

# Thermal and Spectroscopic Investigations of 4-nitrobenzoate Complexes of Ni(II)

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## Abstract

The complexes  $[\text{Ni}(\text{H}_2\text{O})_4(4\text{-nba})_2] \cdot 2\text{H}_2\text{O}$  **1** (4-nba is 4-nitrobenzoate) and  $[\text{Ni}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$  **2** were prepared by the reaction of nickel carbonate or hydroxide with 4-nitrobenzoic acid (4-nbaH) and the formation of these complexes is pH dependent. Complex **1** is isostructural with the corresponding Co complex. The complexes have been characterised by elemental analysis, IR spectra and can be thermally decomposed to the corresponding oxide. Complex **1** can be reversibly hydrated as evidenced by IR spectra and X-ray powder pattern. In contrast the octahydrate complex of Ni(II) cannot be reversibly hydrated. Calcining **2** at 170° results in the formation of the dihydrate and attempts to remove the last two water molecules results in the breakdown of the structure indicating that these water molecules are strongly held in **2**.

## Introduction

In recent years there is a growing interest in the chemistry of metal complexes derived from substituted benzene carboxylic acids in view of their interesting structures [1] as well as their possible applications as useful materials [2]. As part of an ongoing research program, we are investigating the synthesis, spectroscopic and thermal characterization of metal complexes of amino and nitro substituted benzoic acids [3-7]. In earlier work we have demonstrated that the hydrated metal carboxylates of para substituted amino as well as nitrobenzoates can be reversibly hydrated. In the present work we describe the results of our studies on the pH dependent synthesis and thermal characterization of para-nitrobenzoate (4-nba) complexes of nickel(II).

## Experimental

All chemicals used in this investigation were procured from commercial sources. IR spectra of the complexes were recorded as KBr diluted pellets on a Shimadzu FTIR-8101A spectrophotometer. X-ray powder diffraction data were collected on an ITAL SYSTEMS APD 2000 diffractometer using Cu-K $\alpha$  radiation. The TG-DSC studies were performed on a NETZSCH STA 409 PC/4/H (*Luxx*) instrument. The isothermal weight loss studies were performed in an electric furnace fitted with a temperature controller.

## Synthesis of Ni(II) para-nitrobenzoates

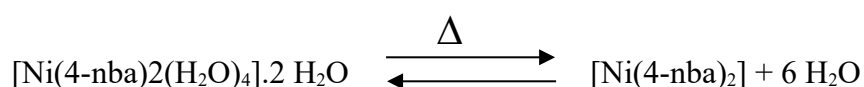
The reaction of nickel carbonate with 4-nitrobenzoic acid (4-nbaH) in water under reflux for ~5 h, followed by filtration of the reaction mixture (pH of the filtrate 9) and crystallization resulted in the formation of the green  $[\text{Ni}(\text{H}_2\text{O})_4(4\text{-nba})_2]\cdot 2\text{H}_2\text{O}$  **1**. In contrast, the reaction of freshly precipitated nickel hydroxide with 4-nbaH dissolved in ammonia (pH of the reaction mixture 12.0) resulted in the formation of the blue hexaquo Ni(II) complex  $[\text{Ni}(\text{H}_2\text{O})_6](4\text{-nba})_2\cdot 2\text{H}_2\text{O}$  **2**. The procedure employed here is a slight modification of the reported procedure for the same complex [8]. Treatment of **1** or **2** with aqueous HCl results in the decomposition of the complexes accompanied by the formation of the insoluble 4-nbaH. The formulation of the complexes was arrived at based on metal analysis and gravimetric analysis of 4-nbaH.

## Results and Discussion

The complexes **1** and **2** are related by a pH dependent equilibrium and at around a pH of 9, complex **1** is the preferred product while under strongly alkaline conditions (pH 12.0) **2** is formed. The synthesized complexes have been formulated based on analytical and isothermal weight loss data (Table 1). The complexes **1** to **2** have been studied by spectroscopic methods. Both the complexes exhibit several sharp signals in the mid IR region many of which are also observed in the free carboxylic acid clearly indicating the presence of the organic moiety in the synthesized complexes. Further, the hydrated complexes **1&2** exhibit a strong and broad absorption signal in the  $3500\text{-}3000\text{ cm}^{-1}$  region, which confirms the presence of water molecules. The presence of water molecules has also been inferred as well as quantified based on isothermal weight loss studies (*vide infra*). The temperatures for the weight loss studies were chosen based on the transition temperatures observed in their DSC thermograms (Fig.1). Although both the complexes decompose exothermically above  $400^\circ\text{C}$ , their differing nature is evident from Fig. 1. Both the complexes **1-2** exhibit several sharp signals in the range ( $2\theta = 10\text{-}50^\circ$ ), in their X-ray powder diffractograms indicating the crystalline nature of the samples. Complex **1** is isostructural with the corresponding Co(II) analogue reported by us earlier [6] as evidenced from the powder X-ray powder data (Fig. 2).

In our earlier work we have shown that hydrated complexes of para-substituted benzoic acids can be reversibly hydrated. The green tetraquo Ni(II) complex **1** exhibits a similar behaviour as evidenced by a comparison of the powder pattern of the pristine

complex and the yellow anhydrous complex (Fig. 3). Interestingly the pattern of the water free complex does not show any sharp lines but only a strong background with Cu-K $\alpha$  radiation. This feature probably indicates the importance of the H-bonding interactions mentioned earlier for the isostructural Co complex, which hold the structure together. The formation of the anhydrous complex is clearly evident from its IR spectra (Fig. 4) wherein the bands due to O-H vibrations are not observed. Exposure of the anhydrous complex to water vapour leads to the formation of the starting green tetraaquo Ni(II) complex **1** as evidenced from the X-ray powder pattern (Fig 3) as well as IR spectra (Fig. 4). The dehydration of complex **1** and the rehydration of calcined complex can be described as shown below.



In contrast the complex **2** cannot be fully dehydrated. Heating complex **2** at 100°C results in a weight loss of 14.5%, which can account for the loss of four moles of water and further heating at 170°C results in the loss of two more moles of water. The IR spectrum of the calcined product (Fig 5) at this stage still exhibits the water band but the profile of the spectrum is different indicating changes in the structure. Efforts to fully dehydrate **2** were not fruitful. The last two water molecules are strongly held and removal of these results in the breakdown of the structure. A similar behaviour has been observed by us earlier for the Mg(II) –nitrobenzoate complexes [5].

## Conclusions

The pH dependent synthesis and characterization of two hydrated para-nitrobenzoate complexes of Ni(II) is reported. Both the complexes can be pyrolysed to the corresponding oxide. Complex **1** can be reversibly hydrated while attempts to fully dehydrate the octahydrate Ni(II) complex **2** were not successful. The differing coordination mode of the 4-nba ligand can be attributed to the differing thermal behaviour of both the complexes.

## Acknowledgements

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Table 1: Analytical data and isothermal decomposition data

Complex	%Ni Obs. (Cal)	% 4-nbaH Obs. (Cal)	% Isothermal weight loss Obs. (Cal)			% residue
			100 <sup>o</sup> C	170 <sup>o</sup> C	230 <sup>o</sup> C	
[Ni(4nba) <sub>2</sub> H <sub>2</sub> O] <sub>4</sub> ·2H <sub>2</sub> O	11.88 (11.7)	67.88 (66.57)	11.4	-	21.60 (21.66) ≈6H <sub>2</sub> O	14.9
[Ni(H <sub>2</sub> O) <sub>6</sub> ](4nba) <sub>2</sub> ·2H <sub>2</sub> O	10.55 (10.9)	63.9 (62.09)	14.5 (13.47) ≈4H <sub>2</sub> O	20.54 (20.2) ≈6H <sub>2</sub> O	-	13.01

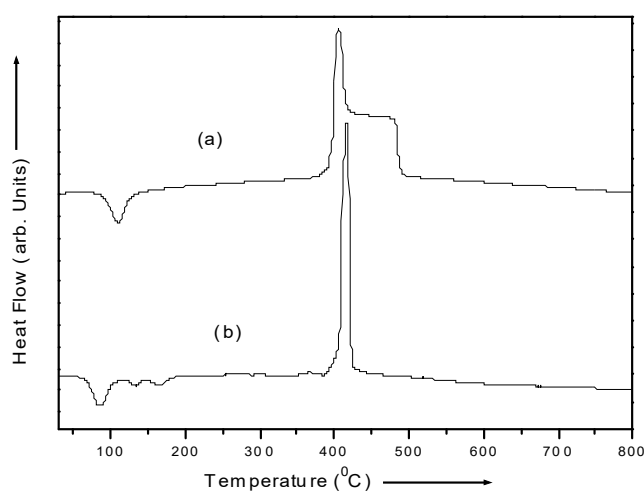


Fig.1. DSC thermograms of a) [Ni(4-nba)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>].2 H<sub>2</sub>O **1** b) [Ni(H<sub>2</sub>O)<sub>6</sub>](4-nba)<sub>2</sub>.2H<sub>2</sub>O **2**

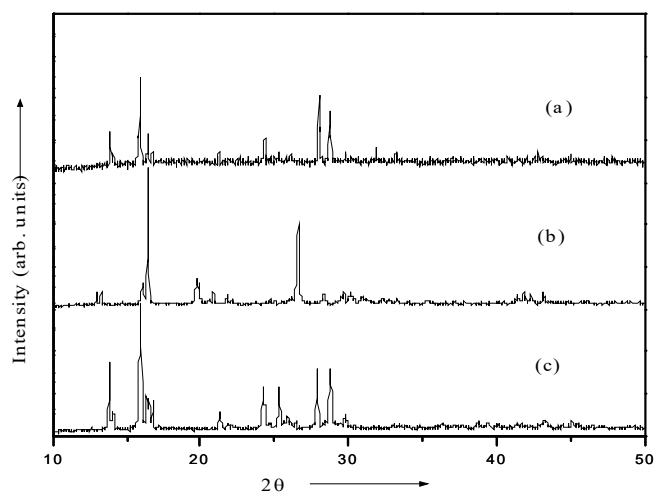


Fig. 2. X-Ray powder pattern of a)  $[\text{Co}(4\text{-nba})_2(\text{H}_2\text{O})_4]2\text{H}_2\text{O}$   
 b)  $[\text{Ni}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$  c)  $[\text{Ni}(4\text{-nba})_2(\text{H}_2\text{O})_4]2\text{H}_2\text{O}$

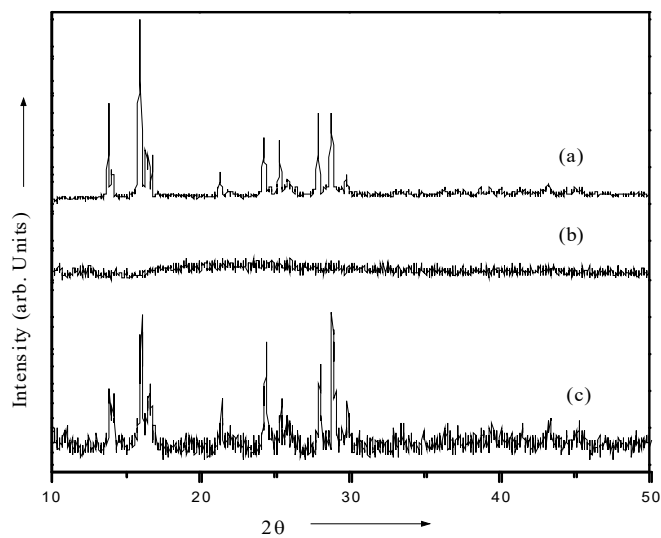


Fig. 3. X-Ray powder pattern of (a)  $[\text{Ni}(4\text{-nba})_2(\text{H}_2\text{O})_4]2\text{H}_2\text{O}$  1 (b) anhydrous  $[\text{Ni}(4\text{-nba})_2(\text{H}_2\text{O})_4]2\text{H}_2\text{O}$  (c)  $[\text{Ni}(4\text{-nba})_2]$  on hydration

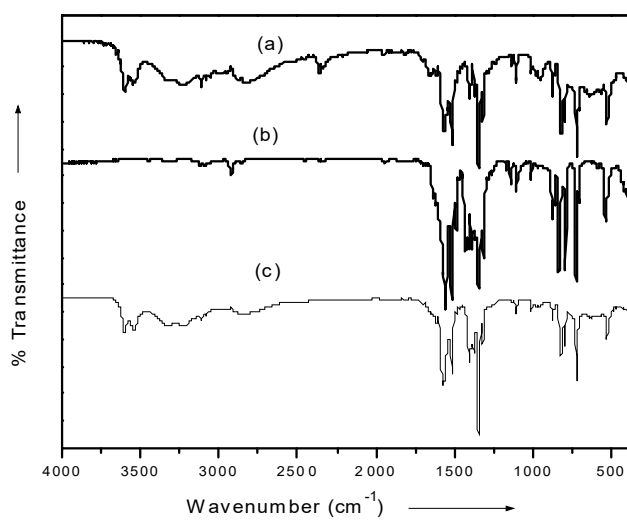


Fig. 4. IR spectra of (a)  $[\text{Ni}(\text{4-nba})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  **1** (b) anhydrous  $[\text{Ni}(\text{4-nba})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  (c)  $[\text{Ni}(\text{4-nba})_2]$  after hydration

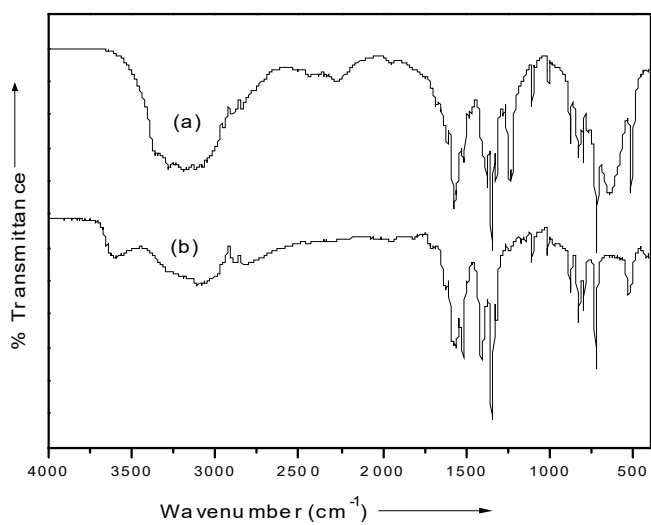


Fig. 5. IR spectra of (a)  $[\text{Ni}(\text{H}_2\text{O})_6](\text{4-nba})_2 \cdot 2\text{H}_2\text{O}$  **2** (b) **2** calcined at  $170^\circ\text{C}$