

CO-ORDINATION BEHAVIOUR OF HYDRAZINE AND ISOMERS OF ACETOXY BENZOIC ACIDS WITH TRANSITION METAL IONS

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ABSTRACT. New hydrazine complexes of some divalent transition metal ions of formulae, $[M\{(2-ab)_2(N_2H_4)\}] \cdot 3H_2O$, $[M\{(3-ab)_2(N_2H_4)\}] \cdot 3H_2O$ and $[M\{(4-ab)_2(N_2H_4)_2\}] \cdot 2H_2O$ where M = Co, Ni, Zn and Cd; 2-abH = 2-acetoxy benzoic acid, 3-abH = 3-acetoxy benzoic acid and 4-abH = 4-acetoxy benzoic acid were prepared using their respective metal nitrates and hydrazine hydrate at pH 6 and 5, respectively, and characterized by elemental analysis, IR and UV-reflectance spectroscopic techniques, thermo analytical technique, powder XRD, SEM-EDX and magnetic susceptibility measurements. All the transition metal complexes were sparingly soluble in water. The IR spectra of complexes showed N-N absorptions of hydrazine in the range of 964-988 cm^{-1} substantiating the bidentate bridging coordination of hydrazine. They showed endothermic decomposition in the range of 67-100 °C, exothermic dehydrazination in the range, 210-281 °C and an oxidative decomposition between 350 and 490 °C to form their respective metal oxides. The electronic spectral and magnetic susceptibility data could substantiate the distorted octahedral geometry of nickel and cobalt complexes and the XRD pattern indicates the existence of isomorphism. Crystals of $[Cd(H_2O)_3((C_6H_4(4-OH)(COO))_2)] \cdot H_2O$ obtained as by-product, was also characterized using single crystal XRD, IR and thermal studies.

KEY WORDS: Acetoxy benzoic acids, Hydrazine, Thermal analysis, Single crystal XRD

INTRODUCTION

The isomers of acetoxy benzoic acids (abH) are capable ligands for the formation of complexes owing to the presence of COOH and CH₃COO- groups attached with benzene ring. The 2-abH isomer, commonly called as aspirin, is a most frequently used antipyretic and 4-abH has been used in polymer synthesis. Literature survey indicates that these acids, especially 2 and 3-abH can form metal complexes having certain therapeutic effects such as due to the complexation of the metallic ion (Cu²⁺, Zn²⁺, Fe²⁺, Mg²⁺, etc.) essential for a certain biochemical process. Obaleye *et al.* reported the anti-bacterial activity of cobalt, nickel and iron complexes of aspirin. They found that 2-abH acted as bidentate chelate coordinating through carbonyl oxygen of carboxyl and ester groups and the metal complexes had greater antibacterial activity than that of ligand [1]. Ashraf *et al.* synthesized 2-acetoxy-4-(picolinamido)benzoic acid, using 2-abH and suggested that it was a promising anti-cancer drugs [2]. Study on modulation of biological properties of aspirin by formation of bio-organometallic derivative has been reported by Ott *et al.* [3]. In another report, biological activities of transition metal complexes based on 2-abH have been studied by Rubner *et al.* In this work, it was shown that there was increased inhibitory action against various tumour cells [4]. Cu(II) complexes of halogen substituted 2-abH have been prepared and their thermal behavior have been studied by Tarulli *et al.* [5]. Further, synthesis, spectroscopic and biological assessment of alkaline earth metal aspirinate complexes have been reported by Refat *et al.* [6]. Biological studies of novel mixed ligand Ag(I) complexes with triphenylphosphine and alicyclic acid were also reported by Poyraz *et al.* [7]. Ogodo *et al.*

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have reported green synthesis of Cu(II) complexes using salicylic acid and 2-abH [8]. Antimicrobial activity of organotin complexes of aspirin has been reported by Kaur *et al.* [9]. Synthesis and characterization of tris-tolylbismuth(V) di-carboxylato complexes and their toxicity towards *Leishmania promastigotes* and human fibroblast cells have been studied by Ong *et al.* [10]. Islam *et al.* have synthesized triphenylbismuth(V) dicarboxylate complexes by the reaction of 2 and 3-acetoxy benzoic acids with Ph_3BiCl_2 [11]. Antitumor-active cobalt-alkyne complexes derived from acetylsalicylic acid have been studied by Ott *et al.* [12]. Using 2-abH, synthesis of ruthenium(II) arene NSAID complexes is also finding place in the literature [13]. Aziz *et al.* studied the synthesis and properties the complexes from a mixture of aspirin (acetylsalicylic acid), paracetamol and methyl dopa with divalent manganese, iron, cobalt, nickel and copper [14].

Despite so many reports on 2 and 3-isomers of acetoxy benzoic acids, no report on metal complexes using 4-acetoxybenzoic acids with metals is found in the literature. The main focus on the use of 4-isomer had been in the synthesis of polymers. Studies have been carried out on thermodynamic parameters of co-polycondensation of 4-abH and 6-acetoxy-2-naphthoic acids [15], kinetics of the polymerization of 4-abH and 6-acetoxy-2-naphthoic acids [16], vapour pressures, enthalpies and entropies of sublimation of para substituted benzoic acids [17], rheological and thermal properties of blended polyester [18] and synthesis of liquid crystalline polymers [19]. Pharmaceutical application of 2-abH was carried out by Chipley *et al.* [20].

In our laboratory, investigation on metal complexes of substituted aromatic carboxylic acids using hydrazine as co-ligand, with the aim of obtaining information about the coordination and thermal reactivity of the hydrazine of such complexes is being carried out. Hydrazine complexes of the first transition metal ions with a variety of carboxylic acids have been reported in the literature. These include simple and substituted aromatic mono [21-25], di [26-27], tricarboxylic [28] and tetracarboxylic acids. [29]. Extension of our idea of using new carboxylic acids made us work with acetoxy benzoic acids. A report was made by us with 3 and 4-abH using hydrazine [30]. Finding the fact that there is no other report on these acids using hydrazine, an attempt was made to synthesize hydrazine complexes of transition metal carboxylates. In this work, synthesis of hydrazine complexes of cobalt, nickel, cadmium and zinc acetoxy benzoates. Further, structural study of cadmium *p*-hydroxybenzoate prepared by an indirect method using 4-abH is also presented.

EXPERIMENTAL

The solvents were distilled prior to use and double distilled water was used for the preparation and chemical analyses. The chemicals used were of AR grade. In all the reactions, 99-100% pure hydrazine hydrate was used as received.

Preparation of $[M\{2\text{-ab}\}_2(\text{N}_2\text{H}_4)] \cdot 3\text{H}_2\text{O}$ and $[M\{3\text{-ab}\}_2(\text{N}_2\text{H}_4)] \cdot 3\text{H}_2\text{O}$ where $M = \text{Co, Ni, Zn and Cd}$

The preparation of $[M(2\text{-ab})_2(\text{N}_2\text{H}_4)] \cdot 3\text{H}_2\text{O}$ was achieved by adding a ligand solution prepared by mixing N_2H_4 (0.2 mL, 4 mmol) with an aqueous solution of 2-abH (0.180 g, 1 mmol in 60 mL of H_2O) to a freshly prepared metal nitrate solution (for example, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.291 g, 1 mmol in 20 mL of H_2O) followed by stirring the reaction mixture vigorously and the pH was found to be 6. Then the reaction mixture was kept over hot water bath at 80 °C. A microcrystalline product (Ni: pale blue, Co: pink, Cd and Zn colourless) was separated out from the mixture within 30 min which was filtered, washed with distilled water and ether and then dried in air.

All other complexes of 2-abH and 3-abH were obtained by adopting similar procedure as described above.

Preparation of $[M(4-ab)_2(N_2H_4)_2].2H_2O$ where $M = Co, Ni, Zn$ and Cd

Hydrazine transition metal complexes of 4-abH were prepared by adding the ligand solution to corresponding hydrated metal nitrate solution with constant stirring at pH 5. Among them Ni, Cd and Zn complexes were formed in the molar ratio, metal : acid : base = 1:1:2 while Co at 1:2:6. Nickel and cobalt complexes were obtained in water medium, whereas cadmium and zinc complexes were recovered using 1:1 aqueous ethanol.

Preparation of $[Cd(H_2O)_3((C_6H_4(4-OH)(COO))_2)].H_2O$

The title compound was prepared by the reaction of 4-acetoxy benzoic acid, hydrazine hydrate and cadmium nitrate tetra hydrate in aqueous medium. Initially the acid (1.8 g, 10 mmol) was mixed in 40 mL of water and hydrazine hydrate (1 g, 20 mmol) was added to dissolve the acid. A complete dissolution occurred on heating the solution at 80 °C over a hot water bath for 10 min. To this hot solution, an aqueous solution of the cadmium nitrate tetrahydrate (3.08 g, 10 mmol in 20 mL of water) was added at pH 5 and heated again at the same temperature for about 6 h till a thick viscous solution was formed. On adding absolute ethanol (50 mL), a white precipitate ($[Cd(4-ab)_2(N_2H_4)_2].2H_2O$) formed immediately was filtered and dried. On slow evaporation of the filtrate, colorless prismatic crystals of the title compound were obtained in 15 days, which was characterized by single crystal XRD-studies.

Physico-chemical methods

The hydrazine content in all the complexes was determined volumetrically using 0.025 M potassium iodate solution under Andrews' conditions [31]. The metal content was determined by EDTA complexometric titration [31] after decomposing a known weight of the sample with 1:1 HNO₃. Magnetic measurements were carried out by the Guoy method using Hg[Co(NCS)₄] as calibrant. The electronic spectra for solid-state complexes were obtained using a Varian, Cary 5000 recording spectrophotometer.

Infra-red 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 in static air using 5-10 mg of the samples at the heating rate of 10 °C/min. The XRD patterns were recorded on a Bruker AXS D8 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 a CHNS Elementar Vario EL III Elemental Analyzer.

RESULTS AND DISCUSSION

All the complexes obtained were polycrystalline powders, which are stable in air and insensitive to light. They are insoluble in ethanol, ether and benzene. The analytical data of the complexes given in Table 1 were compatible with the proposed compositions for the complexes.

Electronic spectra and magnetic susceptibility measurements

The compounds were insoluble in both water and organic solvents. Hence their electronic reflectance spectra were recorded for solid samples. The absorptions 22422-17857, 16447-11933, 8779-5482 cm⁻¹ are assigned to the transitions: $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$, $^4T_{1g} \rightarrow ^4T_{1g}(P)$, $^4T_{1g} \rightarrow ^4A_{2g}$ and $^4A_{2g} \rightarrow ^4T_{2g}$ and the values 21142, 20000-13587, 8467-7128 cm⁻¹ are assigned to $^3A_{2g} \rightarrow ^3T_{1g}$, $^3T_{1g}(P) \rightarrow ^3T_{2g}$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ for cobalt and nickel complexes, respectively. These assignments evidence the distorted octahedral geometry of the complexes [28, 29, 32].

The effective magnetic moments of the cobalt and nickel complexes lie in the range of 4.7-5.2 BM and 2.8-3.3 BM, respectively. The values of cobalt(II) complexes indicated that Co^{2+} is in high spin state. The electronic spectrum of $[\text{Ni}(\text{2-ab})_2(\text{N}_2\text{H}_4)] \cdot 3\text{H}_2\text{O}$ is given as representative image in Figure 1.

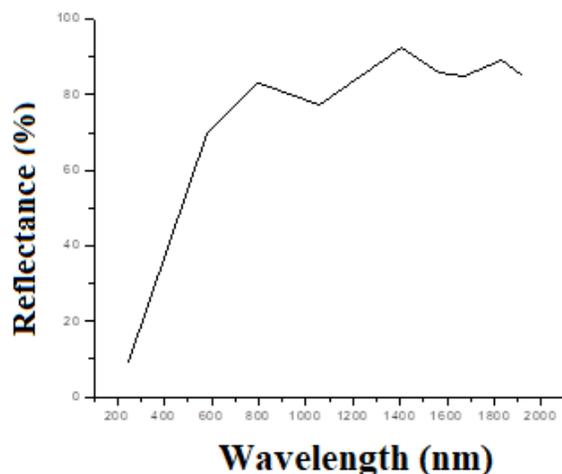


Figure 1. Electronic spectrum of $[\text{Ni}\{2\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4) \cdot 2\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$.

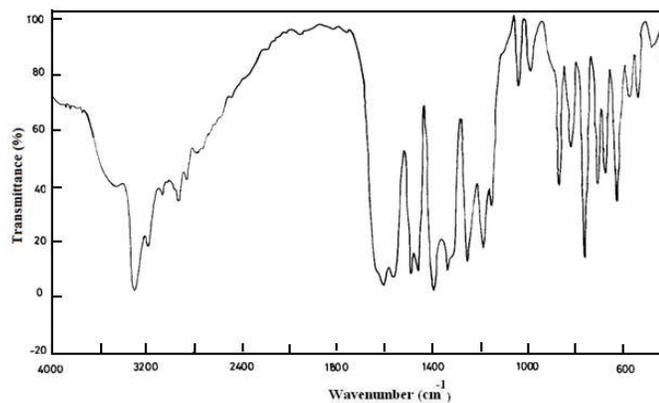


Figure 2. IR spectrum of $[\text{Ni}\{2\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4) \cdot 2\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$.

IR spectra of complexes

IR spectroscopic values of all the complexes are listed in Table 1. The IR spectra of complexes displayed peaks in the range of 1599-1682 and 1391-1454 cm^{-1} corresponding to the asymmetric and symmetric C=O stretching frequencies of the metal bound carboxylates. The difference between $\nu_{\text{C=Oasym}}$ and $\nu_{\text{C=Osym}}$ values was found to be in the range of 172-228 cm^{-1} , which indicated the monodentate coordination of carboxyl group with metal. The complexes displayed the N-N stretching frequency of hydrazine in the range 966-988 cm^{-1} which implied that hydrazine was involved in bridged bidentate coordination with the metal ion. The O-H stretch of

water molecules were noticed between 3329 and 3471 cm^{-1} in all complexes. An additional band observed in the range 818-862 cm^{-1} also supported the presence of lattice water molecules [33]. $\nu_{\text{N-H}}$ bands were found to merged with O-H stretching and seen in the region of 3250-3331 cm^{-1} . The IR spectrum also displayed bands in the range 1705-1777 cm^{-1} for $\nu_{\text{C=O}}$ of acetoxy group, indicating that the acetoxy group was not involved in complexation, due to the fact that the acetoxy group ($-\text{O.COOCH}_3$), is a weak electron contributor [34]. The IR spectrum of the complex $[\text{Ni}\{2\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$ is shown in Figure 2.

Table 1 Analytical and IR data transition metal complexes of isomeric acetoxy benzoic acids and hydrazine.

Compound	Analytical data (%)					IR data (cm^{-1}) b=broad; s=sharp; m=medium						
	Carbon found (calcd.)	Hydrogen found (calcd.)	Nitrogen found (calcd.)	Hydrazine found (calcd.)	Metal found (calcd.)	$\nu_{\text{N-N}}$	ν_{OH}	$\nu_{\text{C=O}}$ sym	$\nu_{\text{C=O}}$ asym	$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$ (acetoxy group)
2-abH complexes												
$[\text{Ni}\{2\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	42.93 (42.94)	4.80 (4.81)	5.58 (5.57)	6.37 (6.36)	11.69 (11.67)	980s	3449m	1410s	1605s	567s	3295s	1757m
$[\text{Co}\{2\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	42.91 (42.92)	4.80 (4.80)	5.57 (5.56)	6.36 (6.36)	11.70 (11.71)	970s	3420m	1391s	1605s	590s	3298s	1760b
$[\text{Cd}\{2\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	38.80 (38.80)	4.34 (4.35)	5.02 (5.03)	5.74 (5.75)	20.18 (20.19)	966s	3448b	1454s	1626s	563s	3315s	1763b
$[\text{Zn}\{2\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	42.39 (42.37)	4.73 (4.74)	5.49 (5.49)	6.26 (6.28)	12.84 (12.83)	964s	3443b	1406m	1605s	571s	3262m	1763s
3-abH complexes												
$[\text{Ni}\{3\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	42.92 (42.94)	4.79 (4.81)	5.57 (5.57)	6.36 (6.36)	11.65 (11.67)	988m	3356m	1447s	1620m	567m	3298s	1705m
$[\text{Co}\{3\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	42.93 (42.92)	4.81 (4.80)	5.58 (5.56)	6.37 (6.36)	11.74 (11.71)	980m	3356b	1404s	1614s	611s	3250s	1705m
$[\text{Cd}\{3\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	38.79 (38.80)	4.36 (4.35)	5.01 (5.03)	5.76 (5.75)	20.20 (20.19)	980m	3329m	1454s	1682m	623s	3271m	1777m
$[\text{Zn}\{3\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	42.38 (42.37)	4.72 (4.74)	5.48 (5.49)	6.27 (6.28)	12.84 (12.83)	974s	3456b	1425b	1609s	621s	3331b	1775s
4-abH complexes												
$[\text{Ni}\{4\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	41.80 (41.78)	5.05 (5.07)	10.81 (10.83)	12.40 (12.38)	11.33 (11.35)	983s	3471b	1443s	1626b	624s	3320b	1750b
$[\text{Co}\{4\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	41.76 (41.76)	5.08 (5.07)	10.82 (10.83)	12.70 (12.37)	11.44 (11.39)	973s	3437b	1405s	1599b	625s	3323b	1768s
$[\text{Cd}\{4\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	37.83 (37.84)	4.55 (4.59)	9.82 (9.81)	11.20 (11.21)	20.40 (19.70)	971s	3469b	1426b	1622b	616s	3324b	1771s
$[\text{Zn}\{4\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$	43.91 (43.92)	5.12 (5.13)	5.60 (5.70)	6.47 (6.50)	13.29 (13.30)	978m	3454b	1447 b	1626 b	574b	3321b	1770s

In the IR spectrum of the compound, the bidentate coordination of carboxylate group was understood by observing bands of $\nu_{\text{C=Oasym}}$ at 1514 cm^{-1} and $\nu_{\text{C=Osym}}$ at 1389 cm^{-1} , respectively, and the difference being 125 cm^{-1} which supports the bidentate coordination of the carboxylate group with metal ion. The presence of lattice water was revealed by the modes 3447, 1672, 1599 and 1514 cm^{-1} . The coordinated water molecules were found by the bands at 844, 775 and 617 cm^{-1} and these values are similar to that reported in the literature [33]. The bands at 499 cm^{-1} and 543 cm^{-1} showed that the oxygen was coordinated with metal, which were also similar to that reported [33].

Thermal analysis of complexes

The TG-DTA of compounds were performed in the temperature range 30-700 $^{\circ}\text{C}$ in static air atmosphere and the thermal degradation data is given in Table 2. The TG-DTA traces of $([\text{Ni}\{(2\text{-ab})_2(\text{N}_2\text{H}_4)\}_2]\cdot 3\text{H}_2\text{O})$, $[\text{Ni}\{(3\text{-ab})_2(\text{N}_2\text{H}_4)\}_2]\cdot 3\text{H}_2\text{O}$ and $[\text{Ni}\{(4\text{-ab})_2(\text{N}_2\text{H}_4)_2]\cdot 2\text{H}_2\text{O}$, are given as representative examples in Figure 3.

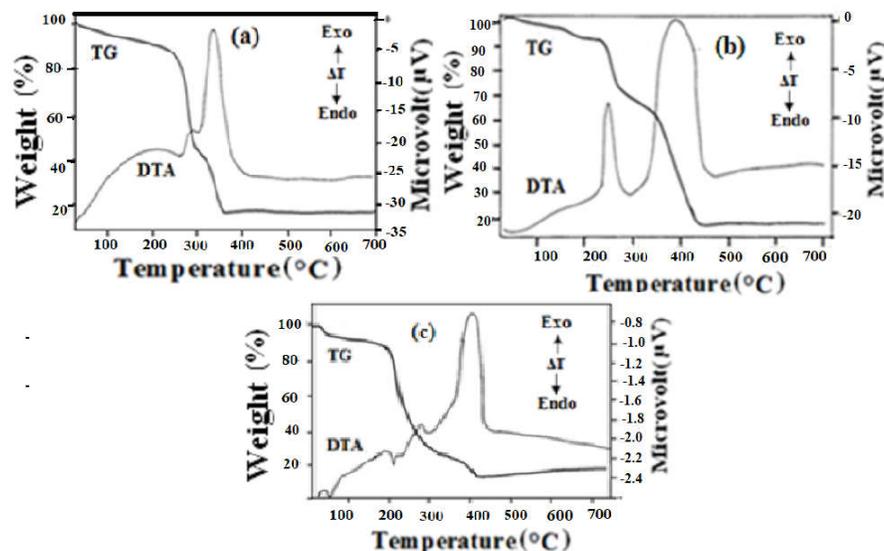


Figure 3. TG-DTA curves of:

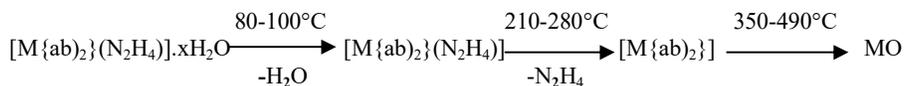
- (a) $[\text{Ni}\{2\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4).2\text{H}_2\text{O}].\text{H}_2\text{O}$,
 (b) $[\text{Ni}\{3\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4).2\text{H}_2\text{O}].\text{H}_2\text{O}$ and
 (c) $[\text{Ni}\{4\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2].2\text{H}_2\text{O}$.

Thermal data of 2-abH and 3-abH complexes

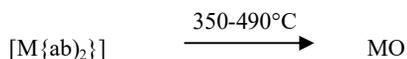
Co, Ni, Zn and Cd complexes of 2-abH and 4-abH and Co, Ni and Cd complexes of 3-abH showed three-step decomposition. They showed endothermic dehydration in the range 80-100 °C and exothermic dehydrazination in the temperature range of 210-280 °C. Further, these metal carboxylates were found to undergo oxidative decomposition to form their respective metal oxide residue, displaying the exotherms between 350 and 490 °C. Our effort to isolate the intermediate from these complexes was unsuccessful, due to their continuous decomposition as evident from their TG.

The dehydrazinated cobalt carboxylate 4-abH underwent exothermic decomposition to form metal phthalate intermediate at 350 °C, and this intermediate further continued to decompose to form its metal oxide residue in the temperature range of 400-467 °C. This decomposition was found to match with the literature reported [35].

Zn complex of 3-abH showed two exotherms at 280 and 440 °C indicating its oxidative decomposition to form its metal oxide, whereas the Zn complex of 4-abH directly decomposed to metal oxide at 271 °C exothermally indicating its high instability behavior. In both of these zinc complexes neither dehydration nor dehydrazination stages were clear. The thermal degradation patterns are given by the following reactions:



(where $x = 3$; $M = \text{Co}, \text{Ni}, \text{Cd}$ and Zn of 2-abH complexes, $x = 3, 2$ and $M = \text{Co}, \text{Ni}$ and Cd of 3-abH and 4-abH complexes).



(where M = Co, Ni, Cd and Zn of 2-abH; M = Co, Ni and Cd of 3-abH and M = Ni and Cd of 4-abH).

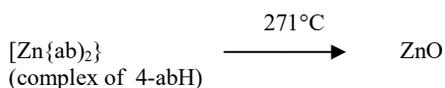
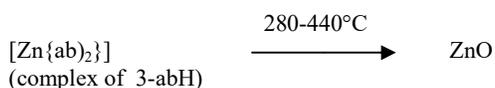
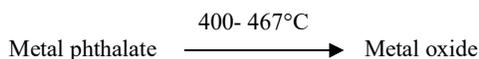
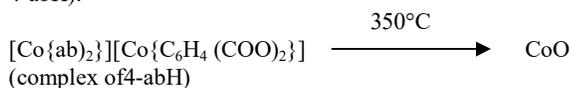


Table 2. Thermal data of transition metal complexes of isomeric acetoxy benzoic acids and hydrazine.

Complex	DTA Temp (°C)	Thermogravimetry			Nature of the reaction
		Temp. range, (°C)	Weight loss %		
			Obsd.	Cald.	
[Ni{2-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄).2H ₂ O].H ₂ O	90(+)	80-150	10.5	10.7	Dehydration Dehydrazination
	210(-)		17.3	17.1	
	300(-)	240-600	85.0	85.2	Decomposition to metal oxide
	350(-)				
[Co{2-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄).2H ₂ O].H ₂ O	100(+)	40-200	10.6	10.7	Dehydration
	190(+)				
	230(-)	200-280	17.0	17.1	Dehydrazination Decomposition to metal oxide
	360(-)		280-600	85.0	
[Cd{2-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄).2H ₂ O].H ₂ O	95(+)	80-198	10.0	9.7	Dehydration Dehydrazination
	190(+)		15.2	15.4	
	210(-)	240-600	77.0	76.9	Decomposition to metal oxide
	480(-)				
[Zn{2-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄).2H ₂ O].H ₂ O	90(+)	75-210	10.5	10.6	Dehydration Dehydrazination
	200(+)		17.0	16.9	
	278(-)	260-600	83.9	84.0	Decomposition to metal oxide
	420(-)				
[Ni{3-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄).2H ₂ O].H ₂ O	80(+)	40-180	10.6	10.7	Dehydration Dehydrazination
	260(-)		17.0	17.1	
	410(-)	280-600	85.1	85.2	Decomposition to metal oxide
[Co{3-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄).2H ₂ O].H ₂ O	80(+)	60-160	10.0	10.7	Dehydration Dehydrazination
	250(-)		17.0	17.1	
	450(-)	270-600	84.9	85.1	Formation of metal oxide

Table 2. Continued.

[Cd{3-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄) ₂ .2H ₂ O].H ₂ O	80(+) 200(+) 240(-) 490(-)	60-210 210-320 320-600	9.9 15.3 77.1	9.7 15.4 76.9	Dehydration Dehydrazination Formation of metal oxide
[Zn{3-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄) ₂ .2H ₂ O].H ₂ O	280(-) 440(-)	200-600	84.1	84.0	Formation of metal oxide
[Ni{4-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄) ₂ .2H ₂ O	67(+) 281(-) 410(-)	40-220 220-250 250-600	6.4 20.0 85.5	7.0 19.3 85.6	Dehydration Dehydrazination Formation of metal oxide
[Co{4-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄) ₂ .2H ₂ O	67(+) 210(-) 350(-) 400(-) 467(-)	50-170 170-250 250-410 410-600	7.0 19.18 37.4 85.7	7.0 19.3 37.6 85.5	Dehydration Dehydrazination Formation of metal phthalate Formation of metal oxide
[Cd{4-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄) ₂ .2H ₂ O	80(+) 250(-) 403(-)	50-150 150-320 320-600	6.0 17.0 78.0	6.3 17.5 77.5	Dehydration Dehydrazination Formation of metal oxide
[Zn{4-C ₆ H ₄ (OCOCH ₃) COO} ₂ (N ₂ H ₄) ₂ .2H ₂ O	271(-)	200-600	84.3	84.5	Formation of metal oxide

Thermal data of [Cd(H₂O)₃((C₆H₄(4-OH)(COO))₂).H₂O

The TG curve showed a medium endothermic weight loss of 4% at 86 °C corresponding to elimination of one water molecule which might be of lattice type and another sharp endothermic weight loss of 12% at 220 °C due to the elimination of three coordinated water molecules. The dehydration was immediately followed by a broad exotherm centered at 290 °C corresponding to oxidative decomposition showing a residual percentage of 27 for cadmium oxide.

X-ray diffraction

X-ray diffraction data of the complexes implies that the complexes with similar formulae showed isomorphism among themselves, which was evidenced from their 'd' spacings.

Crystal structure of [Cd(H₂O)₃((C₆H₄(4-OH)(COO))₂).H₂O

Crystal data of the above crystal are given in the Table 3. The significant bond lengths and bond angles of this crystal are listed in Table 4. Though Wang *et al.* [36] reported this crystal structure using 4-hydroxy benzoic acid as the starting material directly, this compound was obtained by the selective hydrolysis of 4-acetoxy benzoic acid to form 4-hydroxy benzoic acid which reacted with metal nitrate in this method.

The asymmetric unit of the crystal contains two molecules of the formula unit (C₁₄H₁₈Cd₁O₁₀), which were present in the two different planes. Single crystal analysis revealed that the compound has a unique non-centro symmetric three dimensional frame work. The compound crystallized in the orthorhombic space P_n2₁a and there are two crystallographically similar complex units positioned in different planes. The polyhedron of the Cd atom (Cd₂) was a monocapped distorted octahedron formed by four oxygen atoms (O7, O8, O10 and O11) from two bidentately chelating carboxylate ions of 4-hydroxy benzoate ligands, oxygen atom (O8W) of coordinated water and two oxygen atoms of another coordinated (O6W,O7W) water molecules taking apex positions with Cd-O distances (carboxylato oxygen) varying between 2.3499-2.4028Å, Cd-O (water) distances varying between 2.2634(6W), 2.3216 (7W) and 2.3980 Å (8W). The lattice water (O1W) was found to link with O9 via hydrogen bonding (H9A) and

Table 3. Crystal data and structure refinement details of $[\text{Cd}(\text{H}_2\text{O})_3(\text{C}_6\text{H}_4(4\text{-OH})(\text{COO}))_2]\cdot\text{H}_2\text{O}$.

Crystal data and structure refinement details	
Empirical formula	$\text{C}_{14}\text{H}_{18}\text{Cd}_1\text{O}_{10}$
Formula weight	458.690
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P_{n2}2_1a$
Unit cell dimensions	
a (Å)	10.3195
b (Å)	28.103
c (Å)	12.0268
α (°)	90.00
β (°)	90.00
γ (°)	90.00
v (Å ³)	3487.83(8)
Z	8
D _{calcd} (mg m ⁻³)	1.7470
μ (mm ⁻¹)	13.022
F (000)	1840
Crystal size (mm ³)	0.33 x 0.32 x 0.30
θ range for data collection (°)	2.50-27.00
Limiting indices	-13,13; -34,37; -15,15
Reflection collected unique	7995/7308
R _{int}	0.0231
Absorption correlation	Empirical
Refinement method	SHELXL 87 (Sheldrick 2008)
No of parameters	579
Goodness-of-fit on F ²	1.118
Largest diff. Peak and hole (e Å ⁻³)	0.0596 0.0314

Table 4. Significant bond lengths (Å) and angles (°) of $[\text{Cd}(\text{H}_2\text{O})_3(\text{C}_6\text{H}_4(4\text{-OH})(\text{COO}))_2]\cdot\text{H}_2\text{O}$.

Bond lengths and bond angles				
Cd2 – O7	2.3499(26)	Cd2-O8	2.4028 (25)	
Cd2- O10	2.3943(26)	Cd2 – O11	2.3679(21)	
Cd2 - O6W	2.2634(34)	Cd2 - O7W	2.3216(30)	
O1- Cd1 - O5	140.20(0.08)	O10-Cd2-O8W	80.84 (0.09)	
O2- Cd1 -O4	139.60(0.09)	O11-Cd2-O8W	135.33(0.09)	
O2 - Cd1- O5	85.79(0. 09)	O2 - Cd1 – O5W	88.37 (0.10)	
O1- Cd1-O5W	90.58(0.10)	O8- Cd2- O10	141.58 (0.09)	
O7- Cd2 – O10	162.29 (0.09)	O7- Cd2 – O11	141.43 (0.08)	
Cd2-O7W-H7B	103.59(3.86)	Cd2-O8W-H8B	109.49(3.86)	
Cd2-O7W-H7A	114.69(3.25)	Cd2-O8W-H8A	115.73(3.38)	
Hydrogen bonding				
D-H.....A	D-H	H...A	D...A	D-H...A
O6 W -H6A.....O10(4)	0.684(.040)	2.077(.040)	2.730(.004)	160.17(4.45)
O6 W -H6BO1 (0)	0.716(.045)	2.053(.045)	2.758(.004)	168.18(4.85)
O7W -H7A.....O8 (3)	0.754(.043)	1.924(.042)	2.663(.004)	166.23(4.48)
O7W -H7B.....O6 (6)	0.782(.052)	1.986(.052)	2.765(.004)	175.07(5.26)
O8W -H8A.....O11(3)	0.901(.053)	1.882(.052)	2.780(.004)	173.64(4.94)
O8W -H8B.....O12(1)	0.633(.042)	2.233(.042)	2.848(.004)	164.51(4.81)

another lattice water (O2W) was connected with O6 through hydrogen bonding (H6C) in a similar fashion. The planes containing any one carboxylic oxygen atoms (O8 and O7) and (O10 and O11) bore an angle 141.5° . The hydrogen bond distance was found to vary between 1.882-2.077 Å. The packing view of the crystal through axis 'a' is shown in Figure 4.

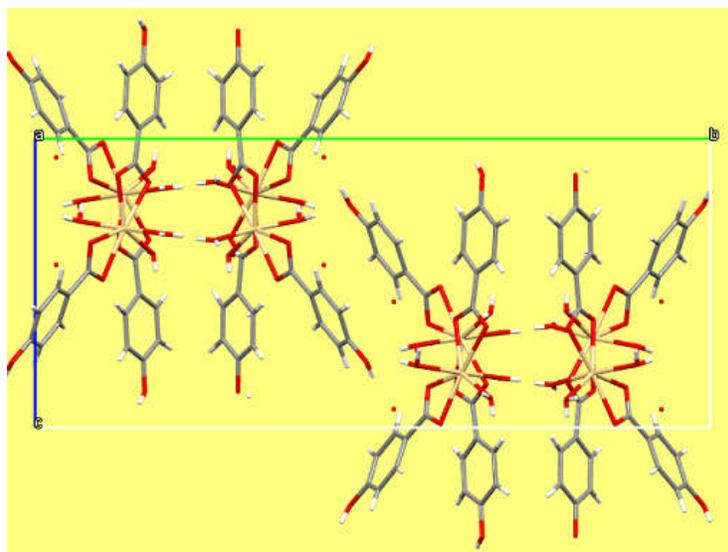


Figure 4. Packing view of $[\text{Cd}(\text{H}_2\text{O})_3(\text{C}_6\text{H}_5(4\text{-OH})\text{COO})_2]\cdot\text{H}_2\text{O}$ via axis 'a'.

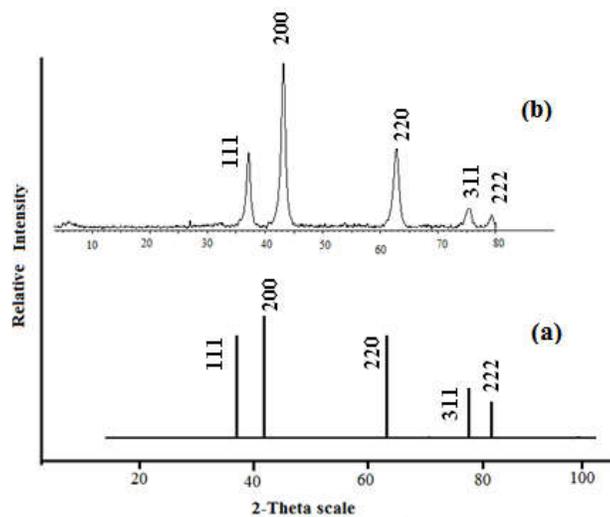


Figure 5. (a) Standard XRD pattern of NiO and (b) XRD pattern of final residue of $[\text{Ni}\{3\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)]\cdot 3\text{H}_2\text{O}$.

SEM-EDX studies

The complexes were calcined in muffle furnace at their decomposition temperatures, kept at the same temperature for 10 min. and then analyzed the cooled products for their morphology and particle size. The SEM-EDX images of residues obtained from $[\text{Ni}(3\text{-ab})_2(\text{N}_2\text{H}_4)] \cdot 3\text{H}_2\text{O}$ and the XRD patterns of the same NiO with the standard are shown in Figure 5. The metal oxide of $[\text{Ni}(3\text{-ab})_2(\text{N}_2\text{H}_4)] \cdot 3\text{H}_2\text{O}$ was found to be in nano scale of 18 nm as calculated from XRD using Scherer's formula [37] $D = K\lambda/B \cos \theta$ 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 Scherer's constant of the order of 0.8. Other two residues were micro sized metal oxides with irregular shapes.

Conductance studies

The molar conductance of selected complexes, $([\text{Zn}\{(2\text{-ab})_2(\text{N}_2\text{H}_4)\}] \cdot 3\text{H}_2\text{O})$, $[\text{Co}\{(3\text{-ab})_2(\text{N}_2\text{H}_4)\}] \cdot 3\text{H}_2\text{O}$ and $[\text{M}(4\text{-ab})_2(\text{N}_2\text{H}_4)_2] \cdot 2\text{H}_2\text{O}$, where $M = \text{Ni}$ and Cd was determined using DMSO as solvent and compared with the reported values [38, 39]. Except zinc and cadmium complexes (76 and $67 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively), other transition metal complexes behaved as low conductivity electrolytes by showing molar conductance values in the range of $10\text{--}12 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating that they were neutral complexes. The high conductivity of zinc and cadmium complexes might be due to solvolysis by DMSO.

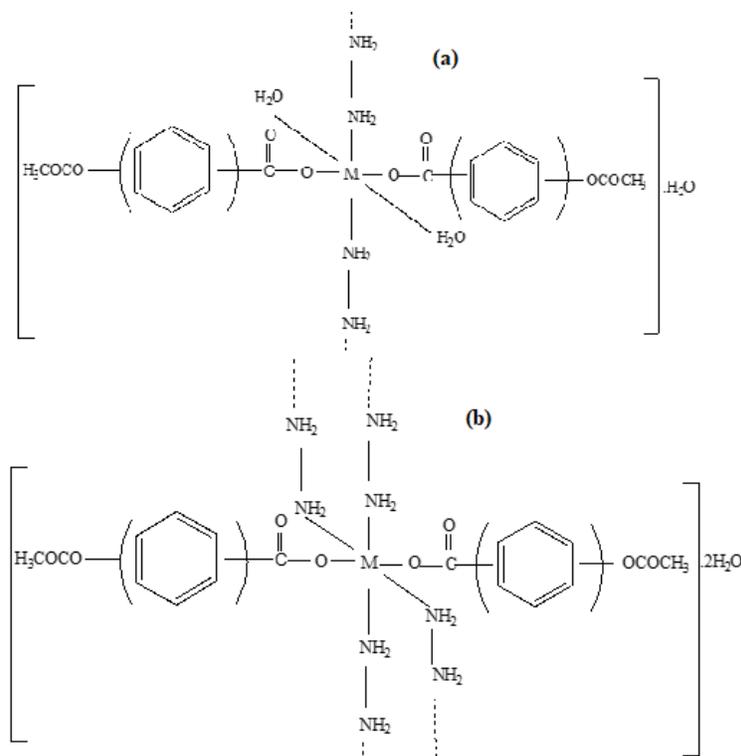


Figure 6. (a) Proposed structure of $[\text{M}\{(2 \text{ and } 3)\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4) \cdot 2\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ and (b) $[\text{M}\{4\text{-C}_6\text{H}_4(\text{OCOCH}_3)\text{COO}\}_2(\text{N}_2\text{H}_4)_2] \cdot 2\text{H}_2\text{O}$, where $M = \text{Ni}, \text{Co}, \text{Cd}$ and Zn .

CONCLUSION

The isomeric acetoxy benzoic acids such as 2-abH, 3-abH and 4-abH yielded the hydrazine complexes of transition metals having formula, $[M(2-ab)_2(N_2H_4)].3H_2O$, $[M(3-ab)_2(N_2H_4)].3H_2O$ and $[M(4-ab)_2(N_2H_4)_2].2H_2O$, where M = Ni, Co, Cd and Zn on reaction with hydrazine hydrate and the respective metal ions. The acids involve in coordination with metal ions only through carboxyl groups and acetoxy group do not involve in coordination. Based on the studies, six coordination has been proposed for central metal ion with distorted octahedral geometry. However, the accurate structures can be known from single crystal XRD studies of the complexes. The proposed structures are given in Figure 6.

Supplementary data

Other crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Code number CCDC 800926. (Supplementary data is available on <http://CCDC.cam.ac.uk> website).

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