

Thermal and spectroscopic characterization of Mg(II) complexes of nitro-substituted benzoic acids

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Abstract

The Mg(II) complexes of the nitro-substituted benzoic acids have been investigated by thermal and spectroscopic methods. Thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), and other spectroscopic methods have been used to investigate the thermal behavior and structure of the compounds $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **1**, $[\text{Mg}(\text{H}_2\text{O})_6](3\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **2**, $[\text{Mg}(\text{H}_2\text{O})_6](2\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **3** (4-nba = *para*-nitrobenzoate; 3-nba = *meta*-nitrobenzoate; and 2-nba = *ortho*-nitrobenzoate). All the complexes are formulated as consisting of the octahedral $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cation with the carboxylates outside the coordination sphere, which is consistent with the IR, UV-Vis and ^1H NMR data. Thermal decompositions of these carboxylates are multi-stage processes. The composition of the complexes and the solid-state intermediates and the resultant products of thermolysis have been identified by IR, elemental analysis and complexometric titration. A possible scheme for the decomposition of the complexes is suggested. Heating the compounds first results in the loss of water molecules. This is followed by the loss of the nitrobenzoate resulting in the formation of oxide. Complex **1** can be reversibly hydrated. The final product of the thermal decomposition in all the cases is MgO.

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Keywords: TG; DTA; DSC; Nitro-substituted benzoic acid; Mg(II) complexes; Reversible hydration

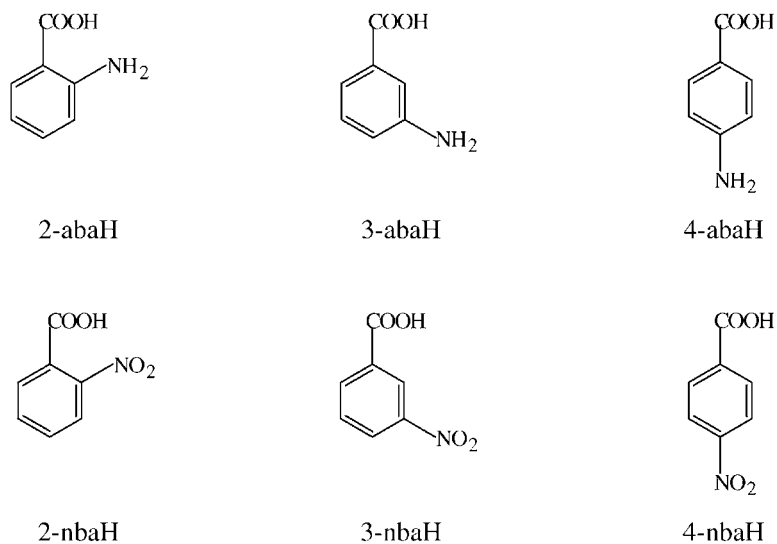
1. Introduction

The chemistry of metal-carboxylates continues to be an area of intense research investigations in view of its diverse applications, ranging from the relevance of metal-carboxylate complexes as model systems for the metalloactive sites in bioinorganic chemistry [1,2] to their usefulness as novel materials in materials science. Metal oxides can be readily prepared from metal-carboxylate precursors by thermal decomposition methods [3]. Metal-carboxylates exhibit fascinating structural features. The structural diversity

encountered in metal-carboxylate complexes can be attributed to the versatile ligational behavior of the carboxylate group which can function like a bidentate ligand binding to a single metal or alternatively as a bridging bidentate ligand coordinating to two metals or as a monodentate ligand [4,5]. Carboxylate ligands that possess additional donor sites for example amino acids (Scheme 1) can result in the formation of metal complexes with novel network structural features. This has been well demonstrated in the case of the alkaline earth metal complexes of aminobenzoic acids [6,7]. An emerging area of interest is the construction of hybrid inorganic–organic polymer network systems [8–10]. In this context, aromatic acids are expected to form rigid stable coordination polymers on account

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Scheme 1.

of their appropriately placed functional groups, which are attached to a rigid template such as a benzene ring.

In view of its widespread occurrence in the body and in nature (e.g. magnesium in chlorophyll) magnesium is considered to be biologically an essential element. Mg(II) plays an essential role in the activation of the enzymes, complexation with nucleic acids, nerve impulse transmission, etc. [11–13]. Consequently many authors have studied several Mg(II) complexes to understand the mode of binding of this metal in vivo and in vitro. These studies are of great importance in enhancing our understanding of magnesium deficiency in the human body arising from controlled diet and modern food habits. These studies have focussed on the use of carboxylate ligands like aspartate, glutamate or polyglutamate, salicylic acid, etc. [14]. Mojumdar et al. have investigated the thermal and spectral characterization of several Mg(II) complexes and have used acetate, chloroacetates and pyridine dicarboxylic acid ligands as well as heterocyclic ligands like pyridine, picoline, etc. [15–18]. Almost all the Mg(II) complexes reported by these workers can be thermally decomposed at high temperatures (above 700 °C in many cases) to MgO. The present work is a continuation of our recent report on the spectral and thermal characteristics of Mg(II) complexes of *ortho* and *para*-aminobenzoic acids [19]. We have earlier shown that the relative instability of the hydrated 2-aba

(aba = aminobenzoate) complex of Mg(II) as compared to that of the 4-aba complex can be attributed to the orientation of the amino group with respect to the carboxylate group in the six-membered ring. In view of the differing electronic nature of the $-\text{NO}_2$ (electron withdrawing) and $-\text{NH}_2$ (electron donating) groups, it is of interest to study the effect of nitro substitution in lieu of the amino group. This paper describes the synthesis, spectral and thermal characterization of Mg(II) complexes of the isomeric nitrobenzoic acids (Scheme 1).

2. Experimental

2.1. Materials and methods

Doubly distilled water was used as the solvent. All the chemicals used in this study were of reagent grade and used as received. 2-Nitrobenzaldehyde was used for the synthesis of the 2-nitrobenzoate complex. The starting materials and reaction products are air stable and hence were routinely prepared under normal laboratory conditions. Infrared spectra were recorded on a Shimadzu (model 8101A) FTIR spectrometer. The samples for the infrared spectra were prepared as KBr diluted pellets in the solid state and the infrared signals referenced to polystyrene bands. The electronic

spectra were recorded in methanol using matched quartz cells on a Perkin-Elmer (Lambda 12) spectrophotometer. NMR spectra were recorded on a Bruker WT 300 MHz FT-NMR spectrophotometer. X-ray powder diffraction data were collected on a Philips Holland PW-3710 diffractometer using Cu K α radiation. The TG–DSC study of compound **1** was performed on a NETZSCH STA 409 PC/4/H (*Luxx*) instrument. The TG, DTA of the complexes **2** and **3** were carried out in air atmosphere in the temperature range 20–1000 °C on a NETZSCH simultaneous thermal analyses apparatus at Universität Dresden. A heating rate of 10 °C/min was chosen for all the measurements.

2.2. Preparation of complexes

The complexes **1**, **2** and **3** were synthesized by reacting MgCO₃ (0.84 g) and the corresponding carboxylic acid (3.34 g) (4-nbaH or 3-nbaH) in a 1:2 mole ratio in water. For the synthesis of **3**, the carboxylic acid was generated in situ by using *ortho*-nitrobenzaldehyde (3.02 g) and H₂O₂ (10 ml). The insoluble organic acids slowly dissolved on heating, with the evolution of carbon dioxide resulting in the formation of a clear solution, whose pH is almost neutral. The reaction mixture was filtered and left undisturbed for crystallization for 2–3 days. The crystals thus obtained were filtered off, washed thoroughly with ether and dried in vacuo.

2.3. Reversible hydration of [Mg(H₂O)₆](4-nba)₂·2H₂O **1**

A powdered sample of [Mg(H₂O)₆](4-nba)₂·2H₂O (500 mg) was taken in a silica crucible and heated in a furnace at 200 °C for 1 h. The crucible was cooled and the resultant sample (356 mg) was equilibrated over water in a desiccator for a day. This resulted in the isolation of 499 mg of the starting material **1**. The infrared spectrum of the final product is identical to that of the starting material.

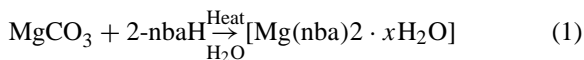
3. Results and discussion

3.1. Synthesis

The reaction of MgCO₃ with nitrobenzoic acids in a 1:2 mole ratio results in the formation of the hydrated

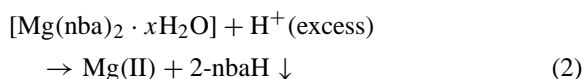
Mg(II) nitrobenzoate complexes in near quantitative yields. The insoluble MgCO₃ goes into solution on heating with the aromatic acids in water and the products can be isolated from the nearly neutral reaction mixture.

A general reaction for the complex formation can be represented as shown below:



where nbaH = nitrobenzoic acid.

When the hydrated Mg(II) nitrobenzoate complexes are acidified with HCl in slight excess, they react as shown in Eq. (2):



The Mg(II) ions go into solution and the insoluble nitrobenzoic acid is precipitated thus permitting the simultaneous analysis of both Mg(II) content by EDTA titration as well as the organic acid (*vide infra*) gravimetrically.

The three nitrobenzoic acids used in this investigation differ in terms of the disposition of the nitro group with respect to the carboxylic acid in the six-membered ring. The positioning of the nitro group is responsible for the differing acidity of the three acids with the *ortho* isomer being the most acidic ($\text{p}K_{\text{a}} = 2.17$) while the *meta* isomer is the least acidic ($\text{p}K_{\text{a}} = 3.49$). The *para* isomer with a $\text{p}K_{\text{a}}$ value of 3.42 is slightly more acidic than the *meta* isomer. In spite of the differing acidity, all the three acids give rise to the Mg(II) complexes. The isolated Mg(II)-*para*-nitrobenzoate complex is sparingly soluble in water although it is obtained from an aqueous solution, while the *ortho* isomer is freely water soluble. The complexes can also be prepared by the reaction of MgCl₂ with sodium nitrobenzoate in a 1:2 mole ratio. All the complexes dissolve in organic solvents like DMF and DMSO.

3.2. Analytical results of the compounds

Mg analysis was performed titrimetrically following a standard procedure [20]. The complexes were acidified with dilute HCl and the precipitated nitrobenzoic acid was filtered, dried and weighed. In the case of the

Table 1
Analytical data of compounds

| Complex | % Mg, found (calcd.) | % nitrobenzoic acid, found (calcd.) | % MgO residue, found (calcd.) |
|--------------------------------------------------------------------------------------|----------------------|-------------------------------------|-------------------------------|
| [Mg(H ₂ O) ₆](4-nba) ₂ ·2H ₂ O 1 | 4.73 (4.86) | 66.20 (66.78) | 8.32 (8.05) |
| [Mg(H ₂ O) ₆](3-nba) ₂ ·2H ₂ O 2 | 4.78 (4.86) | 66.10 (66.78) | 8.16 (8.05) |
| [Mg(H ₂ O) ₆](2-nba) ₂ ·2H ₂ O 3 | 4.77 (4.86) | 65.56 (66.78) | 8.21 (8.05) |

complex **3**, the aqueous solution was extracted with ether to fully recover the aqueous soluble 2-nbaH. The ether was evaporated and the carboxylic acid thus obtained, was dried and weighed. The complexes were converted to MgO by heating at 800 °C for 1 h in an electric furnace fitted with a temperature controller. The formation of MgO was confirmed by Mg analysis. The weights of the MgO residue thus obtained as well as the Mg percentage and the isolated carboxylic acid are in accordance with the proposed formula. Based on the analytical data (Table 1), all the complexes can be formulated as octahydrates. Owing to the fact, that Mg(II) prefers octahedral coordination and [Mg(H₂O)₆]²⁺ is an often encountered species in many Mg(II) complexes [7,21,22], the complexes **1–3** are formulated as consisting of six coordinated waters and two lattice waters with the nitrobenzoate functioning as an anion. This formulation gains credence from the spectroscopic and thermal studies (vide infra).

3.3. Spectral characterization

All the Mg(II) complexes prepared in this work absorb strongly around 260 nm in the UV-region, with the pale yellow *o*-nitrobenzoate showing a band tailing into the visible (Table 2). The UV-Vis spectra of the complexes in methanol are quite similar to the spectra of the free acids recorded in methanol. This feature is indicative of the fact that the carboxylates are outside the coordination sphere and the UV-absorption can be attributed to intramolecular charge transfer transition of the aromatic acids. The molar absorptivities (ϵ_{\max}) of the three Mg(II) complexes are almost twice that of the free carboxylic acid which can be explained in terms of the presence of two molecules of the carboxylate per mole of the complex (Table 2). The NMR spectrum of **1** was recorded in DMSO-*d*₆ while the spectra of the complexes **2** and **3** were recorded in D₂O. All the complexes exhibit characteristic ¹H NMR spectra, which readily confirms the presence of the organic

moiety in these complexes. The complex **1** exhibits a typical AB quartet for the two sets of aromatic protons in the 4-nitrobenzoate at δ 8.2118 and 8.1041 ppm. The *meta*-nitrobenzoate complex of Mg(II) shows four different signals for the four aromatic protons at δ = 8.4454 (s), 8.1571 (tt), 8.0384 (dd) and 7.4844 (t) ppm, respectively while the ortho complex **3** absorbs at δ = 7.9273 (d), 7.5948 (t), 7.4093 (t) and 7.3417 (d) ppm, respectively for the four different aromatic protons. The NMR signals of the Mg(II) complexes are slightly upfield shifted compared to that of the free acids and are indicative of the presence of free carboxylates. A similar trend has been observed in the PMR spectra of aminobenzoate complexes [6,19]. The uncoordinated nature of the carboxylate is further evidenced from the IR spectral studies.

The X-ray powder diffractograms of the complexes **1–3** exhibit several sharp signals, many of which are weak. This is indicative of the fact that the complexes are all crystalline phases. The interplanar spacings of the most prominent peaks are collected in Table 3. The X-ray powder pattern of the residues obtained on heating **1** as well as **2** at 800 °C match with that of the reported data of MgO (periclase) and can be indexed on a cubic cell. The XRD data thus unambiguously confirms the formation of MgO as the final product of thermal decomposition.

All the Mg(II) complexes prepared in this work, have been studied by infrared spectra. For the sake of comparison, the IR spectra of the free nitrobenzoic acids were also recorded and the results are tabulated in Table 2. Since IR has been used as a fingerprint device to confirm the presence and the mode of binding of water, and nitrobenzoate, the spectral assignments for only the water band, carboxylate group and the nitro group are indicated in the Table 2. The IR spectra of the Mg(II) complexes **1**, **2** and **3** exhibit several sharp bands clearly indicating the presence of the organic moiety. The free acids do not exhibit any signals above 3100 cm⁻¹ unlike the Mg(II) complexes.

Table 2
IR and UV-Vis data of compounds **1–3**

| Compound | IR bands (cm ⁻¹) | UV-Vis data, λ_{\max} (nm) |
|--------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|
| 4-nbaH | 3122–2853 (b), 2666, 2549, 1950, 1824, 1696 ^a , 1608, 1544 ^b , 1497, 1433 ^a , 1351 ^b , 1316, 1292, 1280, 1181, 1128, 1111, 1017, 977, 930, 877, 860, 801, 720, 562, 515, 451 | 260 (3505) |
| [Mg(H ₂ O) ₆](4-nba) ₂ ·2H ₂ O 1 | 3600–3000 (b), 2924, 1620, 1573 ^a , 1509 ^b , 1376 ^a , 1347 ^b , 1324, 1166, 1137, 1008, 885, 803, 727, 523, 441 | 260 (8738) |
| 1 calcined at 200 °C | 3100, 2875, 2475, 1650, 1620, 1600, 1560 ^a , 1525 ^b , 1425 ^a , 1350 ^b , 1325, 1175, 1150, 1100, 1020, 975, 880, 850, 840, 800, 775, 600, 550, 525, 440 | |
| 3-nbaH | 3087–2800 (b), 2666, 2549, 1848, 1701 ^a , 1619, 1585, 1538 ^b , 1485 ^a , 1458, 1415, 1362 ^b , 1328, 1292, 1152, 1099, 1000, 924, 901, 830, 813, 778, 725, 702, 661, 567, 532, 444 | 256 (7234) |
| [Mg(H ₂ O) ₆](3-nba) ₂ ·2H ₂ O 2 | 3614, 3426 (b), 3240, 3099, 2935, 1625 ^a , 1593, 1575, 1538 ^b , 1480, 1440 ^a , 1423, 1388, 1353 ^b , 1277, 1160, 1084, 1008, 914, 832, 791, 721, 657, 599, 529, 476 | 261 (16230) |
| 2 calcined at 200 °C | 3610, 3550, 3100, 1630 ^a , 1600, 1560, 1540 ^b , 1500, 1480, 1425, 1400 ^a , 1350 ^b , 1300, 1275, 1160, 1100, 1075, 1000, 940, 925, 900, 850, 830, 800, 775, 675, 650, 550, 475 | |
| 2-nbaH | 3100–2889 (b), 2678, 2549, 1684 ^a , 1608, 1538 ^b , 1491 ^a , 1415, 1368 ^b , 1292, 1152, 1067, 918, 862, 809, 780, 733, 692, 645, 587, 552 | 261 (11993) |
| [Mg(H ₂ O) ₆](2-nba) ₂ ·2H ₂ O 3 | 3578, 3426 (b), 3169, 1684, 1643, 1596 ^a , 1573, 1520 ^b , 1485, 1444, 1386 ^a , 1368 ^b , 1310, 1163, 1140, 1076, 1041, 994, 965, 894, 865, 848, 818, 784, 748, 649, 590, 556, 409 | 265 (20724) |
| 3 calcined at 200 °C | 3600, 3100, 2930, 1600 ^a , 1580, 1530 ^b , 1490, 1460 ^a , 1350 ^b , 1300, 1215, 1150, 1075, 1049, 1000, 950, 860, 849, 798, 749, 700, 650, 600, 550, 475 | |

ϵ_{\max} values are in mol⁻¹ l cm⁻¹ and are given in parentheses.

^a Asymmetric and symmetric vibrations of the (COO)⁻ group.

^b Asymmetric and symmetric vibrations of the (NO₂) group.

Table 3
Interplanar spacings of the most prominent peaks

| Compound | <i>d</i> -values in Å ^a |
|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| [Mg(H ₂ O) ₆](4-nba) ₂ ·2H ₂ O 1 | 7.3630 (24.3), 7.1726 (100.0), 5.9847 (23.1), 5.8857 (12.8), 5.8052 (49.2), 5.1290 (18.0), 5.0635 (73.5), 4.4993 (10.2), 4.0451 (14.5), 3.6702 (11.7), 3.6296 (76.9), 3.3714 (34.4), 3.3558 (75.5), 3.1751 (38.4), 3.1652 (33.3), 3.1212 (30.9), 2.8334 (16.7), 2.5440 (10.4), 2.5280 (10.0) |
| [Mg(H ₂ O) ₆](3-nba) ₂ ·2H ₂ O 2 | 15.8248 (91.2), 7.2874 (12.2), 6.7144 (73.8), 6.1058 (23.5), 5.5710 (54.5), 5.5056 (62.2), 4.9390 (21.3), 4.1535 (42.3), 3.7064 (38.8), 3.6260 (30.8), 3.5187 (32.1), 3.3846 (37.4), 3.3147 (60.4), 3.2494 (100.0), 3.1812 (18.8), 3.0958 (26.3), 2.9757 (17.1), 2.9294 (10.9), 2.7810 (19.3), 2.4927 (11.8), 2.4558 (13.8), 2.3893 (10.0), 2.2792 (18.8), 2.0959 (13.4) |
| [Mg(H ₂ O) ₆](2-nba) ₂ ·2H ₂ O 3 | 7.2695 (11.5), 6.4186 (18.1), 5.8838 (17.4), 5.7231 (6.0), 4.7299 (6.10), 3.8521 (27.7), 3.8259 (100.0), 3.6852 (5.0), 3.3726 (23.4), 3.2658 (15.6), 3.2218 (7.1), 2.8742 (93.6), 2.8035 (5.3), 2.7680 (6.6), 2.5910 (12.4), 2.4222 (7.4), 2.1769 (6.1), 1.4388 (6.2) |
| Residue from 1 | 2.4298 (7.6), 2.1061 (100.0), 1.4910 (43.3), 1.2704 (4.8), 1.2154 (10.2) |
| Residue from 2 | 2.4301 (9.6), 2.1087 (100.0), 1.4910 (43.1), 1.2719 (4.5), 1.2171 (10.6) |
| MgO (periclase) ^b | 2.11 (100.0), 1.49 (50.0), 1.22 (10.0) |

^a Values in parentheses are the relative intensities.

^b Data from JCPDS file 4-829.

Table 4
Thermal decomposition data

| Complex | DSC/DTA results | | TG results | | | |
|---------------------------------------------------------------------------------------------------|------------------------------------------|--|-------------------------------------------|--------------------------------------|-------------------|---------|
| | T_{peak} ($^{\circ}\text{C}$) | | T_{range} ($^{\circ}\text{C}$) | Mass loss (%), found (calculated) | Loss | Residue |
| [Mg(H ₂ O) ₆](4-nba) ₂ ·2H ₂ O 1 ^a | 88 endo | | 60–200 | 29.51 (28.77) | 8H ₂ O | MgO |
| | 101 endo | | 200–375 | | | |
| | 213 exo | | 375–495 | 25.79 (17.58) | 2CO ₂ | |
| | 396 exo | | 495–750 | Decomposition | | |
| | 429 exo | | | | | |
| | 560 exo | | | | | |
| [Mg(H ₂ O) ₆](3-nba) ₂ ·2H ₂ O 2 | 120 endo | | 80–129 | 12.30 (10.79) | 3H ₂ O | MgO |
| | 162 endo | | 129–193 | 7.50 (7.19) | 2H ₂ O | |
| | 248 exo | | 193–314 | | | |
| | 320 endo | | 314–381 | 13.90 (10.79) | 3H ₂ O | |
| | 365 exo | | 381–640 | Decomposition | | |
| | 417 exo | | | | | |
| [Mg(H ₂ O) ₆](2-nba) ₂ ·2H ₂ O 3 | 140 endo | | 31–174 | 15.30 (14.38) | 4H ₂ O | MgO |
| | 337 exo | | 174–298 | 4.20 (3.60) | 1H ₂ O | |
| | 381 exo | | 298–347 | 17.70 (10.79) | 3H ₂ O | |
| | 577 exo | | 347–640 | Decomposition | | |
| | | | | | | |

^a DSC data.

This indicates that the –OH group of the carboxylic acid is strongly H-bonded to the nitro substituent in the solid state. All the three Mg(II) complexes exhibit very strong and broad absorption bands in the region 3500–3000 cm⁻¹. These bands correspond to the antisymmetric and symmetric stretching vibrations of water. These signals clearly confirm the presence of water in the synthesized complexes. The absorptions of the symmetric and antisymmetric vibrations of the nitro group in the aromatic ring are observed at around 1550–1500 and 1360–1290 cm⁻¹, as expected [23]. The carbonyl absorption, which is observed at around 1700 cm⁻¹ in the free acids, is shifted to lower energies in the Mg(II) complexes and this is a typical feature observed in carboxylates [24]. Further, the difference between the symmetric and antisymmetric stretching vibrations of the carboxylate is of the order 200 cm⁻¹ which is indicative of the fact that the carboxylate is not coordinated and only functions as an anion in all the complexes [24]. The IR spectrum of a sample of **1** heated at 200 °C shows several IR bands while the broad signal due to water disappears. The absence of the broad –OH bands in the heat-treated sample can be attributed to the formation of the cor-

responding anhydrous complex. Further, the IR vibrations of the carboxylate group are quite closer in the calcined complex and the bands are split. This feature indicates that on removal of the coordinated water, the nitrobenzoate is coordinated to the central metal.¹ In contrast, the IR spectra of the complexes **2** and **3** calcined at 200 °C still exhibit the –OH absorption signals indicating the presence of water. In addition, the signals characteristic of the aromatic acid are also observed (Table 2). The IR spectra of the residues left after thermally decomposing the complexes **1–3** at 800 °C are featureless and devoid of any absorption down to 600 cm⁻¹ indicating oxide formation. The IR spectra of the residue formed in all the cases are identical indicating that the product formed is same.

3.4. Thermal characterization

The TG, and DSC/DTA results of the Mg(II) complexes **1–3** are summarized in Table 4. All the complexes start decomposing below 100 °C. Thermal decomposition of all the compounds is a multi-stage

¹ We thank a reviewer for drawing our attention to this feature.

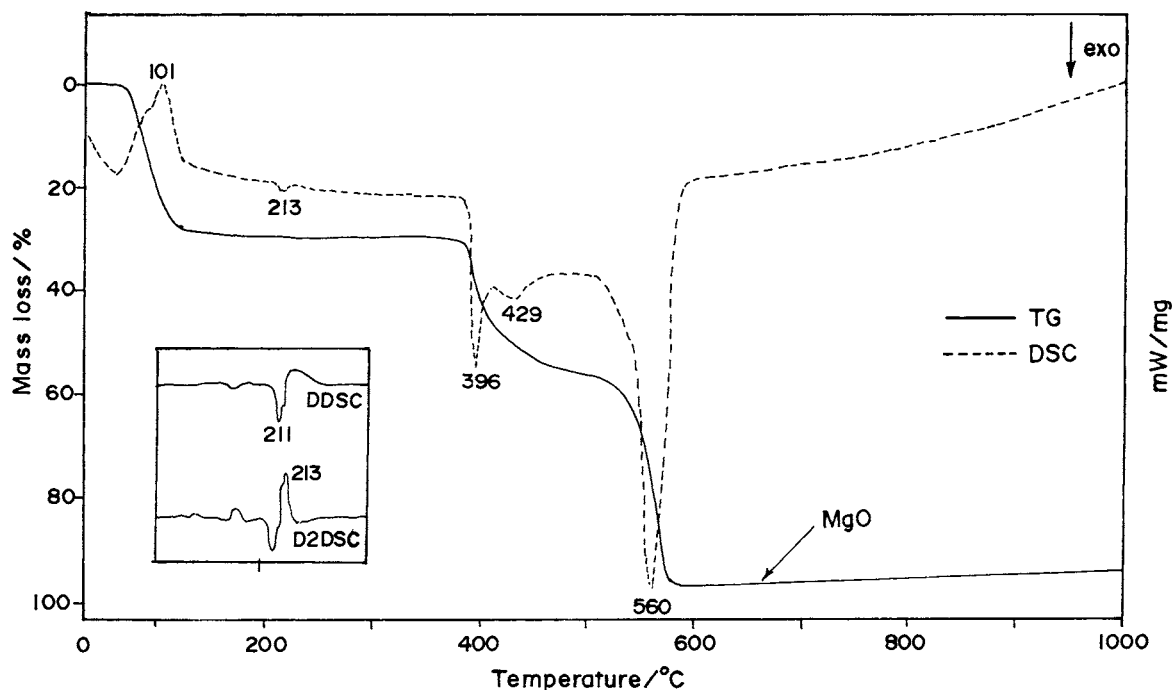
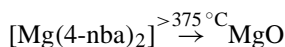
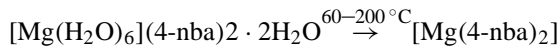


Fig. 1. TG and DSC curves of $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **1**.

process. Although, all the complexes differ in their thermal behavior, in all the cases, the final solid product of thermal decomposition was always identified as MgO.

The TG and DSC curves of the complex $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **1** are reproduced in Fig. 1. The TG curve of this complex indicates that the complex is thermally stable up to 60 °C, when the slow decomposition to MgO begins. The TG curve shows the first mass loss between 60 and 200 °C corresponding to the loss of 8 mol of water resulting in the formation of the anhydrous complex. This assignment gains further support, based on infrared spectral studies. The infrared spectrum of a sample of **1** recorded after heating it at 200 °C is devoid of the broad signal at around 3500 cm^{-1} . The IR spectrum of the heat-treated (at 200 °C) sample, after exposure to moisture is identical to that of the starting material. In addition, the IR spectrum of **1** recorded after heating it to 420 °C is featureless and does not show any bands indicating the decomposition of the organic moiety. This is indicative of the fact that the carboxylates are not lost in two steps. The most probable thermal

decomposition scheme can be shown as below:

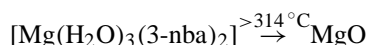
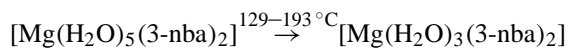
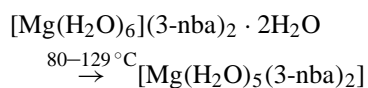


The DSC curve for complex **1** displays two closely spaced endothermic peaks at 88 and 101 °C. The inflexion point at 88 °C can be attributed to the loss of 2 mol of water while the signal at 101 °C can be assigned to the removal of 6 mol of water. The rapid drop of the TG curve in this region indicates, that initially 2 mol of water (probably crystal water) are lost, which immediately results in the loss of the remaining 6 mol of coordinated water. A weak exothermic signal is observed at 213 °C. As the TG curve is parallel to the X-axis in the temperature region 200–375 °C, the signal at 213 °C can be assigned to a phase change. The observation of the first and second derivative signals at 211 and 213 °C, respectively adds credence to this assignment. The derivative thermograms in the region 150–250 °C (DDSC and D2DSC) are shown as an inset in Fig. 1. Heating a sample of complex **1**

isothermally at 250 °C results in the formation of a bright yellow complex. It is probable that this phase may correspond to a different binding mode of the carboxylate ligand. However, the exact nature of the phase formed is not clear. The DSC curve shows an exothermic signal at 403 °C followed by a weak peak at 429 °C. These signals can be attributed to the removal of 2 mol of CO₂. However, the observed mass loss (25.80%) is much more than that expected (17.58%) for the loss of 2 mol of CO₂, indicating that decarbonylation results in the decomposition of **1**. The exothermic signal at 560 °C can be attributed to the decomposition reaction of the intermediate formed in the previous step, involving the loss of the nitrobenzoate with simultaneous formation of MgO.

The TG, and DTA curves of the complex [Mg(H₂O)₆](3-nba)₂·2H₂O are presented in Fig. 2. Unlike the para isomer, this complex exhibits several steps. The TG curve of this complex indicates that the complex is thermally stable up to 80 °C, when the slow decomposition to MgO begins. The mass losses observed between 80 and 129, and 129 and 193 °C can be attributed to the removal of 3 and 2 mol of water, respectively. In the region 193–314 °C, the TG curve is parallel to the temperature axis and the observed mass loss (0.3%) is negligible. The observed mass loss between 314 and 381 °C is more than that expected for the last 3 mol of water. This can be explained due to the fact that these waters are very strongly bound

and removal of these, result in the breakdown of the structure resulting in decomposition. It is this factor which is probably responsible for the higher observed mass loss. Further decomposition occurs resulting in the formation of pure MgO at 640 °C. The most probable thermal decomposition scheme is



The DTA of **2** exhibits several events. The endothermic peaks at 120 and 162 °C can be assigned to the loss of 3 and 2 mol of water, respectively. The exothermic peak at 248 °C is probably due to a phase change as the TG curve is parallel to the X-axis in this region. The nature of the phase formed is not very clear. The endothermic peak at 320 °C can be assigned to the loss of the remaining 3 mol of water. The observed mass loss is much more than that expected for the loss of 3 mol of water indicating that these waters are more strongly bound and removal of these result in the decomposition of the complex. The exothermic peak at 365 °C can be attributed to the decomposition of the organic anion probably involving a decarbonylation reaction. The exothermic peaks seen at 417 and 606 °C

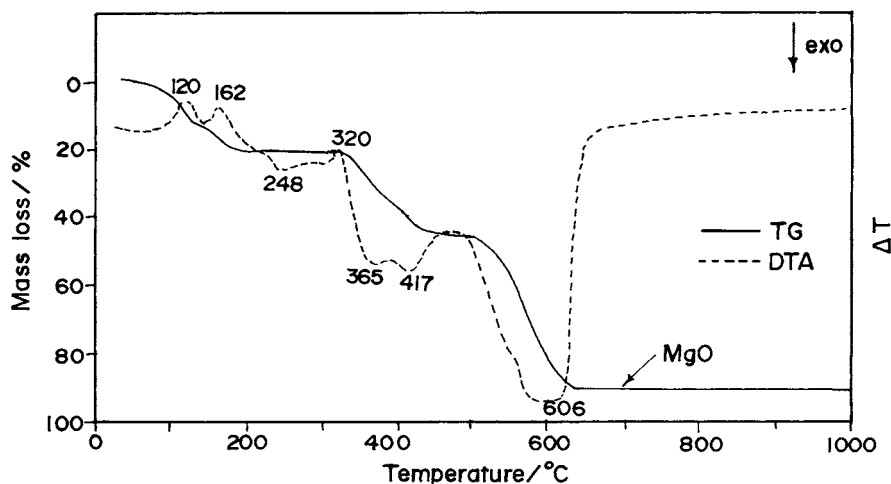


Fig. 2. TG and DTA curves of [Mg(H₂O)₆](3-nba)₂·2H₂O **2**.

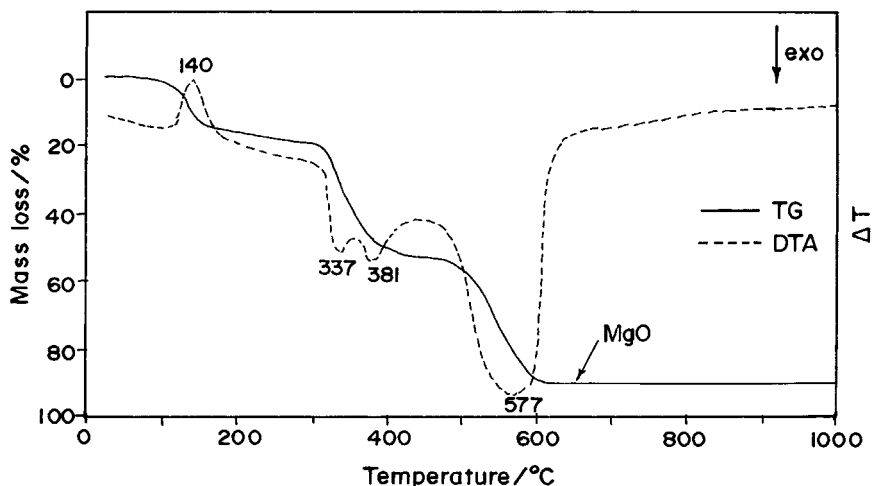
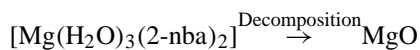
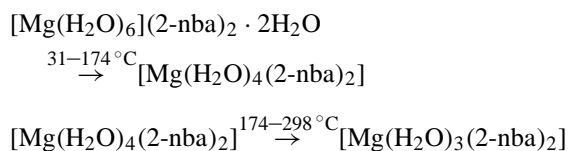


Fig. 3. TG and DTA curves of $[\text{Mg}(\text{H}_2\text{O})_6](2\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **3**.

can be assigned to the formation of intermediate products due to decomposition of the nitrobenzoate as well as oxidation. The broad DTA signal centered at around 606°C is indicative of a very complex process.

The TG and DTA curves of the complex $[\text{Mg}(\text{H}_2\text{O})_6](2\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **3** are shown in Fig. 3. The first mass loss of 15.3% observed between 31 and 174°C can be attributed to the loss of 4 mol of water. It may be noted that a higher temperature range is needed for the first dehydration step than in the complex **2** indicating that the water is more strongly bound. The thermal behavior of this complex is entirely different compared to that of **2** which can be attributed to the positioning of the $-\text{NO}_2$ group in the six-membered ring. The observed mass loss of 4.2% between 174 and 298°C can be assigned to the loss of 1 mol of water. The third mass loss of 17.7% between 298 and 347°C is more than the expected mass loss for the last 3 mol of water. This can be attributed to the decomposition of **3** when it is fully dehydrated. The decomposition of the organic carboxylate continues, ultimately resulting in the formation of MgO above 600°C . The most probable thermal decomposition scheme can be as shown below:



The DTA shows an endothermic peak at 140°C , which can be assigned to the loss of 4 mol of water. The exothermic event at 337°C can be attributed to the loss of the last 3 mol of waters, which are very strongly bound. Removal of these, results in the breakdown of the structure. The exothermic peaks observed at 381 and 577°C can be assigned to the formation of intermediate products due to decomposition of the organic moiety as well as oxidation resulting in the formation of MgO. The observation of a broad DTA signal centered at around 577°C is indicative of a very complex process. The exact nature of this process is not clear.

3.5. Comparative chemistry of Mg(II) complexes of nitro- and aminobenzoates

The hydrated Mg-nitrobenzoate complexes **1–3** prepared in this work exhibit certain similarities and yet they are different. The complexes can be prepared by the reaction of MgCO_3 with the isomeric nitrobenzoic acids. Their molecular weights and stoichiometries are the same. All the complexes can be formulated as octahydrates and consist of the same octahedral $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cation. The complexes decompose on heating in air to give MgO as the final product. The complexes **1–3** also show some resemblance with the previously reported hydrated

Mg(II)-aminobenzoates. The aminobenzoates of Mg(II) prepared from 4- and 2-abaH are octahydrates and have been formulated as consisting of the octahedral $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cation [7,19]. In these complexes, the aminobenzoates are outside the coordination sphere of the bivalent metal and function as anions. The reported crystal structure of the complex $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-aba})_2 \cdot 2\text{H}_2\text{O}$ has been explained in terms of secondary H-bonding interactions between the coordinated water molecules of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and the 4-aminobenzoate both at the $-\text{NH}_2$ and $-\text{COO}^-$ sites [7]. The amino ($-\text{NH}_2$) functionality forms $\text{N}-\text{H} \cdots \text{O}$ bonds (H-donor bonds) with the O atom of a coordinated water molecule. Similar weak $\text{N}-\text{H} \cdots \text{O}$ bonds have also been observed in Ca, Sr and Ba-aminobenzoates [6]. Although no X-ray structural studies have been done by us for the complexes **1–3**, the structural data of the complex $[\text{Co}(\text{H}_2\text{O})_4(4\text{-nba})_2] \cdot 2\text{H}_2\text{O}$ can be used to draw a comparison. In the hydrated Co-*para*-nitrobenzoate complex, short H-bonding contacts are observed between the O atom of the $-\text{NO}_2$ group and a H atom of the coordinated water [25]. The presence of such weak interactions in the form of $\text{O} \cdots \text{H}-\text{O}$ bonds (H acceptor bonds) between the O atom of the nitro group and the H of a coordinated water is an important difference between the amino and nitrobenzoates. The differing capabilities of the $-\text{NH}_2$ and $-\text{NO}_2$ groups to form H-bonds with the coordinated water can then be used to explain the difference in thermal behaviour of these complexes. The Mg(II) complex **1** prepared in this work can be fully dehydrated at 200°C while the analogous aminobenzoate complex can be fully dehydrated at a slightly higher temperature of 215°C . Both the complexes can be reversibly hydrated. The hydrated Mg(II) complex of 2-aba can be fully dehydrated at 200°C to yield the anhydrous complex [19]. However, the anhydrous complex cannot be rehydrated [19]. In contrast, the analogous nitrosubstituted complex **3** cannot be fully dehydrated without decomposition indicating that H-bonding interactions are quite strong in this case. This further indicates that the positioning of the amino or nitro substituent in the aromatic ring with respect to the $-\text{COO}^-$ group can also influence the structure and hence the properties. The H-bonding interactions present in these complexes are probably responsible for the higher temperature ranges needed for the dehydration processes. Hence, this

subtle difference in the type of secondary H-bonding interactions is an important factor to be taken into consideration while discussing the chemistry of these systems.

4. Conclusions

The thermal and spectral characterization of the Mg(II) complexes of substituted nitrobenzoic acids have been investigated in this work. The isomeric nitrobenzoate complexes prepared in this study differ from each other in terms of the orientation of the nitro group with respect to the carboxylate group in the six-membered ring. In the ortho isomer, the nitro group is disposed at an angle of 60° with respect to the carboxylate functionality, while in the para isomer it is trans to the $-\text{COO}^-$ group. In the meta isomer the nitro group is disposed in an intermediate way, i.e. at 120° with respect to the carboxylate. The positioning of the $-\text{NO}_2$ group seems to affect the structure of the complexes. In all the complexes, the nitrobenzoate anions are outside the coordination sphere of Mg(II) as evidenced from spectral studies. All the complexes can be thermally decomposed to MgO at around 600°C . The decomposition temperature for oxide formation in these complexes is quite low compared to the Mg(II) carboxylate complexes reported by Mojumdar et al. using heterocyclic ligands [15–18]. The formation of MgO at relatively lower temperatures, indicates that the Mg(II)-nitrobenzoate complexes **1–3** prepared in this work, can be used as precursors for the generation of high-area metal oxides of wide applications.

The differing nature of the thermal decomposition processes of the Mg(II) complexes **1**, **2**, and **3** can be explained in terms of the orientation of the nitro group. While complex **1** (para isomer) can be cleanly dehydrated to get the anhydrous complex, the ortho and meta isomers cannot be fully dehydrated without decomposition, indicating that the para isomer is structurally different as compared to the ortho and meta isomers. For the isomeric aminophenols, it has been reported that the ortho and meta isomers have a very different crystal structure from that of *para*-aminophenol which is explained based on the supramolecular architecture of these compounds with the aid of H-bonds (see the footnote 1, [26,27]). Further complex **1** can be reversibly hydrated. Higher

temperatures are required to dehydrate **2** and **3** indicating that the water molecules are more strongly bound in these complexes compared to **1**. This behavior can be attributed to possible secondary H-bonding interactions between the coordinated water molecules and the nitrobenzoate anion. In the absence of single crystal X-ray data, a definite structure cannot be described for the different components. However, the present spectroscopic and thermal studies do indicate that the positioning of the $-\text{NO}_2$ group in the benzene ring does influence the structure.

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