

3-Hydroxy-2-naphthoate Complexes of Transition Metals with Hydrazine - Preparation, Spectroscopic and Thermal Studies

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Received 19 June 2009; Accepted 10 August 2009

Abstract: Reaction of hydrazine and 3-hydroxy-2-naphthoic acid with some transition metal ions forms two types of complexes: (i) $[M(N_2H_4)(C_{10}H_6(3-O)(2-COO)(H_2O)_2)]$ where $M=Ni, Co, Cd$ and Zn , at pH 9 and (ii) $[M(N_2H_5)_2\{C_{10}H_6(3-O)(2-COO)\}_2].xH_2O$ where $M=Ni$ & $x=1$; $M=Co, Cd, Mn$ & $x=3$; and $M=Zn, Cu$ & $x=0$ at pH 4. Analytical data confirms the compositions of the complexes. The acid shows dianionic nature in these complexes. The magnetic moments and electronic spectra suggest the geometry of the complexes. IR data indicates the nature of hydrazine and presence of water in the complexes. Simultaneous TG-DTA studies shows different thermal degradation patterns for the two types of complexes. The first type shows formation of no stable intermediates whereas the second type shows the respective metal hydroxy naphthoate intermediates. The final products in both the types are found to be metal oxides of nano size. XRD patterns show isomorphism among the complexes with similar molecular formulae.

Keywords: Hydrazine complexes, Hydrazinium complexes, 3-Hydroxy-2-naphthoic acid, IR, Thermal analysis.

Introduction

Hydrazine complexes of the first row transition metal ions with a variety of carboxylic acids have been reported in the literature. These include simple aliphatic mono and dicarboxylic acids^{1,2}, aromatic mono and *di* carboxylic acids^{3,4} and heterocyclic carboxylic acids⁵. The hydrazinium metal carboxylates⁶ and their hydrates are crystalline solids and mostly water soluble but hydrazine complexes are amorphous powder and are insoluble in water. Many *bis*-hydrazine and hydrazinium metal carboxylates are used as precursors for metal oxides and mixed metal oxides such as ferrites, cobaltites, chromites *etc*^{7,8}.

3-Hydroxy-2-naphthoic acid is one example of a naphthalene derivative that has been frequently used as the chelating agent. Bin Liu *et al.* prepared Cr(III) complex with this chelating agent⁹. Fluorescence property and stability constant have been studied¹⁰. In this paper we report the preparation, characterization and thermal decomposition of some new hydrazine and hydrazinium complexes with this acid.

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 Fluka Chemicals. The hydrazine hydrate was used as such as received.

Preparation of $[M(N_2H_4)\{C_{10}H_6(3-O)(2-COO)\}(H_2O)_2]$ where $M = Ni, Co, Cd \& Zn$

These complexes were prepared by stirring the aqueous solution of the ligands (60 mL) containing 3-hydroxy-2-naphthoic acid (0.188 g, 1 mmol) and hydrazine hydrate (0.5 mL, 10 mmol) with 20 mL of added metal nitrate solution (*i.e.* 0.291 g of $Co(NO_3)_2 \cdot 6H_2O$, 1 mmol in 20 mL of distilled water) at pH 9.

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 90 °C 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 $CaCl_2$.

Preparation of $[M(N_2H_5)_2\{C_{10}H_6(3-O)(2-COO)\}_2] \cdot xH_2O$, where $M = Ni, x = 1$; $M = Co, Cd \& Mn, x = 3$ and $M = Zn \& Cu, x = 0$

A similar procedure was adopted for the preparation of these complexes, with a molar ratio of acid: base: metal ion = 1:2:2, in 60 mL of water-alcohol (1:1) mixture at 60 °C. Cadmium complex was formed with 1:1:4 ratio. The micro crystalline precipitate was formed immediately and the mixture was kept in water bath for 20 min. It was cooled, filtered and washed with distilled water, ethanol and then with ether. The precipitate was dried in a desiccator over anhydrous $CaCl_2$.

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 acid¹¹.

IR spectra of the complexes in the region $4000\text{-}400 \text{ cm}^{-1}$ 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 $Cu\text{-}K\alpha$ 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 $10 \text{ }^\circ\text{C min}^{-1}$ 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

A band appears in the range 19890-20350 cm^{-1} and is assigned to the ${}^4\text{T}_{1g}(\text{P}) \rightarrow {}^4\text{T}_{1g}$ transition of typical six coordinated Co(II) hydrazine complexes. The corresponding nickel complexes show two bands in the region 10480-10790 and 17370-17690 cm^{-1} which are ascribable to ${}^3\text{A}_{2g} \rightarrow {}^2\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^2\text{T}_{1g}(\text{F})$ transitions, respectively, of octahedral Ni(II). The magnetic moment values obtained for the nickel and cobalt complexes, 3.2 and 4.8 BM respectively, confirm the high spin octahedral structures.

The cobalt complexes of hydrazinium transition metal complexes register a band in the regions of 18300 and 20080 cm^{-1} due to transitions ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ of typical six coordinated Co(II) complexes. The corresponding nickel complexes show bands in the regions 16200, 18210 and 26370 cm^{-1} which are ascribable to transition ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and the copper complex shows bands in the regions 13610 and 18620 cm^{-1} assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transitions, respectively, evidence the octahedral geometry of the complexes¹². The magnetic moment values obtained for the nickel, cobalt, copper and manganous complexes, 3.35, 4.97, 1.83 and 5.8 BM respectively, confirm the high spin octahedral structures.

The axial ESR spectrum for copper complex shown in Figure 1 has features at $g_{\parallel} = 2.1$ and $g_{\perp} = 1.9$ which indicate that the copper(II) ion geometry is that of a distorted octahedron.

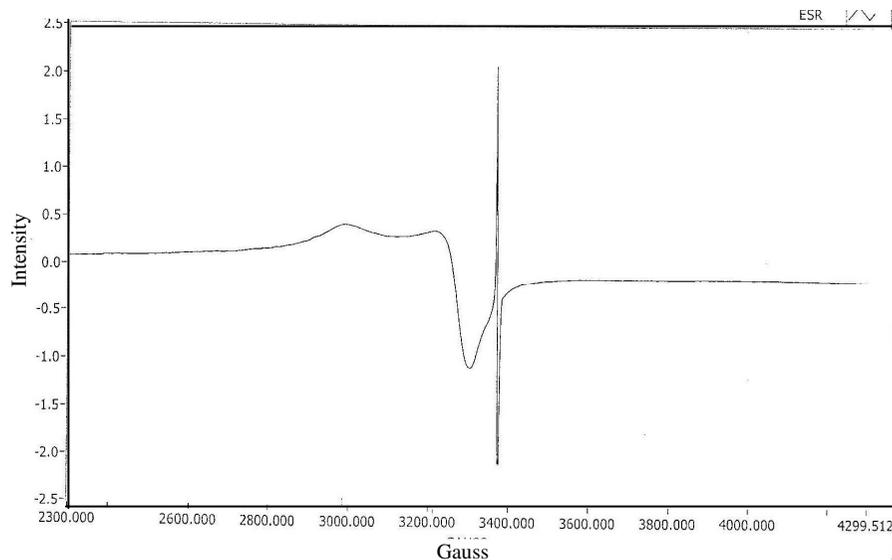


Figure 1. ESR spectrum of $[\text{Cu}(\text{N}_2\text{H}_5)_2\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})_2\}]$.

IR spectra of complexes

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

Table 1. Analytical and IR data of the complexes.

Molecular Formula of Complexes	Colour	D.pt / °C	Analytical data, %					IR data							
			C Found. (calcd.)	H Found. (calcd.)	N Found. (calcd.)	Hydra zine Found. (calcd.)	Metal Found. (calcd.)	ν OH cm^{-1}	$\rho_r(\text{H}_2\text{O})$ cm^{-1}	$\nu_{\text{C=O}}$ asym cm^{-1}	$\nu_{\text{C=O}}$ sym cm^{-1}	ν_{asy^-} ν_{sy^-} cm^{-1}	$\nu_{\text{M-O}}$ cm^{-1}	$\nu_{\text{N-N}}$ cm^{-1}	ν_{NH} cm^{-1}
[Ni(N ₂ H ₄){C ₁₀ H ₆ (3-O)(2-COO)}(H ₂ O) ₂]	Green	135	41.9 (42.2)	4.5 (4.5)	8.7 (8.9)	10.0 (10.2)	18.6 (18.8)	3384(b)	838(s)	1627(m)	1382(m)	245	474(s)	981(s)	3180(s)
[Co(N ₂ H ₄){C ₁₀ H ₆ (3-O)(2-COO)}(H ₂ O) ₂]	Pink	170	42.1 (42.2)	4.4 (4.5)	8.8 (8.9)	10.1 (10.2)	18.7 (18.8)	3384(b)	841(s)	1654(s)	1382(s)	272	470(s)	972(s)	3298(s)
[Cd(N ₂ H ₄){C ₁₀ H ₆ (3-O)(2-COO)}(H ₂ O) ₂]	White	180	36.2 (36.0)	3.7 (3.8)	7.5 (7.6)	8.8 (8.7)	30.6 (30.7)	3325(b)	841(s)	1647 (s)	1375 (s)	272	474(s)	960(s)	3288(s)
[Zn(N ₂ H ₄){C ₁₀ H ₆ (3-O)(2-COO)}(H ₂ O) ₂]	White	195	41.3 (41.3)	4.3 (4.4)	8.7 (8.8)	10.2 (10.0)	20.5 (20.5)	3384(b)	840(s)	1649(s)	1394(s)	255	470(s)	977(s)	3292(s)
[Ni(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O)(2-COO)} ₂].H ₂ O	Green	140	51.3 (51.3)	4.6 (4.7)	10.9 (10.9)	12.4 (12.4)	11.4 (11.4)	3384(b)	517(s)	1618(m)	1348(b)	270	466(s)	1016 (s)	3299 (s)
[Co(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O)(2-COO)} ₂].3H ₂ O	Pink	65	47.9 (47.9)	5.1 (5.1)	10.1 (10.2)	11.6 (11.6)	10.7 (10.7)	3398(b)	580(s)	1604(s)	1334(m)	270	470 (s)	1016 (s)	3298(s)
[Cd(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O)(2-COO)} ₂].3H ₂ O	White	60	43.7 (43.7)	4.7 (4.6)	9.2 (9.3)	10.6 (10.6)	18.5 (18.6)	3386(b)	573(s)	1600(m)	1326(m)	274	470(s)	1016(s)	3282(s)
[Zn(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O)(2-COO)} ₂]	Dull white	280	52.5 (52.4)	4.3 (4.4)	11.1 (11.1)	12.7 (12.7)	12.9 (13.0)	-	596(s)	1649(s)	1363(m)	286	476 (s)	1014(s)	3265 (s)
[Mn(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O)(2-COO)} ₄].3H ₂ O	Dull white	130	48.3 (48.3)	5.1 (5.1)	10.2 (10.2)	11.7 (11.7)	10.0 (10.0)	3346(b)	596(s)	1649(s)	1363(m)	286	470 (s)	1014(s)	3265 (s)
[Cu(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O)(2-COO) ₂ }]	Grass green	175	52.6 (52.6)	4.4 (4.4)	11.2 (11.2)	12.8 (12.8)	12.6 (12.7)	-	594(s)	1647(m)	1396(m)	251	472(s)	1014(s)	3286 (s)

s = sharp; m = medium; b = broad

All the hydrated complexes, except zinc and copper in hydrazinium complexes, display a medium broad peak centered on 3440 cm^{-1} , indicating the O-H stretch of water molecules. An additional sharp peak in the region $838\text{-}841\text{ cm}^{-1}$ is observed which may be due to the presence of coordinated water molecules in $[\text{M}(\text{N}_2\text{H}_4)\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}(\text{H}_2\text{O})_2]$ and sharp peak in the region $517\text{-}596\text{ cm}^{-1}$ is due to presence of lattice water in $[\text{M}(\text{N}_2\text{H}_5)_2\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}_2].x\text{H}_2\text{O}$. Infrared technique serves as finger print technique and the presence of bidentate N_2H_4 in $[\text{M}(\text{N}_2\text{H}_4)\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}(\text{H}_2\text{O})_2]$ is indicated by the characteristic *N-N* frequency in the range $960\text{-}981\text{ cm}^{-1}$. The presence of coordinated hydrazinium cation in $[\text{M}(\text{N}_2\text{H}_5)_2\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}_2].x\text{H}_2\text{O}$ has been indicated by the presence of $\nu_{\text{N-N}}$ in the region $1014\text{-}1016\text{ cm}^{-1}$ ¹³. All the compounds show moderately strong bands in the region $3180\text{-}3299\text{ cm}^{-1}$ due to N-H stretching. The asymmetric and symmetric stretching frequencies of carboxylate ions are seen in the range $1600\text{-}1654$ and $1326\text{-}1396\text{ cm}^{-1}$, respectively with a ($\nu_{\text{asy}} - \nu_{\text{sy}}$) separation of $245\text{-}286\text{ cm}^{-1}$ indicating the monodentate linkage of both the carboxylate group.

Thermal analysis

The thermal data of the complexes are listed in Table 2. The compositions of the intermediates and the final products are those, which fit with the observed mass losses in TG. Thermogravimetric results are in good agreement with the DTA data. As a representative example, TG-DTA of $[\text{Ni}(\text{N}_2\text{H}_4)\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}(\text{H}_2\text{O})_2]$ and $[\text{Ni}(\text{N}_2\text{H}_5)_2\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}_2].\text{H}_2\text{O}$ are shown in Figure 2(a) & 2(b).

Table 2 . Thermal Analysis of the complexes.

Molecular formula of the complexes	DTA peak Temp, ° C	TG		Decomposition products
		Temp. Range, °C	Weight loss, % obsd. calcd.	
$[\text{Ni}(\text{N}_2\text{H}_4)\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}(\text{H}_2\text{O})_2]$	140 (+) 223(-)	40 - 259	21.3 -	unstable intermediate
	352 (-)	259 - 700	76.1 76.1	NiO
$[\text{Co}(\text{N}_2\text{H}_4)\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}(\text{H}_2\text{O})_2]$	238 (-)	179 - 257	21.3 -	unstable intermediate
	365 (-)	257 - 700	74 74.4	Co_3O_4
$[\text{Cd}(\text{N}_2\text{H}_4)\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}(\text{H}_2\text{O})_2]$	227 (-)	189 - 244	24.4 -	unstable intermediate
	431 (-)	244 - 700	64.8 64.9	CdO
$[\text{Zn}(\text{N}_2\text{H}_4)\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}(\text{H}_2\text{O})_2]$	215 (+)	196 - 233	11.1 11.3	$[\text{Zn}(\text{N}_2\text{H}_4)\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}]$
	267 (-)	233 - 359	21.5 -	unstable intermediate
	453 (-)	359 - 700	74.4 74.5	ZnO
$[\text{Ni}(\text{N}_2\text{H}_5)_2\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}_2].\text{H}_2\text{O}$	146 (+)	57-166	3.5 3.5	$(\text{N}_2\text{H}_5)_2\text{Ni}\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}_2$
	296 (-) 318 (-) 498 (-)	166 - 700	85.3 85.5	NiO
$[\text{Co}(\text{N}_2\text{H}_5)_2\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}_2].3\text{H}_2\text{O}$	79 (+)	43 - 100	10.1 9.8	$(\text{N}_2\text{H}_5)_2\text{Co}\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}_2$
	279 (-)	100 -	84.7 85.4	Co_3O_4
	429 (-)	700		
$[\text{Cd}(\text{N}_2\text{H}_5)_2\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}_2].3\text{H}_2\text{O}$	61 (+)	40 - 100	8.6 8.9	$(\text{N}_2\text{H}_5)_2\text{Cd}\{\text{C}_{10}\text{H}_6(3\text{-O})(2\text{-COO})\}_2$
	409 (-)	100 - 700	78.6 78.7	CdO

Contd...

[Zn(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O)(2-COO)} ₂]	282 (+)	200 - 330	12.3	12.5	Zn{C ₁₀ H ₆ (3-O)(2-COO)} ₂ ZnO
	496 (-)	330 - 700	83.5	83.8	
[Mn(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O)(2-COO)} ₄].3H ₂ O	135 (+)	42 - 200	10.0	9.9	(N ₂ H ₅) ₂ Mn{C ₁₀ H ₆ (3-O)(2-COO)} ₂ MnO ₂
	424 (-)	200 - 700	84.2	84.0	
[Cu(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O)(2-COO)} ₂]	178 (+)	100 - 237	12.6	12.8	Cu{C ₁₀ H ₆ (3-O)(2-COO)} ₂ CuO
	354 (-)	237 - 700	84.1	84.2	

(+) = endotherm; (-) = exotherm

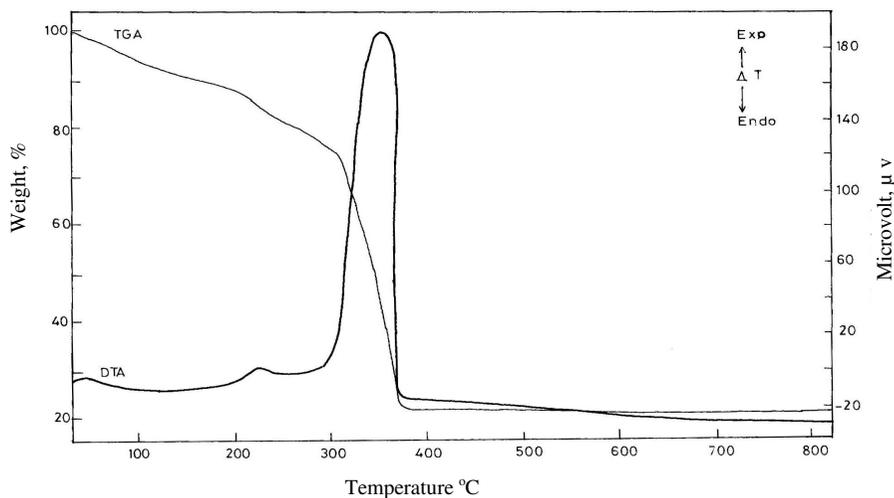


Figure 2(a). TG-DTA of [Ni(N₂H₄){C₁₀H₆(3-O)(2-COO)}(H₂O)₂].

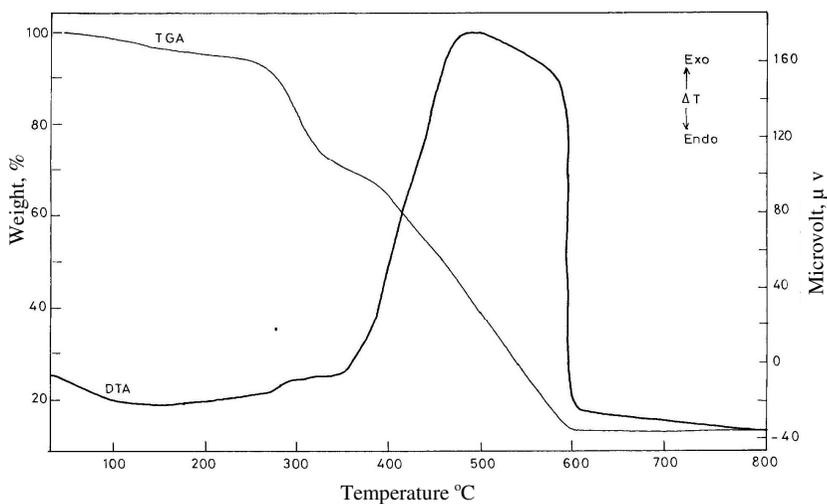


Figure 2(b). TG-DTA of [Ni(N₂H₅)₂{C₁₀H₆(3-O)(2-COO)}₂].H₂O

$[M(N_2H_4)\{C_{10}H_6(3-O)(2-COO)\}(H_2O)_2]$ where $M = Ni, Co, Cd$ and Zn

Nickel, cobalt and cadmium complexes lose hydrazine and water simultaneously showing exotherms at 223, 238 and 227 °C forming an unstable intermediate which could not be made out. Dehydration normally accompanies heat absorption. A broad endotherm centred at 140 °C due to dehydration appears initially in the case of nickel complex. But in the case of other complexes, this step appears to combine with dehydrazination resulting in exotherms in the range 227-238 °C. During the last step of decomposition of the complexes, the unstable intermediate degrades to the respective metal oxide showing a strong exothermic peak in the range 352-431 °C.

A clear distinct mass loss is observed in the TG of Zn complex, showing endothermic dehydration at 215 °C, followed by an exothermic decomposition at 267 °C with the formation of unstable intermediate. During the last step this intermediate undergoes exothermic decomposition at 453 °C forming ZnO as final product.

$[M(N_2H_5)_2\{C_{10}H_6(3-O)(2-COO)\}_2].xH_2O$, where $M = Ni, Co, Cd, Mn, Zn$ & Cu

All the complexes undergo two stages of decomposition upon heating. For Ni, Co, Cd and Mn complexes, the first stage of decomposition occurs in the range 61-146 °C which is attributed to the loss of water molecules present outside the co-ordination sphere. On further heating, the anhydrous complexes decomposes directly to NiO, Co₃O₄, CdO and MnO₂ in the temperature range 279-498 °C which was confirmed by their XRD pattern.

Zinc and copper complexes undergoes dehydrazination, forms an unstable intermediate, probably $[M\{C_{10}H_6(O)(COOH)\}_2]$, at 282 & 178 °C. In the next step both the complexes undergo exothermic decomposition to form corresponding metal oxides as final product at 496 °C and 354 °C.

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 about 3-4 h were found to be pure and uniform in nano scale (20-25 nm) as found from XRD using Scherrer's formula¹⁴, $D = K\lambda / B \cos\theta$ where λ is the X-ray wavelength, B is the full width of height maximum (FWHM) of a diffraction peak, θ is the diffraction angle and K is the Scherrer's constant of the order of 0.8. The SEM image of MnO₂ from hydrazinium complex is shown as representative example (Figure 3).

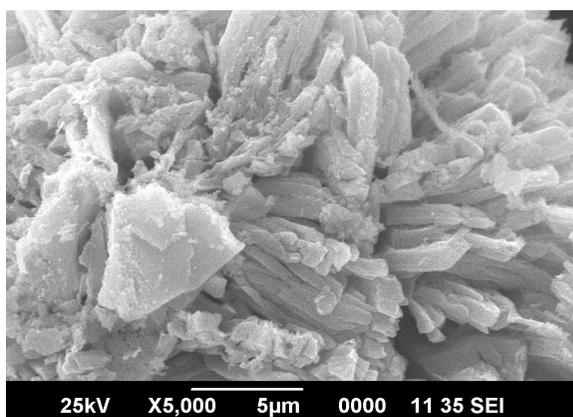


Figure 3. SEM image of MnO₂.

Table 3. X ray powder diffraction data of 3-hydroxy - 2-naphthoic acid complexes (d spacings in Å° and relative intensities in parentheses).

[M(N ₂ H ₄){C ₁₀ H ₆ (3-O)(2-COO)}(H ₂ O) ₂]				[Ni(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O) (2-COO)} ₂].H ₂ O	[M(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O) (2-COO)} ₂].3H ₂ O			[M(N ₂ H ₅) ₂ {C ₁₀ H ₆ (3-O)(2-COO)} ₂]		
Ni	Co	Cd	Zn		Co	Cd	Mn	Zn	Cu	
11.7505 (28.8)	11.6308 (14.4)	11.6382 (8.3)	11.5048 (13.8)	19.52 (65.9)	17.01 (12)	17.14 (100)	17.15 (45.9)	17.57 (100)	18.48 (100)	
10.3741 (24.2)	10.4457 (24.1)	10.3094 (7.5)	10.3069 (15.8)	4.7821 (95.3)	15.66 (16)	15.55 (8.4)	15.74 (100)	6.31 (12.3)	6.32 (68)	
9.28272 (29.1)	9.3959 (33)	9.3429 (6.5)	9.0835 (9.4)	4.0107 (99.7)	5.9737 (100)	5.86 (14.1)	5.33 (59.4)	5.06 (28.3)	5.09 (72.9)	
6.0387 (100)	5.9346 (78.5)	6.4373 (100)	5.9402 (100)	3.8499 (89.5)	3.6045 (74.4)	3.16 (21.3)	3.89 (92.9)	4.54 (18.5)	4.55 (75.5)	
4.4285 (67.3)	4.4601 (78.3)	4.4828 (8.1)	4.4856(16.1)	3.3456 (89.6)	2.7845 (70.5)	2.68 (4.3)	2.67 (98.1)	3.65 (25.3)	3.63 (80.9)	
3.9974 (89.8)	3.7084 (100)	3.6301(10.1)	3.6664 (25.6)	2.0471 (63.1)	2.1104 (59.2)	2.28 (8)	2.28 (93.8)	2.10 (5.3)	2.22 (57.3)	
2.8967 (70.1)	2.8126 (85)	2.7999 (5.4)	2.8192 (20.7)	1.9974 (61.7)	1.8303 (57.1)	1.93 (5.9)	1.92 (92)	1.57 (3.3)	1.57 (45.3)	
				1.9512 (63.4)	1.5988 (51.2)	1.58 (6.6)	1.58 (89.5)			
				1.3345 (54)						
				1.46 (48.1)						
				1.3006 (35.3)						
				1.2584 (34.5)						

X-ray diffraction

X-ray powder diffraction data of the complexes are summarized in Table 3. It is found that the diffraction patterns of hydrazine complexes of Ni, Co, Cd & Zn, hydrazinium complexes of Co, Cd & Mn and hydrazinium complexes of Zn & Cu show similarity among the individuals in each set implying isomorphism

Conclusion

Transition metal ions such as Ni(II), Co(II), Cd(II), Mn(II), Zn(II) & Cu(II) react with 3-hydroxy-2-naphthoic acid and hydrazine hydrate yield hydrazine metal naphthoates at pH 9 and hydrazinium metal naphthoates at pH 4. The magnetic moment and electronic spectra suggest the high-spin octahedral nature of the complexes. Infrared spectra indicate the monodentate nature of carboxylate ions, bidentate bridged nature of hydrazine in *bis*-hydrazine complexes and coordinated hydrazinium cation in hydrazinium complexes. TG-DTA studies shows different thermal degradation patterns for the two types of complexes. The first type shows formation of no stable intermediates whereas the second type shows the respective metal hydroxy naphthoate intermediates. During the last step of decomposition all the complexes undergo oxidative decomposition to form corresponding metal oxides as final product. Because of the evolution of various gases during decomposition (N₂, H₂ and CO₂), the metal oxides formed are fine particles probably with nano size 20-25 nm.

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