ii) $[Zn(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$

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Evaluation of kinetic parameters

From the TG curves, the kinetic parameters i.e. n (order of reaction), E (energy of activation), A (pre-exponential factor) and ΔS (entropy change) were determined (shown in TABLE 3). The linear plots are constructed for the different decomposition steps using integrated Coats- Redfern equation[20] and correlation coefficient values were evaluated. The best linear plot obtained for each of the decomposition stages was chosen as the mechanism of the reaction, in which the correlation coefficient value was close to unity. By using different values of order of reaction, straight line was fitted by regression. The highest value of r (correlation coefficient) gave the correct value 'n'. From the slope and intercept, E and A values were calculated. Using E and A values, the value of ΔS was determined.

TABLE 3 : Kinetic parameters of the complexes

Molecular formula of the Complexes	Reaction	E in KJ	A	n	ΔS in KJ
$(N_2H_5)_2[Ni\{(C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	Dehydration	68.2182	3.0605×10^6	0.1	0.02789
	Decomposition	69.2407	2.3077×10^6	3	0.02678
$(N_2H_5)_2[Co\{(C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	Dehydration	98.5421	6.5417×10^9	3	0.05557
	Decomposition	75.6678	7.00349×10^6	3	0.03079
$(N_2H_5)_2[Cd\{(C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	Dehydration	48.2186	6.7225×10^5	0.1	0.02243
	Decomposition	38.8321	6.7212×10^6	0.3	0.03061
$(N_2H_5)_2[Zn\{(C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	Dehydration	113.227	9.5317×10^{11}	3	0.07355
	Decomposition	21.6869	4.3343×10^7	3	0.0373
$(N_2H_5)_2[Mn\{C_{10}H_6(COO)(O)\}_2(H_2O)_2]$	Dehydration	127.591	7.1443×10^{13}	3	0.08918
	Decomposition	39.3826	6.1887×10^6	3	0.03034
$(N_2H_5)_2[Cu\{(C_{10}H_6(COO)(O)_2\}(H_2O)_2]$	Dehydration	102.8363	1.1668×10^{12}	3	0.07436
	Decomposition	88.4917	2.3335×10^{19}	0.1	0.1349
$[Ni(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$	Dehydration	33.0399	5.5116×10^7	0.1	0.03834
	Decomposition	28.3845	4.0126×10^7	3	0.0371
$[Co(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$	Dehydration	27.5704	1.21927×10^8	0.1	0.04121
	Decomposition	32.7214	3.23377×10^7	2	0.03633
$[Cd(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$	Dehydration	48.9052	9.97768×10^5	0.1	0.02387
	Decomposition	17.4716	3.37916×10^8	3	0.04479
$[Zn(N_2H_4)\{C_{10}H_6(COO)(O)\}(H_2O)_2]$	Dehydration	80.2489	5.8413×10^7	0.1	0.03858
	Decomposition	11.1275	6.8738×10^8	3	0.04729

CONCLUSION

New anionic complexes of 2 -hydroxy -1- naphthoic acid with transition metals and $N_2H_5^+$ as cation with the general formula, $(N_2H_5)_2[M\{(C_{10}H_6(COO)(O)\}_2(H_2O)_2]$ where M = Ni, Co, Cd, Zn, Mn and Cu and neutral hydrazine complexes with the formula $[(N_2H_4)M\{C_{10}H_6(COO)(O)\}(H_2O)_2]$ where M(II) = Ni, Co, Cd and Zn have been prepared. Electronic spectra and magnetic moment values indicate that Ni, Co and Cu complexes may be of octahedral geometry with CN 6. The infrared spectrum implies their nature of coordination. However, the exact structure of the complexes may be known
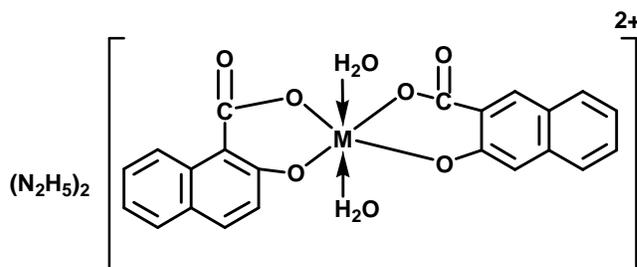
Figure 7a : Structure of hydrazinium complexes
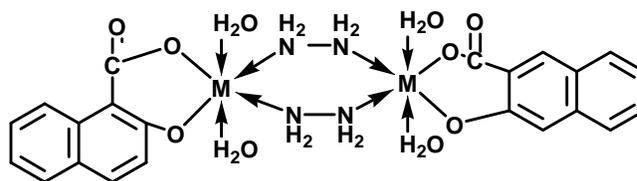
Figure 7b : Structure of hydrazine complexes

only from single XRD analysis. The proposed structures of the complexes are as shown in Figure 7a and Figure 7b.

The thermal behaviour of the complexes indicates that they undergo oxidative degradation in the temperature 336 ºC - 465 ºC to form metal oxides. Because of the evolution of various gases during decomposition N_2, H_2 and CO_2, the metal oxides are produced as fine particles probably with nano size, 25-50 nm suggesting the fact that these complexes may be used as precursors for nanometal oxides.

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