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Spectral and Thermal Studies of Transition Metal Complexes of Acetamido Benzoic Acids with Hydrazine

E. HELEN PRICILLA BAI[1] and S. VAIRAM[2,*]

[1]Department of Chemistry, Park College of Engineering and Technology, Coimbatore-641 659, India
[2]Department of Chemistry, Government College of Technology, Coimbatore-641 013, India

*Corresponding author: E-mail: vamshen@yahoo.com

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The metal complexes of isomeric acetamido benzoic acids with Co, Ni, Zn and Cd metals have been prepared and characterized by analytical, spectroscopic (IR, UV reflectance), micro elemental analysis, simultaneous TG-DTA, powder XRD, magnetic susceptibility measurements and SEM-EDS studies: $[Ni(2\text{-acamb})_2(N_2H_4)].2H_2O$; $[M(2\text{-acamb})_2(N_2H_4)].H_2O$, where M = Co, Cd and Zn; $[M(3\text{-acamb})_2(N_2H_4)].H_2O$, where M = Ni and Co and $[M(3\text{-acamb})_2(N_2H_4)].2H_2O$ where M = Cd and Zn; $[Co(4\text{-acamb})_2(N_2H_4)].H_2O$ and $[M(4\text{-acamb})_2(N_2H_4)].2H_2O$ where M = Ni, Cd and Zn, 2-acambH = 2-acetamido benzoic acid, 3-acambH = 3-acetamido benzoic acid and 4-acambH = 4-acetamido benzoic acid. Among them Ni, Co and Cd complexes of 2-acambH and 4-acambH were obtained at pH 5 and 6 respectively, whereas Zn complexes of both acids were formed at pH 3. 3-acambH complexes were prepared at pH 5. The IR spectra of the compounds display the *N-N* stretching frequency absorptions in the range of 984-926 cm^{-1}, which reveals the bridging bidentate coordination of hydrazine. The compounds show ν(C=O) (asym) values in the range 1611-1582 cm^{-1} and the ν(C=O) (sym) values at 1555-1422 cm^{-1}. The difference of ν(C=O) (asym) and ν(C=O) (sym), which is found to be 48-162 cm^{-1}, indicates that the carboxylate anion is coordinated to the metal ion in the bidendate fashion. These complexes undergo dehydration in the range of 140-177 ºC first and then oxidative decomposition showing exotherms in the range of 200-278 ºC and in the range of 400-682 ºC to their respective metal oxides. Cadmium and zinc complexes show their intermediates as carbonates. The electronic spectra and the magnetic susceptibility values suggest that the coordination number of the complexes is 6 with distorted octahedral geometry. XRD patterns show isomorphism among the complexes with similar molecular formulae. The SEM-EDS studies reveal the presence of respective metal oxides.

Key Words: IR, Simultaneous TG-DTA, Acetamido benzoate, Electronic spectra.

INTRODUCTION

Hydrazine is the simplest diamine containing two lone pair of electrons. It forms variety of compounds with more number of carboxylic acids, such as simple aliphatic mono and di carboxylic acids[1,2] aromatic mono and di carboxylic acids[3,4] tri and tetra carboxylic acids[5,6], which have been reported in the literature. Many *bis*-hydrazine and hydrazinium metal carboxylates are used as precursors for metal oxides and mixed metal oxides[7-15]. Though studies have been done on 4-acetamido benzoate synthesis of lanthanide coordination polymers using 4-acetamido benzoic acid and various modes of coordination of 4-acetamido benzoate (monodentate, chelating and multidentate bridging nature)[16-20], a detailed study of transition metal complexes of isomeric acetamido benzoic acids in the presence of hydrazine has not been attempted so far. In this paper, we report the synthesis, spectral and thermal studies of some transition metal complexes of 2-acetamido, 3-acetamido and 4-acetamido benzoates with hydrazine. The structures of the isomeric forms acetamido benzoic acids are given in the Figs. 1-3.

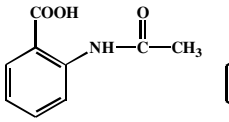

Fig. 1. 2-Acetamido benzoic acid (2-acambH)

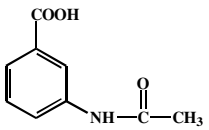

Fig. 2. 3-Acetamido benzoic acid (3-acambH)

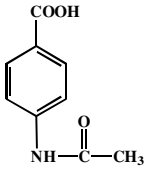

Fig. 3. 4-Acetamido benzoic acid (4-acambH)

EXPERIMENTAL

The chemicals and solvents used were of AR grade received from Fluka chemicals. The double distilled water was used for the preparation and chemical analyses. Hydrazine hydrate 99.99 % pure was used as such.

Preparation of $[M\{(2\text{-}),(3\text{-}) \text{ and } (4\text{-}) \text{ acamb}\}_2(N_2H_4)].xH_2O$, where 2-acambH =2-acetamido benzoic acid, M =

Ni and x = 2 and M = Co, Cd and x = 1; where 3-acambH = 3-acetamido benzoic acid, M = Ni, Co and x = 1 and M = Cd and x = 2; where 4-acambH = 4-acetamido benzoic acid M = Ni, Cd and x = 2 and M = Co and x = 1.

The complexes were prepared by adding an aqueous solution of metal nitrate [*e.g.*, $Ni(NO_3)_2.6H_2O$, 0.291 g, 1 mmol in 20 mL of H_2O] to a clear solution obtained by mixing hydrazine hydrate (99.99 % pure, 0.1 g, 2 mmol) with a slurry of acetamido benzoic acid (0.1792 g, 1 mmol in 60 mL of hot water). Crystalline products of complexes were formed when the solution mixture was heated over a hot water bath at 80 ºC.

2-Acetamido benzoic acid complexes were formed at pH 5 immediately whereas 3-acetamido and 4-acetamido benzoic acid complexes formed at pH 5 when the reaction mixture is heated for 90 min and at pH 6 when heated for 2h 30 min respectively.

The complexes formed were filtered through filter paper, washed with distilled water, ethanol then with ether and dried in a desiccator.

Preparation of $[Zn(acamb)_2(N_2H_4)].xH_2O$, where 2-acambH = 2-acetamidobenzoic acid and x = 1 and 3-acambH = 3-acetamido benzoic acid, 4-acambH = 4-acetamidobenzoic acid and x = 2.

These complexes were also prepared by the same procedure in absolute alcohol medium. As mentioned above, complexes of **2** isomer were formed immediately at pH 3 and those of **3** and **4** isomers were formed at pH 5 and 3 in 90 min and 2 h 30 min respectively.

The complexes were filtered, washed and dried as mentioned above.

Physico-chemical techniques: The composition was established by chemical analysis. Hydrazine content was determined by titrating against standard KIO_3 solution (0.025 mol L^{-1}) under Andrew's conditions[20]. The metal content was determined by EDTA (0.01 mol L^{-1}) complexometric titration[20] after decomposing a known weight of the sample with 1:1 HNO_3. Magnetic measurements were carried out by using Guoy balance and Gauss meter DGM102 (Besto) keeping $Hg[Co(NCS)_4]$ as calibrant. The electronic spectra for solid state complexes were obtained using a Varian, Cary 5000 recording spectrophotometer. Infrared spectra were recorded using KBR disc (4000-400 cm^{-1}) on a Shimadzu FTIR-8201 (PC)S spectrophotometer. The simultaneous TG-DTA studies were done on a Perkin Elmer, Diamond TG/DTA analyzer and the curves were obtained using 5-10 mg of the samples at the heating rate of 10 ºC per min in air atmosphere. Platinum cups were employed as sample holders and alumina as reference and the temperature range was ambient to 700 ºC. The XRD patterns were recorded on a Bruker AXS D_8 advance diffractometer with an X-ray source Cu, wavelength 1.5406 Å using a Si (Li) PSD detector. The elemental analysis was carried out using an Elementar Vario ELIII CHNS elemental analyzer. The SEM with EDS analysis was obtained using JEOL model JSM-6390 LV and JEOL model JED-2300 instrument.

RESULTS AND DISCUSSION

Electronic spectra and magnetic susceptibility: The absorption maximum and assignments are summarized in Table-1. Since the complexes were insoluble in water and organic solvents, the electronic reflectance spectra were recorded in solid-state. Based on the absorptions term states assigned are $^4T_{1g}$ (P) → $^4T_{2g}$ and $^4A_{2g}$ for cobalt and $^3T_{2g}$ → $^3T_{1g}$ and ^1E_g for nickel complexes. These assignments evidence the distorted octahedral geometry of the complexes[21]. The magnetic moment values obtained for the cobalt and nickel complexes were 5.20 and 3.31 BM respectively, which supports the geometry of cobalt and nickel compounds.

TABLE-1
ELECTRONIC SPECTRA VALUES OF THE COMPLEXES

Complex	Absorption maximum (cm^{-1})	Assignment
$[Ni(2\text{-acamb})_2N_2H_4].2H_2O$	20534, 16807 and 15408	$^3T_{1g}$
	8313, 7257 and 6725	$^3T_{2g}$
$[Ni(3\text{-acamb})_2(N_2H_4)].H_2O$	20000, 16447, 13459 and 12136	$^3T_{1g}$
	8224 and 7257	$^3T_{2g}$
$[Ni(4\text{-acamb})_2(N_2H_4)].2H_2O$	20000 and 13459	$^3T_{1g}$
	11933	^1E_g
	7955 and 6064	$^3T_{2g}$
$[Co(2\text{-acamb})_2(N_2H_4)].H_2O$	21186	$^4T_{1g}(P)$
	11806	$^4A_{2g}$
	8467, 7348 and 6667	$^4T_{2g}$
$[Co(3\text{-acamb})_2(N_2H_4)].H_2O$	23148	$^4T_{1g}(P)$
	11561	$^4A_{2g}$
	8313, 7117, 6489 and 5780	$^4T_{2g}$
$[Co(4\text{-acamb})_2(N_2H_4)].H_2O$	12755	$^4A_{2g}$
	8224, 7184, 6667 and 6017	$^4T_{2g}$

IR spectra of complexes: The IR spectral data of the complexes are summarized in Table-2. The pka values of 2-acambH, 3-acambH and 4-acambH were found to be 3.63, 4.07 and 4.28 respectively. These indicate that 4-isomer is least acidic and the lowest value of ν(C=O) 1672 cm^{-1} of the same may be due to its highest pka value.

The IR spectra of pure acids show absorption at 1707, 1694 and 1672 cm^{-1} corresponding to ν(C=O) (acid). But the spectra of complexes show ν(C=O) asym (acid) at 1582-1611 cm^{-1} and ν(C=O) sym (acid) in the range 1555-1422 cm^{-1} with the difference of 48-162 cm^{-1} between ν(C=O) (asym) and ν(C=O) (sym), which supports the bidental coordination of carboxylate ions to metal. The absorption at 984-926 cm^{-1} observed in IR spectra of complexes is assigned to ν(N-N) stretching of hydrazine present in the complexes, which reveals that N_2H_4 is coordinated to metal ion in bridged bidentate fashion. The O-H stretch of water molecules are noticed at 3543-3304 cm^{-1} in all complexes. An additional band observed at 594-518 cm^{-1} also supports the presence of lattice water molecules[22]. The C=O frequency of amide group of the compounds is observed at 1709-1635 cm^{-1}. The N-H stretching frequencies of amide and that of hydrazine are found to be a merged broad band at 3281-3173 cm^{-1}.

Thermal data of all the complexes are given in Table-3.

Thermal data of $[M(2\text{-acamb})_2(N_2H_4)_2].xH_2O$ complexes, where M = Ni and x = 2, where M = Co, Cd and Zn and x = 1

The 2-acambH complexes show endothermic dehydration in the range 140-177 ºC. The high temperature dehydration reveals that these lattice water molecules are held up strongly[22]. Co and Cd complexes show exothermic dehydrazi-nation at 214-275 ºC, whereas the dehydrazination was not clearly visible in Ni and Zn compounds.

TABLE-2
ANALYTICAL AND IR DATA OF COMPLEXES

m.f.	Analytical data: C Found (calc.)	H Found (calc.)	N Found (calc.)	N_2H_4 Found (calc.)	M Found (calc.)	IR data (cm^{-1}) b = broad; s = sharp; m = medium: ν (C=O) asym	ν (C=O) sym	ν (N-N)	ν (OH)	ν (N-H)	ν (C=O) (amido gp)	ρ_r H_2O	ν (M-O)
2-acambH complexes													
$[Ni(2\text{-acamb})_2N_2H_4]\cdot 2H_2O$	45.6(44.7)	4.4(5.0)	12.0(11.6)	6.4(6.6)	12.9 (12.2)	1595 b	1433 b	964 s	3464 b	3233 b	1684 m	527 s	422 m
$[Co(2\text{-acamb}_2(N_2H_4)]\cdot H_2O$	46.0(46.4)	4.3(4.8)	12.1(12.0)	6.4(6.9)	12.4(12.7)	1589 s	1439 s	966 s	3304 m	3175 m	1661 s	594 s	438 s
$[Cd(2\text{-acamb})_2(N_2H_4)]\cdot H_2O$	41.8(41.6)	4.3(4.3)	10.7(10.8)	6.3(6.2)	21.3(21.7)	1584 b	1422 b	959 s	3543 s	3235 b	1676 m	594 s	509 s
$[Zn(2\text{-acamb})_2(N_2H_4)]\cdot H_2O$	45.3(45.8)	4.5(4.7)	11.8(11.9)	6.8(6.8)	13.7(13.9)	1599 s	1447 s	970 s	3320 s	3219 b	1661 s	567 s	463 s
3-acambH complexes													
$[Ni(3\text{-acamb})_2(N_2H_4)]\cdot H_2O$	46.5(46.4)	4.5(4.8)	12.0(12.0)	6.7(6.9)	12.4(12.6)	1582 s	1460 s	984 s	3392 b	3227 b	1709 b	525 s	476 m
$[Co(3\text{-acamb})_2(N_2H_4)]\cdot H_2O$	46.4(46.4)	4.7(4.8)	12.1(12.0)	6.9(6.9)	(12.6(12.7)	1611 m	1487 s	980 s	3339 s	3271 b	1635 b	552 s	459 s
$[Cd(3\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$	41.3(40.2)	4.2(4.5)	10.9(10.4)	6.5(6.0)	20.1(20.9)	1611 s	1462 s	926 m	3376 b	3281 s	1659 s	559 s	459 s
$[Zn(3\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$	43.9(44.1)	4.7(4.9)	11.6(11.4)	7.0(6.5)	14.3(13.4)	1607 s	1487 s	974 s	3305 s	3215 b	1607 b	559 s	430 s
4-acambH complexes													
$[Ni(4\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$	44.4(44.7)	4.5(5.0)	11.8(11.6)	7.4(6.6)	13.2(13.1)	1609 b	1530 b	964 s	3360 m	3183 b	1672 m	544 s	500 s
$[Co(4\text{-acamb})_2(N_2H_4)]\cdot H_2O$	46.2(46.4)	4.7(4.8)	12.0(12.0)	6.7(6.9)	12.8(12.7)	1601 b	1528 b	968 s	3335 b	3173 b	1680 b	546 s	500 s
$[Cd(4\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$	41.2(40.2)	3.8(4.5)	11.3(10.4)	6.2(6.0)	21.3(20.9)	1603 b	1555 b	964 s	3377 b	3260 b	1668 b	581 s	500 s
$[Zn(4\text{-acamb})_2(N_2H_4)\cdot 2H_2O]$	44.7(44.1)	4.1(4.9)	12.4(11.4)	7.0(6.5)	14.4(13.4)	1597 s	1521 s	972 s	3315 s	3270 b	1672 m	518 s	503 s

The cadmium complex shows a broad exotherm at 400 ºC indicating the formation of metal carbonate intermediate[23,24] and the corresponding weight loss is observed between 300-470 ºC in its thermogravimetric curve. It is also inferred that the complex undergoes oxidative decomposition to form the metal oxide residue, which is accompanied by an exothermic doublet at 490 and 556 ºC indicating the weight loss temperature of 470-700 ºC.

The TG-DTA curves of Ni, Co and Zn complexes show that the dehydrazinated metal carboxylates decompose to give the metal oxide as their final residue. As the intermediates are highly unstable and they could not be isolated. They show exotherms in the range 420-500 ºC attributing the formation of metal oxide residue with the mass loss temperature in the range of 200-700 ºC is observed in their TG.

Reaction Scheme-I

The reaction scheme of the 2-acambH complexes is given below:

$$[M\{C_6H_4(CH_3CONH)COO\}_2(N_2H_4)]\cdot xH_2O \xrightarrow[-H_2O]{140\text{-}177\ ^\circ C} [M\{C_6H_4(CH_3CONH)COO\}_2(N_2H_4)]$$

where, M = Ni, Co, Cd and Zn

$$[M\{C_6H_4(CH_3CONH)COO\}_2(N_2H_4)] \xrightarrow[-N_2H_4]{214\text{-}275\ ^\circ C} M\{C_6H_4(CH_3CONH)COO\}_2$$

where, M = Co and Cd

$$M\{C_6H_4(CH_3CONH)COO\}_2 \xrightarrow{420\text{-}500\ ^\circ C} MO$$

where, M = Ni, Co and Zn and CoO = Co_3O_4)

$$[Cd\{C_6H_4(CH_3CONH)COO\}_2] \xrightarrow{400\ ^\circ C} CdCO_3 \xrightarrow{490\text{-}556\ ^\circ C} CdO$$

Thermal data of $[M(3\text{-acamb})_2(N_2H_4)_2].xH_2O$; where M = Ni, Co and x = 1; M = Cd, Zn and x = 2

Similar to 2-acambH complexes, 3-acambH complexes show an endothermic dehydration at 122-160 ºC. Ni and Co complexes show exothermic dehydrazination in the range of 230-260 ºC, while Cd and Zn complexes do not. The intermediates of Ni, Co and Zn compounds were unstable and could not be identified. They further decompose to their respective metal oxides at 500-600 ºC. In case of cadmium oxidative decomposition occurs *via* its carbonate intermediate. Its decomposition temperature, 494 ºC was comparable to that of the reported[6], with the corresponding weight loss between 400-700 ºC.

Reaction Scheme-II

The reaction scheme of 3-acetamidobenzoate complexes is given as follows:

$$[M\{C_6H_4(CH_3CONH)COO\}_2(N_2H_4)]\cdot xH_2O \xrightarrow[-H_2O]{122\text{-}160\ ^\circ C} [M\{C_6H_4(CH_3CONH)COO\}_2(N_2H_4)]$$

where, M = Ni, Co, Cd and Zn

$$[M\{C_6H_4(CH_3CONH)COO\}_2(N_2H_4)] \xrightarrow[-N_2H_4]{230\text{-}260\ ^\circ C} [M\{C_6H_4(CH_3CONH)COO\}_2]$$

where, M = Ni and Co

$$[M\{C_6H_4(CH_3CONH)COO\}_2)] \xrightarrow{446\text{-}600\ ^\circ C} [MO]$$

where, M = Ni, Co, and Zn and CoO = Co_3O_4

$$[Cd\{C_6H_4(CH_3CONH)COO\}_2)] \xrightarrow{210\text{-}317\ ^\circ C} CdCO_3 \xrightarrow{494\text{-}700\ ^\circ C} CdO$$

Thermal data of $[M(4\text{-acamb})_2(N_2H_4)_2].xH_2O$; where M = Ni, Cd, Zn and x = 2; M = Co and x = 1

TABLE-3
THERMAL DATA OF COMPLEXES

Complex	DTA Temp. (ºC)	Thermogravimetry			Nature of the reaction
		Temp. Range	Weight Loss (%)		
			Obsd.	Calcd.	
$[Ni(2\text{-acamb})_2N_2H_4]\cdot 2H_2O$	150(+)	60-200	7.1	7.2	Dehydration
	278(-) }				
	420(-) }	200-700	84.3	84.5	Formation of nickel oxide
$[Co(2\text{-acamb}_2(N_2H_4)]\cdot H_2O$	177(+)	60-190	4.0	3.9	Dehydration
	214(-)	190-300	10.5	10.7	Dehydrazination
	400(-)	300-700	82.6	82.8	Formation of cobalt oxide (Co_3O_4)
$[Cd(2\text{-acamb})_2(N_2H_4)]\cdot H_2O$	160(+)	40-180	3.6	3.5	Dehydration
	275(-)	180-300	9.8	9.6	Dehydrazination
	400(-)	300-480	57.1	57.1	Formation of cadmium carbonate
	490(-) }	480-700	75.0	75.2	Formation of cadmium oxide
	556(-) }				
$[Zn(2\text{-acamb})_2(N_2H_4)]\cdot H_2O$	140(+)	100-180	3.9	3.8	Dehydration
	274(-)	180-700	83.0	82.7	Formation of zinc oxide
	500(-)				
$[Ni(3\text{-acamb})_2(N_2H_4)]\cdot H_2O$	140(+)	100-200	3.6	3.9	Dehydration
	260(-)	200-400	10.7	10.8	Dehydrazination
	500(-) }				
	590(-) }	4000-700	84.7	84.9	Formation of nickel oxide
$[Co(3\text{-acamb})_2(N_2H_4)]\cdot H_2O$	160(+)	120-200	3.8	3.9	Dehydration
	230(-)	200-340	10.5	10.7	Dehydrazination
	446(-) }				
	540(-) }	340-700	83.8	83.9	Formation of cobalt oxide
	600(-) }				
$[Cd(3\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$	122(+)	80-200	6.6	6.7	Dehydration
	210(-) }	200-400	55.2	55.0	Formation of cadmium carbonate
	317(-) }				
	494(-) }	400-700	76.1	76.0	Formation of cadmium oxide
	620(-) }				
$[Zn(3\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$	145(+)	100-200	7.2	7.5	Dehydration
	240(-) }				
	468(-) }	200-700	83.4	83.3	Formation of zinc oxide
	553(-) }				
$[Ni(4\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$	175(+)	50-190	7.4	7.5	Dehydration
	251(-)	190-390	14.0	14.1	Dehydrazination
	401(-) }	390-700	85.3	85.5	Formation of nickel oxide
	486(-) }				
$[Co(4\text{-acamb})_2(N_2H_4)]\cdot H_2O$	120(+)	60-180	4.0	3.9	Dehydration
	239(-)	180-280	10.6	10.7	Dehydrazination
	324(-) }				
	390(-) }				
	450(-) }	280-700	82.6	82.8	Formation of cobalt oxide (Co_3O_4)
$[Cd(4\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$	150(+)	50-180	6.8	6.7	Dehydration
	240(-)	180-320	12.9	12.7	Dehydrazination
	401(-) }	320-460	55.0	55.2	Formation of cadmium carbonate
	625(-) }	460-800	75.8	76.0	Formation of cadmium oxide
	682(-) }				
$[Zn(4\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$	145(+)	75-160	7.2	7.4	Dehydration
	236(-) }				
	350(-) }	160-400	63.8	64.0	Formation of zinc carbonate
	533(+)	400-600	83.9	84.0	Formation of zinc oxide

4-acambH complexes show endothermic dehydration at 120-175 ºC. Exothermic dehydrazination is observed between 239-251ºC for Ni, Co and Cd complexes and no distinct step was observed in case of Zn complex.

Ni and Co complexes undergo oxidative decomposition to their metal oxide as final residue accompanied by the exotherms in the range 324-486 ºC with a corresponding weight loss between 230-700 ºC.

In the final step, cadmium and zinc show exothermic decomposition at 350 and 401 ºC *via* the carbonate intermediate[5,6], which decompose further to their metal oxides showing broad exotherms in the range of 533-682 ºC showing the mass loss between 400-800 ºC, to 75.8 % for cadmium and 83.9 % for zinc.

The TG-DTA of $[Ni(2\text{-acamb})_2(N_2H_4)].2H_2O$, $[Cd(3\text{-acamb})_2(N_2H_4)].2H_2O$ and $[Zn(4\text{-acamb})_2(N_2H_4)].2H_2O$ complexes are shown as representative examples in Figs. 4-6.

Reaction Scheme-III

The reaction scheme of 4-acetamidobenzoate complexes are given as follows:

$$[M\{C_6H_4(CH_3CONH)COO\}_2(N_2H_4)]\cdot xH_2O \xrightarrow[-H_2O]{122\text{-}175\ ^oC} [M\{C_6H_4(CH_3CONH)COO\}_2(N_2H_4)]$$

where, M = Ni, Co, Cd and Zn

$$[M\{C_6H_4(CH_3CONH)COO\}_2(N_2H_4)] \xrightarrow[-N_2H_4]{239\text{-}251\ ^oC} [M\{C_6H_4(CH_3CONH)COO\}_2]$$

where, M = Ni and Co

$$[M\{C_6H_4(CH_3CONH)COO\}_2] \xrightarrow{324\text{-}486\ ^oC} [MO]$$

where, M = Ni and Co and CoO = Co_3O_4

$$[Cd\{C_6H_4(CH_3CONH)COO\}_2)] \xrightarrow{401\ ^oC} CdCO_3 \xrightarrow{625\text{-}682\ ^oC} CdO$$

$$[Zn\{C_6H_4(CH_3CONH)COO\}_2(N_2H_4)] \xrightarrow{350\ ^oC} ZnCO_3 \xrightarrow{553\ ^oC} ZnO$$

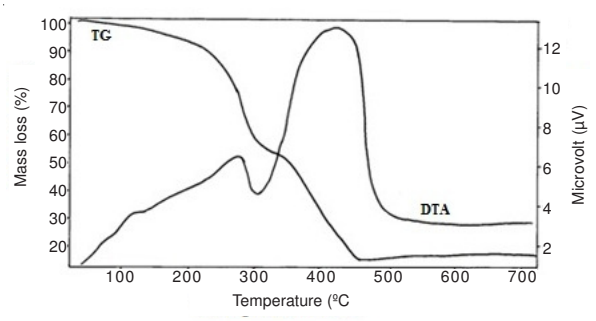

Fig. 4. TG-DTA of $[Ni(2\text{-acamb})_2N_2H_4\cdot 2H_2O$

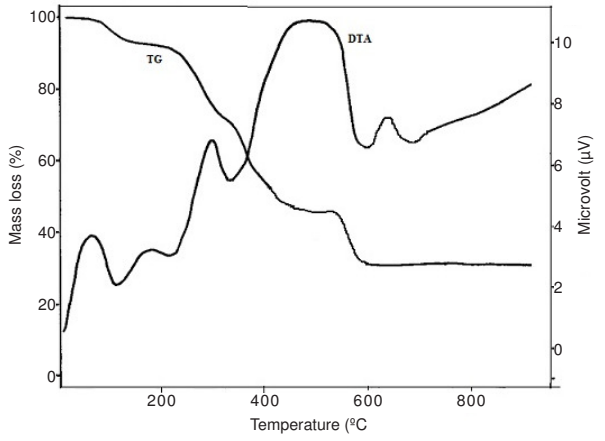

Fig. 5. TG-DTA of $[Cd(2\text{-acamb})_2N_2H_4\cdot 2H_2O$

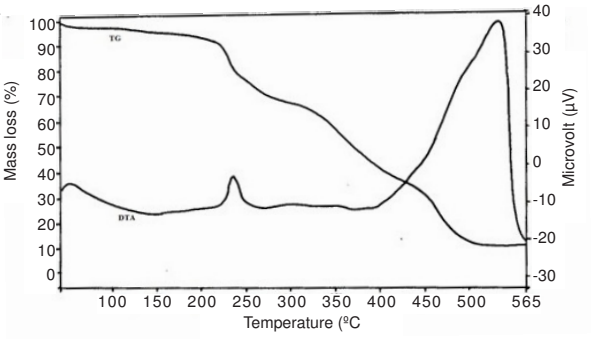

Fig. 6. TG-DTA of $[Zn(4\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$

XRD-data of complexes: The powder XRD patterns with their d-spacings are given in Table-4. They imply that each set of complexes with similar composition possesses isomorphism among them.

All the complexes were found to be crystalline even though compounds of 2-acambH show more crystallinity.

SEM-EDX studies: The SEM-EDX images of metal oxides of the complexes $[Co(2\text{-acamb})_2(N_2H_4)]\cdot H_2O$, $[Cd(3\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$ and $[Zn(4\text{-acamb})_2(N_2H_4)]\cdot 2H_2O$ are given as representative examples in Figs. 7-12. These metal oxides are obtained by incinerating the corresponding complexes at their decomposition temperature followed by sintering them for 0.5 h. They have yielded probably nanosized metal oxides.

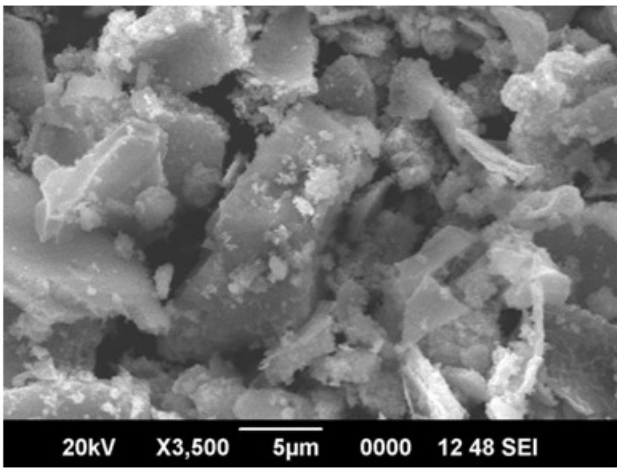

Fig. 7. SEM image of CoO obtained from $[Co(2\text{-acamb})_2(N_2H_4).H_2O$

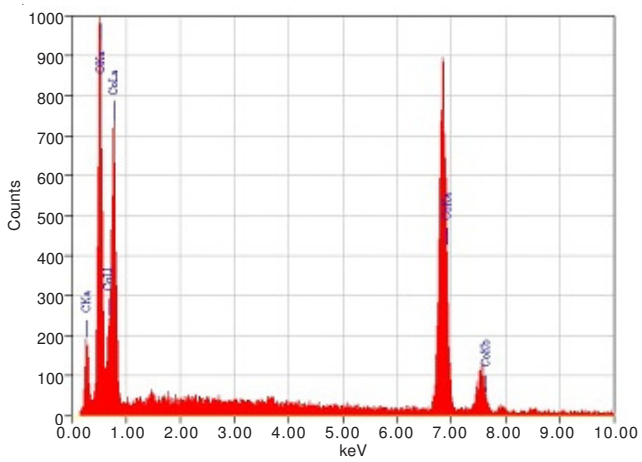

Fig. 8. SEM-EDX picture of CoO

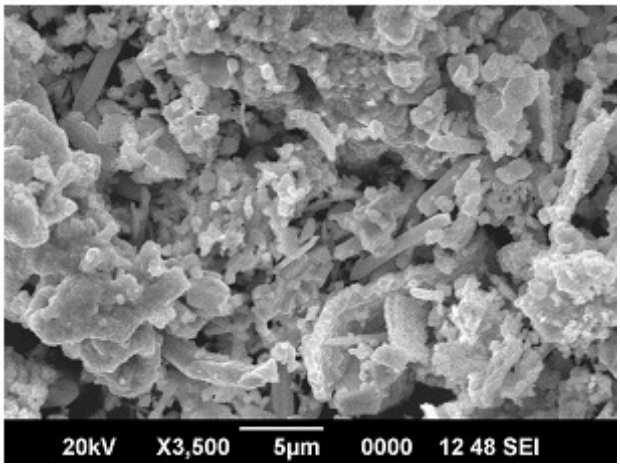

Fig. 9. SEM image of CdO obtained from $[Cd(3\text{-acamb})_2(N_2H_4)].2H_2O$

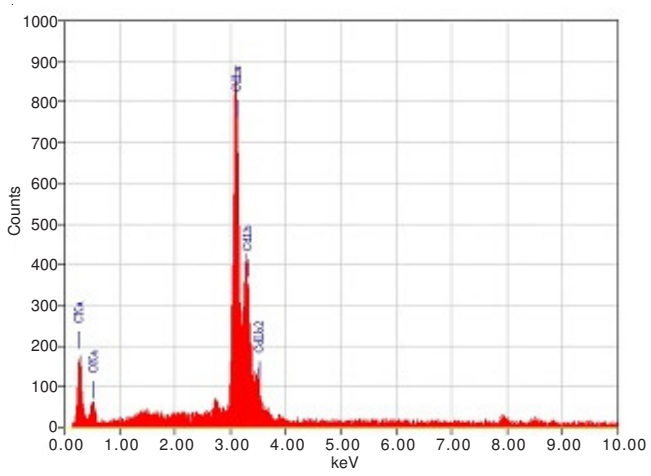

Fig. 10. SEM-EDX picture of CdO

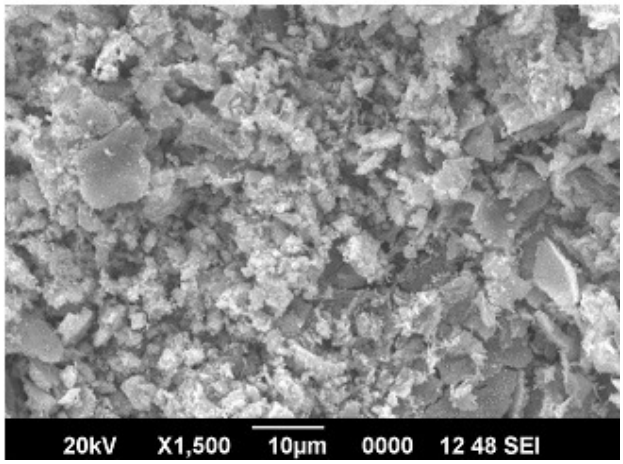

Fig. 11. SEM image of ZnO obtained from $[Zn(4\text{-acamb})_2.N_2H_4]_2H_2O$

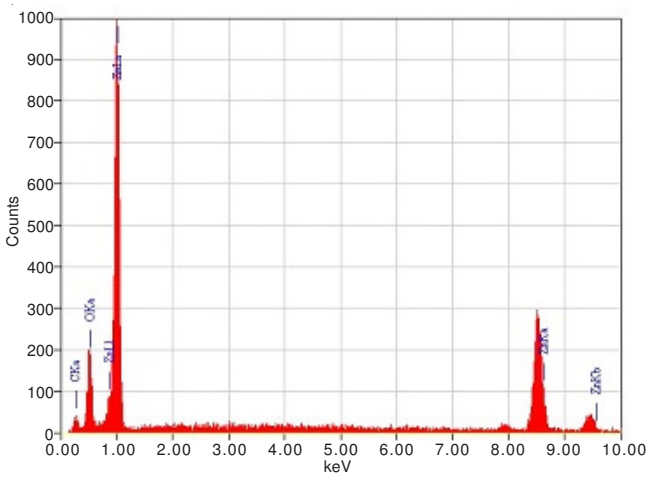

Fig. 12. SEM-EDX picture of ZnO

Conclusion

All the three isomeric acetamido benzoic acids have formed two categories of hydrated neutral hydrazine complexes with the formulae $[M\{(2\text{-}),(3\text{-}) \text{ and } (4\text{-}) \text{ acamb})\}_2(N_2H_4)].xH_2O$ where 2-acambH = 2-acetamido benzoic acid, M = Ni and x = 2; M = Co, Cd and Zn and x = 1, 3-acambH = 3-acetamido benzoic acid, M = Ni, Co and x = 1; M = Cd and Zn and x = 2 and 4-acambH = 4-acetamido benzoic acid, M = Co and x = 1; M = Ni, Cd and Zn and x = 2 The $NHCOCH_3$ group is both larger and less strongly electron donating than the NH_2 group and hence has not involved in complexation.

The IR frequencies reveal the coordination of the hydrazine with metal and the coordination mode of the carboxylate ion to metal. XRD patterns show isomorphism among the complexes with similar molecular formulae. The SEM-EDS studies confirm the formation of respective metal oxides. The thermal data reveals that various steps of decomposition of the compounds to form their metal oxide. The electronic spectra and the magnetic susceptibility values reveal the coordination and geometry. They suggest that Ni, Co, Cd and Zn complexes possesses distorted octahedral geometry with coordination number[6]. The proposed structures of these complexes are represented in the Figs. 13-15. However, they may be confirmed by single crystal XRD only.

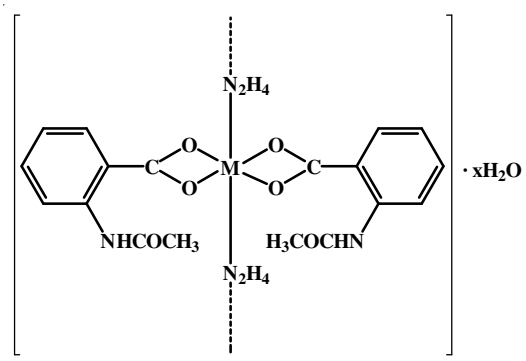

Fig. 13. Proposed structures of transition metal complexes of 2-acetamido benzoate with formula $[M(2\text{-acamb})_2(N_2H_4)].xH_2O$, where M = Ni and x = 2; M = Co, Cd, Zn and x = 1

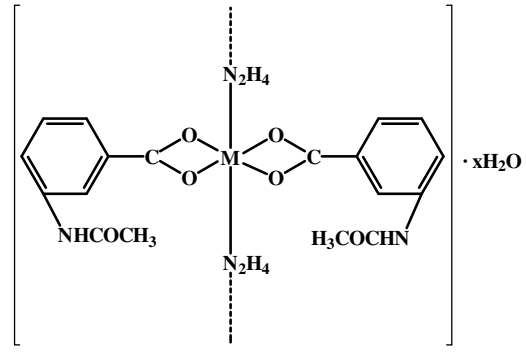

Fig. 14. Proposed structures of transition metal complexes of 3-acetamido benzoate with formula $[M(3\text{-acamb})_2(N_2H_4)].xH_2O$, where M = Ni, Co and x = 1; M = Co, Cd, Zn and x = 2

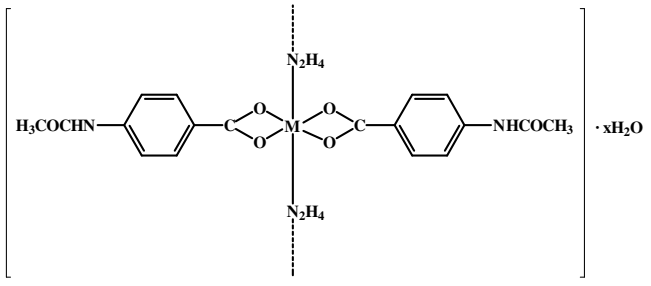

Fig. 15. Proposed structures of transition metal complexes of 4-acetamido benzoate with formula $[M(4\text{-acamb})_2(N_2H_4)].xH_2O$, where M = Ni, Cd, Zn and x = 2; M = Co and x = 1

TABLE-4
XRD DATA OF COMPLEXES (d-SPACING IN Å UNITS AND INTENSITY IN PARENTHESES)

$[M(2\text{-acamb})_2N_2H_4].xH_2O$, (where M = Ni and x = 2 and M=Co, Cd, Zn and x = 1) 2-acambH = 2-acetamido benzoic acid				$[M(3\text{-acamb})_2N_2H_4].xH_2O$, (where M = Ni, Co and x = 1 and M = Cd, Zn and x = 2) 3-acambH = 3-acetamido benzoic acid				$[M(4\text{-acamb})_2N_2H_4].xH_2O$, where M = Co and x =1 and M = Ni, Cd, Zn and x = 2) 4-acambH = 4-acetamido benzoic acid			
Ni	Co	Cd	Zn	Ni	Co	Cd	Zn	Ni	Co	Cd	Zn
	15.30 (22.20)	22.34 (3.23)						20.17 (41.67)	20.57 (65.00)		21.92 (100.00)
13.79 (29.10)	13.30 (40.00)	11.37 (100.00)	11.35 (5.56)				9.43 (33.00)	11.11 (19.00)	10.45 (32.00)	11.30 (34.00)	12.44 (42.00)
10.51 (100.00)	10.12 (100.00)	10.25 (12.90)	9.46 (100.00)								
8.95 (38.20)	8.95 (15.56)	9.19 (6.45)	9.05 (29.63)				8.00 (10.00)		8.57 (68.00)		
8.30 (45.50)	7.47 (35.56)	7.12 (4.84)	7.48 (94.44)				7.30 (8.33)	7.44 (100.00)		7.57 (50.00)	7.54 (13.00)
6.40 (54.50)	6.76 (4.44)	6.47 (6.45)	6.05 (85.19)			6.49 (98.3)	6.70 (20.00)	6.44 (19.00)	6.36 (47.00)	6.18 (12.00)	6.91 (9.00)
5.55 (32.70)	6.19 (40.00)	5.73 (29.00)	5.77 (18.52)	5.48 (71.19)		5.64 (71.67)	5.65 (30.00)	5.99 (10.00)	5.83 (100.00)	6.48 (22.00)	6.45 (36.00)
5.32 (38.20)	5.41 (37.78)	5.53 (22.58)				5.34 (30.00)	5.37 (100.00)		5.29 (63.00)		5.35 (15.00)
4.44 (5.50)	5.11 (35.56)	5.07 (16.67)	4.96 (29.63)		3.32 (87.50)	4.71 (15.00)	4.73 (48.33)	4.44 (31.00)	4.44 (58.00)	4.56 (38.00)	4.83 (58.20)
	4.86 (17.78)	4.58 (3.23)	4.75 (29.63)	4.04 (100.00)	2.50 (100.00)	4.25 (51.66)	4.17 (28.33)				4.42 (9.00)
3.98 (27.30)	4.47 (2.20)	3.95 (3.23)	4.63 (33.33)			3.96 (40.00)	3.93 (18.30)		3.78 (42.00)	3.71 (12.00)	4.11 (16.00)
3.42 (25.50)	4.13 (4.44)	3.83 (4.84)	4.39 (3.50)			3.73 (50.00)	3.69 (76.66)	3.65 (13.00)	3.31 (53.00)	3.32 (20.00)	3.95 (11.00)
	3.96 (13.33)	3.72 (3.23)	4.13 (22.22)			3.40 (46.00)	3.42 (36.00)			3.10 (16.00)	3.66 (100.00)
	3.59 (8.89)	3.56(6.45)	4.05 (16.67)			3.17 (26.66)	3.17 (70.00)			2.84 (14.00)	3.40 (60.00)
2.81 (16.40)	3.41 (6.67)	3.39 (4.84)	3.94 (57.41)			2.92 (41.67)	3.07 (33.00)				3.11 (16.00)
2.63 (9.10)	3.11 (4.44)	3.21 (3.23)	3.87 (2.60)			2.89 (100.00)	2.91 (6.60)				2.99 (11.00)
2.50 (7.30)		3.06 (3.23)	3.76 (2.60)			2.81 (18.30)	2.83 (10.00)		2.66 (47.00)		2.84 (27.27)
2.38 (9.10)		2.89 (3.23)	3.67 (9.26)			2.72 (23.33)	2.59 (15.00)		2.60 (63.00)		2.75 (7.00)
			3.39 (57.41)			2.60 (13.33)	2.48 (18.30)		2.54 (63.00)		2.58 (7.00)
			3.35 (29.63)			2.44 (20.00)	2.24 (10.00)		2.30 (47.00)		2.40 (15.00)
			3.25 (33.33)			2.24 (13.33)	2.19 (10.00)		2.14 (37.00)		2.28 (6.00)
			3.17 (7.40)			2.17 (20.00)	2.04 (15.00)		2.05 (42.00)	1.90 (14.00)	2.22(9.00)
			2.90 (11.11)			2.09 (15.00)	1.85 (5.00)		1.97 (47.00)		2.17 (7.00)
			2.84 (9.26)			2.03 (16.66)	1.80 (5.00)		1.91 (74.00)		2.05 (7.00)
			2.49 (7.40)			1.96 (20.00)	1.61 (5.00)		1.84 (58.00)		1.89 (7.00)
			2.36 (11.11)			1.87 (23.33)			1.73 (37.00)		1.82 (4.00)
			2.22 (12.96)			1.79 (6.66)					1.77 (6.00)
			2.18 (7.40)			1.67 (8.33)					1.65 (4.00)
			1.98 (7.40)			1.61 (8.33)					1.55 (4.00)
						1.56 (5.00)			1.55 (47.00)		1.45 (4.00)
						1.52 (5.00)			1.46 (53.00)		
						1.45 (6.66)			1.42 (53.00)		

$[M(2\text{-acamb})_2N_2H_4].xH_2O$, (where M = Ni and x = 2 and M=Co, Cd, Zn and x = 1) 2-acambH = 2-acetamido benzoic acid				$[M(3\text{-acamb})_2N_2H_4].xH_2O$, (where M = Ni, Co and x = 1 and M = Cd, Zn and x = 2) 3-acambH = 3-acetamido benzoic acid				$[M(4\text{-acamb})_2N_2H_4].xH_2O$, where M = Co and x =1 and M = Ni, Cd, Zn and x = 2) 4-acambH = 4-acetamido benzoic acid			
Ni	Co	Cd	Zn	Ni	Co	Cd	Zn	Ni	Co	Cd	Zn
						1.42 (5.00)			1.38 (42.00) 1.37 (32.00) 1.34 (42.00) 1.32 (32.00 1.29 (47.00) 1.27 (53.00) 1.25 (53.00) 1.22 (47.00)				

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