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## Synthesis, X-ray structure and properties of a calcium(II) coordination polymer showing $\mu_2$ - $\eta^1$ : $\eta^1$ and $\mu_3$ - $\eta^2$ : $\eta^1$ coordination modes of 4-nitrobenzoate

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### Abstract

The reaction of the monomeric compound  $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-nba})(\eta^2\text{-4-nba})]$  **1** (4-nba = 4-nitrobenzoate) with N-methylimidazole (N-MeIm) or imidazole (Im) at 100°C results in the formation of the anhydrous mixed ligand complexes of composition  $[\text{Ca}(\text{L})(4\text{-nba})_2]$  (L=N-MeIm **2**; L=Im **3**). The compounds were characterized by elemental analysis, IR, UV-Vis and <sup>1</sup>H NMR spectra, TG-DSC thermograms, weight loss studies and the structure of **2** was determined by single crystal X-ray crystallography. Compounds **2** and **3** can be transformed into **1** by heating with water. At elevated temperatures all compounds (**1-3**) are thermally decomposed to CaO. Compound **2** crystallizes in the centrosymmetric triclinic space group  $P\bar{1}$  with all atoms located in general positions. The structure reveals that **2** is a polymer and can be formulated as *catena*-poly[[N-methylimidazole]calcium(II)]( $\mu_2$ - $\eta^1$ : $\eta^1$ -4-nitrobenzoato)( $\mu_2$ - $\eta^2$ : $\eta^1$ -4-nitrobenzoato)]. The structure of  $[[\text{Ca}(\text{N-MeIm})](\mu_2$ - $\eta^1$ : $\eta^1$ -4-nba)( $\mu_3$ - $\eta^2$ : $\eta^1$ -4-nba)]<sub>n</sub> **2**

consists of a central Ca(II) ion, a terminal N-MeIm ligand and two crystallographically independent 4-nba ligands. In the crystal structure, each Ca(II) is bonded to a nitrogen atom of N-MeIm and five oxygen atoms from five symmetry related 4-nba ligands resulting in a distorted  $\{CaO_5N\}$  octahedron. One of the unique 4-nitrobenzoate in each formula unit functions as a bridging bidentate ligand ( $\mu_2\text{-}\eta^1\text{:}\eta^1\text{-4-nba}$ ) and is linked to two symmetry related Ca(II) ions leading to the formation of an infinite chain extending along  $a$  axis with a long Ca $\cdots$ Ca separation of 5.531(1) Å. The second independent 4-nba ligand ( $\mu_3\text{-}\eta^2\text{:}\eta^1\text{-4-nba}$ ) is coordinated to three different Ca(II) ions with both the carboxylate oxygen atoms linked to the same infinite chain formed earlier and one of the carboxylate oxygen atoms functions as a monoatomic bridge between two symmetry related Ca(II) ions. This bridge links two chains with a shorter Ca $\cdots$ Ca separation of 3.8585(7) Å resulting in the formation of a one-dimensional ladder structure. The oxygen atoms of the nitro groups are involved in C-H $\cdots$ O interactions. A comparative study of thirty Ca(II) coordination polymers is described.

*Keywords:* 4-nitrobenzoate; N-methylimidazole; imidazole; bridging bidentate; monoatomic bridge; one-dimensional ladder; C-H $\cdots$ O interactions.

## 1. Introduction

The design of coordination polymers employing carboxylic acids as ambidentate and templating ligands with metals providing interesting connectivity is an area of current research [1-3]. Recently several reports have appeared on the synthesis and structural characterization of metal-carboxylate based materials using benzene carboxylic acids [4-11]. The ready availability of benzene based carboxylic acids in pure form, combined with the fact that the carboxylate group is a versatile donor that can bind in a variety of ways [12-14], has contributed to these recent advances in the area of organic-inorganic hybrid materials. An added advantage of using benzene-based systems is the introduction of potential donor groups like -NH<sub>2</sub>, -OH, -SH, or another -COOH into the rigid six-membered ring. Further the positioning of these groups can be altered with respect to the carboxylate functionality. The introduction of additional groups affects the acidity of the carboxylic acid, which is useful from a synthetic point of view of metal carboxylates. Substituents present on the benzene ring like -NO<sub>2</sub>, -F, -Cl, -Br, etc. lack the donor characteristics to form a strong metal-ligand bond. However the resulting carboxylic acids are stronger acids as compared to benzoic acid and hence can exhibit different reactivity characteristics when treated with metal sources. In addition, substituents like -NO<sub>2</sub> can participate in secondary interactions by forming H-acceptor bonds, which can direct the assembly of novel structures. In view of this, we are investigating the synthesis, thermal properties [15] and structure characteristics [16] of metal-4-nitrobenzoate (4-nba) complexes, to prepare new compounds by exploiting the H-bonding characteristics of the -NO<sub>2</sub> group.

The structural chemistry of alkaline-earths with carboxylate ligands is an area of current research as evidenced by the several recent reports in literature [17-23]. In our metal carboxylate research programme we have unraveled a rich structural chemistry of the 4-nitrobenzoates of the alkaline-earths [24-28]. The triad of compounds  $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Mg}(\text{H}_2\text{O})_2(\text{Im})_2(\eta^1\text{-4-nba})_2]$  (Im = imidazole) and  $[\text{Mg}(\text{H}_2\text{O})(\text{N-MeIm})_2(\eta^1\text{-4-nba})(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-4-nba})_2]$  (N-MeIm = N-methylimidazole) demonstrate a rich and variable chemistry of 4-nitrobenzoates of Mg in terms of the binding modes of 4-nba anions as well as secondary H-bonding interactions. For calcium we reported on the structure and properties of a seven coordinated monomeric complex  $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-nba})(\eta^2\text{-4-nba})]$  **1** [24], which exhibits both mono ( $\eta^1$ ) and bidentate ( $\eta^2$ ) coordination of 4-nba and  $[\text{Ca}(\text{H}_2\text{O})_3(\text{Im})(\eta^1\text{-4-nba})_2] \cdot \text{Im}$  [25] which shows  $\eta^1$  ligation of 4-nba and contains coordinated as well as free imidazole. In this paper, we present the details of the investigation of the thermal reaction of the seven coordinated Ca compound **1** in the presence of N-methylimidazole (N-MeIm) and imidazole (Im), resulting in the formation of the anhydrous mixed ligand complexes of composition  $[\text{Ca}(\text{L})(4\text{-nba})_2]$  (L=N-MeIm **2**; L=Im **3**).

## 2. Experimental

### 2.1. Materials and methods

All the chemicals used in this study were of reagent grade and were used as received. The starting materials and reaction products are air stable and hence were prepared under normal laboratory conditions. The complex  $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-nba})(\eta^2\text{-4-nba})]$  **1** was prepared as described earlier [24]. Infrared (IR) spectra were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range 4000-400  $\text{cm}^{-1}$ . The

samples for the IR spectra were diluted with KBr in the solid state and the signals referenced to polystyrene bands. Electronic spectra were recorded using matched quartz cells on a Shimadzu (UV-2450) spectrophotometer.  $^1\text{H}$  NMR spectra were recorded in DMSO- $d_6$  on a Bruker 400 MHz FT-NMR spectrometer. TG-DSC measurements were performed in  $\text{Al}_2\text{O}_3$  crucibles on a STA-409PC simultaneous thermal analyzer from Netzsch in flowing air. A heating rate of  $10\text{ K min}^{-1}$  was employed for all measurements. X-ray powder pattern were recorded on a Phillips PW-3710 diffractometer using  $\text{Cu-K}\alpha$  radiation over  $2\theta$  range of  $15\text{-}75^\circ$  at a scan rate of  $3^\circ\text{ min}^{-1}$ . The insoluble 4-nbaH obtained on acid treatment of the complexes was weighed as described earlier [15] and metal analysis was performed titrimetrically following a standard procedure. Isothermal weight loss studies were performed in an electric furnace fitted with a temperature controller.

### 2.2 Preparation of $[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]$ **1a**

A powdered sample of **1** (0.444 g) was heated on a steam bath for ~30 minutes. The heat-treated sample was kept in a dessicator and allowed to cool to room temperature and weighed to obtain **1a**. The observed decrease in weight (12.15%) corresponds to the removal of three moles of water. The yield was quantitative. The compound is insoluble in MeOH,  $\text{CH}_3\text{CN}$  etc.

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{10}\text{CaN}_2\text{O}_9$  : Ca, 10.25; 4-nbaH, 85.68; CaO, 14.35. Found: Ca, 10.01; 4-nbaH, 84.8, CaO, 14.0

IR data: 3611-3100 (br), 3113(s), 2849(w), 1944(w), 1813(w), 1612(s), 1558(s), 1524(m), 1493(sh), 1414(s), 1346(s), 1319(s), 1171(m), 1142(m), 1107(s), 1015(s), 980(s), 880(s), 839(s), 799(s), 725(s), 511(s)  $\text{cm}^{-1}$ .

DSC data (in  $^\circ\text{C}$ ) : 260 (exo), 410 (exo), 447 (exo) 558 (exo).

### 2.3 Preparation of $[Ca(N-MeIm)(4-nba)_2]_n$ **2**

#### 2.3.1 Method 1

N-Methylimidazole (0.082 g, 1 mmol) was added into a freshly prepared sample of **1a** and the reaction mixture was left in a dessicator for ~30 min. The reaction mixture was washed with ether and dried to obtain **2**. Alternatively **2** can also be prepared by directly heating a mixture of a finely powdered sample of **1** (0.45 g, 1 mmol) and N-MeIm (0.082 g, 1 mmol) in a steam bath for ~30 min. The hot reaction mixture was cooled and washed well with ether and dried in air. Yield: (quantitative).

*Anal.* Calcd for  $C_{18}CaH_{14}N_4O_8$  (454.43) **2** : Ca, 8.8; 4-nbaH, 73.11; CaO, 12.34; C, 47.53; H, 3.0; N, 12.32 Found: Ca, 8.8; 4-nbaH, 73, CaO, 12.2; C, 47.6; H, 3.03; N, 11.81.

IR data: 3121(s), 2967(s), 2855(w), 1614(s), 1584(s), 1520(m), 1402(s), 1375(s), 1344(s), 1321(s), 1279(s), 1230(m), 1107(s), 1014(s), 1082(m), 934(s), 878(s), 822(s), 800(s), 752(s), 727(s), 667(s), 621(s), 559(s), 509(s)  $cm^{-1}$ .

UV-Vis 274 nm (23775  $L \cdot mol^{-1} \cdot cm^{-1}$ )

$^1H$  NMR (DMDO- $d_6$ )  $\delta$  (in ppm) : 3.63 (s, 3H); 6.86 (s, 1H); 7.09 (s, 1H); 7.55 (s, 1H); 8.16 (m, 4H )

DSC data (in  $^{\circ}C$ ): 188 (endo) 412 (exo) 558 (exo)

#### 2.3.2 Method 2

A powdered sample of **1** (1.78g, 4 mmol) was heated with N-MeIm (1.4 ml, 17 mmol) on a steam bath for ~1 h to obtain a light yellow solid. To this hot mass distilled water (~8 ml) was added and the mixture reheated to obtain a pale yellow solution. The hot solution was quickly filtered and kept aside for crystallization. Fine colourless blocks of crystals suitable for X-ray study, which separated were washed with ether (5ml) and dried in air. Yield: 60%. The use of reduced amounts of N-MeIm in the thermal

reaction or excess water for recrystallisation results in the formation of the tetraaqua compound **1** in accordance with its hydration characteristics (*vide infra*). The infrared spectrum and the DSC thermogram of this product is identical with that of the product obtained in the thermal reaction.

#### 2.4 Preparation of $[Ca(Im)(4-nba)_2]$ **3**

Imidazole (0.068 g, 1 mmol) was added into a freshly prepared sample of **1a** and the reaction mixture was left in a dessicator for ~30 min. The reaction mixture was washed with ether and dried to obtain **3**. Alternatively **3** can also be prepared by directly heating a mixture of a finely powdered sample of **1** (0.45g, 1mmol) and Im (0.068 g, 1mmol) in a steam bath for ~30 min. The hot reaction mixture was cooled and was washed well with ether and dried in air. Yield: (quantitative).

*Anal.* Calcd for  $C_{17}CaH_{12}N_4O_8$  **3** : Ca, 9.08; 4-nbaH, 75.88; CaO, 12.73; C, 46.31; H, 2.72; N, 12.71 Found: Ca, 8.9; 4-nbaH, 74.28; CaO, 12.3; C, 45.95; H, 3.13; N, 10.94. IR data: 3381 (s), 3223(s), 3061(w), 2941(w), 1604(w), 1570 (s), 1516(s), 1490(m), 1402 (s),1348 (s),1321 (s), 1261 (s), 1171 (m),1142 (m),1107 (s),1066 (s),1014 (s), 935 (s), 918 (s), 860 (s), 825 (s), 802 (s), 752 (s), 740 (s), 723 (s), 659 (s), 617 (s), 497 (s), 511(s)  $cm^{-1}$ .

$^1H$  NMR (DMDO- $d_6$ )  $\delta$  (in ppm) : 7.00 (s, 2H); 7.63 (s, 1H); 8.13 (m, 4H ).

DSC data (in  $^{\circ}C$ ): 198 (endo), 415 (exo), 547 (exo)

#### 2.5 Rehydration studies

A powdered sample of **2** (200 mg) was suspended in water (~5 ml) and the reaction mixture left undisturbed overnight. The reaction mixture was filtered and the residue was washed with alcohol followed by ether and dried to obtain **1** in quantitative yields. The formation of **1** is evidenced by its characteristic IR spectrum and DSC thermogram. Alternatively **2** can be transformed to **1** by suspending an amount (200 mg) of **2** in water (5 ml) and heating the solution till dissolution of the solid. The hot

solution is cooled to obtain **1** in quantitative yield. The equilibration of a powdered sample of **3** over water vapour, resulted in the formation of the starting compound **1** in quantitative yield in about a day as evidenced by its characteristic IR spectrum and DSC thermogram.

### 2.6 X-ray crystallography

Intensity data for **2** were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo-K $\alpha$  radiation. The data integration and reduction were processed with SAINT software [29]. An empirical absorption correction was applied to the collected reflections with SADABS [30]. The structure was solved with direct methods using SHELXS-97 and refinement was done against F<sup>2</sup> using SHELXL-97 [31]. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms. The technical details of data acquisition and some selected refinement results for **2** are listed in Table 1.

## 3. Results and discussion

### 3.1 Synthesis and spectroscopy

Heating of a solid sample of the tetrahydrate **1** at 100 °C resulted in the loss of three moles of water leading to the formation of a monohydrate [Ca(H<sub>2</sub>O)(4-nba)<sub>2</sub>] **1a** (Scheme 1). The presence of water in **1a** is evidenced by the strong and broad absorption around 3500 cm<sup>-1</sup> in its infrared spectrum assignable to O-H vibration. It is to be noted that the profile of the O-H signal of compound **1a** is quite different as compared to that of the tetrahydrate compound **1**. In addition the IR signals of the nitro and carboxylate functionalities, which occur between 1300 to 1650 cm<sup>-1</sup> are broadened



in **1a** as compared to the spectrum of **1** (Figure 1). On exposure to moisture the monohydrate rapidly transforms into the seven coordinated starting material **1**. Interestingly, the reaction of N-MeIm or Im with the monohydrate **1a** results in the displacement of water by the N-donor ligands and the formation of anhydrous mixed ligand compounds **2** or **3** having molar composition of Ca:4-nba:N-MeIm(Im) 1:2:1 (Scheme 1). The use of excess N-MeIm or Im in the thermal reaction did not result in the formation of new products containing additional N-donor ligands. The anhydrous mixed ligand compounds **2** or **3** can also be synthesized in a single step by directly heating a mixture of powdered sample of **1** and N-MeIm in a 1:1 mole ratio. The presence of the N-donor ligands in compounds **2** and **3** can be readily confirmed by their NMR spectra which exhibit the characteristic signals of 4-nba, N-MeIm or Im. The formation of the anhydrous compounds **2** or **3** is evidenced by their IR spectra, which are devoid of the signals for O-H vibrations of water and is further confirmed by the appearance of additional bands due to the incorporation of the N-donor ligand in its mid IR spectrum (Figure 1). Compounds **2** and **3** are relatively stable compared to the moisture sensitive monohydrate **1a**. However, both **2** and **3** can be transformed to **1** by suspending them in water overnight or alternatively by heating **2** or **3** in water (Scheme 1). Crystals of **2** suitable for structure determination were prepared by heating a mixture of **1** and excess N-MeIm at 100°C followed by recrystallisation from minimum water. Similar attempts to prepare compound **3** in crystalline form suitable for X-ray structure determination by solution method always resulted in the formation of the known monomeric compound  $[\text{Ca}(\text{H}_2\text{O})_3(\text{Im})(\eta^1\text{-4-nba})_2]\cdot\text{Im}$ . The compounds **1a**, **2** and **3** were formulated based on the elemental analysis and the mass loss leading to the formation of CaO on pyrolysis in a Bunsen flame. All the compounds exhibit several

signals in the mid IR region indicating the presence of the organic moieties. However based only on the infrared data the exact nature of the binding of the 4-nba ligand cannot be confirmed. The UV-Vis spectra of all compounds exhibit an absorption in the UV region around 274 nm assignable to the charge transfer of the aromatic 4-nba ligand.

### 3.2 Crystal structure description of **2**

Compound **2** crystallises in the triclinic space group  $P\bar{1}$  and all atoms are situated in general positions. The structure reveals that **2** is a polymer and can be formulated as *catena*-poly[[ $(N\text{-methylimidazole})\text{calcium(II)}(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-4-nitrobenzoato})(\mu_2\text{-}\eta^2\text{:}\eta^1\text{-4-nitrobenzoato})$ ]]. The structure of  $[[\text{Ca}(\text{N-MeIm})](\mu_2\text{-}\eta^1\text{:}\eta^1\text{-4-nba})(\mu_3\text{-}\eta^2\text{:}\eta^1\text{-4-nba})]_n$  **2** consists of a central Ca(II) ion, a terminal N-MeIm ligand and two crystallographically independent 4-nba ligands. In the crystal structure, each Ca(II) is bonded to a nitrogen atom of N-MeIm and five oxygen atoms from five symmetry related 4-nba ligands resulting in a distorted  $\{\text{CaO}_5\text{N}\}$  octahedron (Fig. 2). The geometric parameters of the 4-nba anions and N-MeIm are in the normal range and are comparable with literature values [24-27]. The Ca-O distances in **2** range from 2.2823(12) to 2.4507(11) Å (Table 2) and are in agreement with literature values [24, 25]. The Ca-N bond is longer at 2.5088(14) Å. The cis O-Ca-O and O-Ca-N angles range from 73.71(4) to 107.39(4)° while the trans O-Ca-O and O-Ca-N angles range from 163.97(4) – 175.54(4)° indicating a distorted octahedron. It is interesting to note that both 4-nitrobenzoates in each formula unit are coordinated to the central Ca(II) in different bridging modes (Fig. 2). One of the two 4-nba anions in each formula unit functions as a bridging

bidentate ligand ( $\mu_2\text{-}\eta^1\text{:}\eta^1\text{-4-nba}$ ) (Supplementary Fig. 1)<sup>§</sup> and is linked to two symmetry related Ca(II) ions via O5 and O6 atoms resulting in the formation of an infinite chain extending along *a* axis with a Ca $\cdots$ Ca separation of 5.531(1) Å. The second independent ligand ( $\mu_3\text{-}\eta^2\text{:}\eta^1\text{-4-nba}$ ) is coordinated to three different Ca(II) ions with both the carboxylate oxygen atoms O1 and O2 linked to the same infinite chain formed earlier and one of the carboxylate oxygen atoms (O1) functioning as a monoatomic bridge between two symmetry related Ca(II) ions (Supplementary Fig. 2 & 3)<sup>§</sup>. This monoatomic bridge serves to link the two infinite chains with a shorter Ca $\cdots$ Ca separation of 3.8585(7) Å resulting in the formation of a one-dimensional ladder structure [Fig. 3].

It is to be noted that Ca(II) forms a polymeric compound with 4-nba in the presence of N-MeIm unlike Mg(II) which forms a centrosymmetric dimeric complex [Mg(H<sub>2</sub>O)(N-MeIm)<sub>2</sub>( $\eta^1\text{-4-nba}$ )( $\mu_2\text{-}\eta^1\text{:}\eta^1\text{-4-nba}$ )<sub>2</sub>] [26]. The coordination polymer **2** and the previously reported monomeric compounds [Ca(H<sub>2</sub>O)<sub>4</sub>( $\eta^1\text{-4-nba}$ )( $\eta^2\text{-4-nba}$ )] **1** [24] and [Ca(H<sub>2</sub>O)<sub>3</sub>(Im)( $\eta^1\text{-4-nba}$ )<sub>2</sub>]·Im [25] constitute a triad of Ca(II) compounds having Ca:4-nba in a 1:2 mole ratio and showing different binding modes of the 4-nba ligand. In terms of secondary interactions **1** shows only O-H $\cdots$ O interactions while the monomeric imidazole compound is involved in three varieties of H-bonding interactions namely O-H $\cdots$ O, N-H $\cdots$ O and O-H $\cdots$ N. The absence of coordinated water as well as methylation of the nitrogen atom in N-MeIm in **2** blocks the O-H $\cdots$ O, N-H $\cdots$ O and O-H $\cdots$ N interactions. An analysis of the structure of **2** reveals that the anhydrous compound is involved in only C-H $\cdots$ O interactions (Supplementary Fig. 4)<sup>§</sup> with the oxygen atoms of the nitro groups functioning as H-acceptors and the methyl

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<sup>§</sup> Supplementary Material for online publication

group of imidazole as well as H atoms on the aromatic ring functioning as H-donors.

The geometric parameters of these hydrogen bonds are listed in [Table 3](#).

### 3.3 Comparative study of Ca(II) coordination polymers

A survey of the reported structures of Ca(II) carboxylates reveals that formation of a polymeric chain due to the bridging nature of the carboxylate ligand is a characteristic structural feature of many Ca(II) carboxylates. Several polymeric Ca(II) carboxylates of varying dimensionalities (D) [[17-23](#), [32-52](#)] have been reported in the literature many of which are 1-D polymers ([Table 4](#)). A comparative study of 30 different Ca(II) 1-D polymers reveals that the coordination number of Ca(II) in these compounds varies from 6 to 10, with eight coordination observed in many cases. Hexacoordination around Ca(II) is observed in compound **2** as well as  $[\text{Ca}(\text{Sa})_2(\text{Phen})]_n$  and  $[\text{Ca}(\text{H}_2\text{O})_2(\text{C}_9\text{H}_8\text{NO}_4)_2] \cdot 2.5\text{H}_2\text{O}]_n$  (for abbreviations see [Table 4](#)). Of the several Ca(II) coordination polymers reported in the literature using substituted benzene carboxylic acids, compound **2** constitutes the first example of a Ca(II) coordination polymer derived from 4-nba ligand as the two other known Ca(II) compounds of 4-nba are monomeric in nature. A wide range of Ca $\cdots$ Ca distances between 3.612(1) and 9.816(1) Å are observed for the different Ca(II) 1-D polymeric compounds listed in the comparative [Table](#). The Ca $\cdots$ Ca separation of 3.8585(7) Å between the chains in the ladder compound is comparable with the Ca-Ca distance of around 4.0 Å observed in several coordination polymers listed in [Table 4](#) while the Ca $\cdots$ Ca separation of 5.531(1) Å across the chains in **2** is relatively longer. A very long Ca $\cdots$ Ca distance of 9.816(1) Å is observed in the one-dimensional polymer  $[\text{Ca}(\text{H}_2\text{O})_4(\text{AIP})_2](\text{H}_2\text{O})_n$  containing the 5-aminoisophthalate dianion. Interestingly in the related 1-D Ca(II)

polymer derived from isophthalic acid which exhibits a triple helix structure, Ca $\cdots$ Ca separations of 3.6402(3) and 3.8705(4) Å are reported. These observations indicate that the Ca $\cdots$ Ca distances across the polymeric chain in the coordination polymers are determined by a combination of several factors, which include the electronic and steric requirements of the central metal, the denticity, flexibility, bridging behaviour, H-bonding characteristics of the carboxylate ligand, presence of ancillary ligands etc.

### 3.4 Thermal studies

The temperature for the thermal synthesis of compounds **2** and **3** was chosen based on the thermal characteristics of compound **1**. A comparison of the thermal behaviour of the tetrahydrate **1** and the monohydrate **1a** reveals that the DSC thermograms of **1a** is identical to that of compound **1** above 100 °C when the tetrahydrate **1** emits three moles of water forming the monohydrate (See Supplementary Figures 5 and 6)<sup>§</sup>. Both **1** and **1a** decompose at higher temperatures forming CaO as the final product as evidenced by the observed mass loss and also the featureless infrared spectra of the residues indicating the loss of organics. The DSC thermogram of **2** (Fig. 4) exhibits an endothermic peak at 188 °C, which can be attributed to the removal of N-methylimidazole and exothermic events above 400 °C assignable to the decomposition of the carboxylate ligand resulting in the formation of CaO. This assignment gains more credence as all the compounds **1**, **1a**, **2** and **3** exhibit the first exothermic event at around 410°C. The removal of N-MeIm leads to further decomposition of **2** as evidenced by a steep drop in the TG curve of **2**. A scrutiny of **2** by isothermal weight loss studies at 185°C, revealed a weight loss of 21.67 % corresponding to the loss of one mole of N-MeIm, while further heating to 800 °C resulted in a total mass loss of

88% with 12% residue corresponding to the formation of CaO. However our efforts to prepare the anhydrous compound  $[\text{Ca}(4\text{-nba})_2]$  by heating **2** were not successful. The TG-DSC thermogram of **3** exhibits three thermal events at 198, 415 and 547°C respectively (Fig. 5). The endothermic signal at 198°C can be assigned for the loss of the neutral Im ligand. This process appears to be complex and is not well resolved as evidenced by further drop in the TG curve. The exothermic signals at 415 and 547°C can be attributed to the degradation of the carboxylate moieties leading to the decomposition of **3** to CaO with a residual mass of 12.3%, which is in good agreement with the calculated value. In the absence of associated mass spectral data of the emitted fragments the exact nature of the thermal decomposition taking place above 400°C can not be commented upon for both **2** and **3**. The formation of CaO as the final residue can be unambiguously confirmed by weight loss studies of compounds **2** and **3** in a temperature controlled furnace, as well as their characteristic X-ray powder pattern (See Supplementary Figures 7 and 8)<sup>5</sup>. The diffractograms of the residues are in very good agreement with that of the reported CaO phase in the JCPDS file No. 37-1497.

#### 4. Conclusions

In summary, we have shown that the zero dimensional mononuclear tetraaqua Ca(II) compound **1** can be transformed into the Ca(II) coordination polymer  $[\text{Ca}(\text{N-MeIm})(4\text{-nba})_2]_n$  **2** by heating it in the presence of N-MeIm. The key step in this transformation is the formation of an intermediate monohydrate compound, which undergoes ligand substitution and incorporation of N-donor ligand into the coordination sphere of Ca(II). The use of imidazole instead of N-MeIm in the thermal reaction resulted in the formation of the anhydrous mixed ligand compound  $[\text{Ca}(\text{Im})(4\text{-nba})_2]_n$  **3**.

### **Supplementary Material**

Additional figures related to the crystal structure of **2**, comparative DSC thermograms of compounds **1**, **1a**, **2** and **3**, X-ray powder pattern of the residue of compounds **2** and **3** are available as Supplementary material. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 658462. These can be obtained, free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: +44-(0)1223-336033 or email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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Table 1 Crystal data and structure refinement for [Ca(N-MeIm)(4-nba)<sub>2</sub>]<sub>n</sub> **2**

Empirical formula	C <sub>18</sub> H <sub>14</sub> CaN <sub>4</sub> O <sub>8</sub>	
Formula weight	454.41 g mol <sup>-1</sup>	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	$a = 5.5313(5)$ Å	$\alpha = 113.08(1)^\circ$
	$b = 12.7904(12)$ Å	$\beta = 95.72(1)^\circ$
	$c = 14.9226(15)$ Å	$\gamma = 97.64(1)^\circ$
Volume	950.11(16) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.588 mg/m <sup>3</sup>	
Absorption coefficient	0.388 mm <sup>-1</sup>	
$F(000)$	468	
Crystal size	0.38 × 0.28 × 0.20 mm <sup>3</sup>	
Theta range for data collection	1.50 to 26.0°	
Index ranges	-6 ≤ $h$ ≤ 6, -15 ≤ $k$ ≤ 15, -18 ≤ $l$ ≤ 18	
Reflections collected	9475	
Independent reflections	3696 [ $R(\text{int}) = 0.0205$ ]	
Completeness to theta = 26.0°	99.3 %	
Refinement method	Full-matrix least-squares on $F^2$	
Data/restraints/parameters	3696 / 0 / 285	
Goodness-of-fit on $F^2$	1.057	
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0348$ , $wR2 = 0.0900$	
$R$ indices (all data)	$R1 = 0.0392$ , $wR2 = 0.0929$	
Largest diff. peak and hole	0.338 and -0.235 e.Å <sup>-3</sup>	

Table 2 Selected bond lengths (Å) and bond angles (°) for [Ca(N-MeIm)(4-nba)<sub>2</sub>]<sub>n</sub> **2**

Ca(1)-N(3)	2.5088(14)	Ca(1)-O(5)	2.3074(12)
Ca(1)-O(1)	2.3710(11)	Ca(1)-O(6)	2.2823(12)
Ca(1) <sup>i</sup> -O(1)	2.4507(11)	Ca(1)-Ca(1) <sup>iii</sup>	5.531(1)
Ca(1)-O(2)	2.3292(11)	Ca(1)-Ca(1) <sup>i</sup>	3.8585(7)
O(6)-Ca(1)-O(5)	96.22(5)	O(2)-Ca(1)-O(1) <sup>i</sup>	93.23(4)
O(6)-Ca(1)-O(2)	92.78(4)	O(1)-Ca(1)-O(1) <sup>i</sup>	73.71(4)
O(5)-Ca(1)-O(2)	165.10(4)	O(6)-Ca(1)-N(3)	88.01(5)
O(6)-Ca(1)-O(1)	90.60(4)	O(5)-Ca(1)-N(3)	84.47(5)
O(5)-Ca(1)-O(1)	91.47(4)	O(2)-Ca(1)-N(3)	84.00(4)
O(2)-Ca(1)-O(1)	100.31(4)	O(1)-Ca(1)-N(3)	175.54(4)
O(6)-Ca(1)-O(1) <sup>i</sup>	163.97(4)	O(1) <sup>i</sup> -Ca(1)-N(3)	107.39(4)
O(5)-Ca(1)-O(1) <sup>i</sup>	81.25(4)	O(6)-Ca(1)-Ca(1) <sup>i</sup>	128.09(4)

Symmetry transformations used to generate equivalent atoms: i) -x+1,-y+1,-z+1  
iii) x-1, y, z

Table 3 — Hydrogen-bonding geometry (Å, °) for [Ca(N-MeIm)(4-nba)<sub>2</sub>]<sub>n</sub> **2**

D-H...A	<i>d</i> (D-H)	<i>d</i> (H...A)	<i>D</i> (D...A)	<DHA
C13-H13...O8 <sup>iv</sup>	0.93	2.67	3.456(3)	143
C13-H13...O4 <sup>v</sup>	0.93	2.69	3.586(2)	161
C6-H6...O7 <sup>vi</sup>	0.93	2.63	3.519(2)	160
C4-H4...O3 <sup>v</sup>	0.93	2.62	3.495(2)	157
C18-H18B...O7 <sup>vii</sup>	0.93	2.44	3.378(3)	167

Symmetry codes: iv) -x+1, -y,- z , v) -x, -y+1, -z , vi) -x+1, y+1, -z , vii) x+1, y, z+1

Table 4 Ca...Ca distances across the chain in reported one dimensional (1-D) Ca(II) coordination polymers

Compound	C.N.	Ca...Ca distance (Å)	Reference
[[Ca(H <sub>2</sub> O) <sub>3</sub> (4-fba)](4-fba)] <sub>n</sub>	8	3.612(1)	32
[[Ca(H <sub>2</sub> O) <sub>3</sub> (benz) <sub>2</sub> ]] <sub>n</sub>	8	3.6146(4)	33
[Ca(H <sub>2</sub> O) <sub>4</sub> (1,4-bdc)] <sub>n</sub>	8	3.637(2)	34
[[Ca(H <sub>2</sub> O) <sub>2</sub> (1,3-bdc)] <sub>2.5</sub> .4 H <sub>2</sub> O] <sub>n</sub> *	8,8,9	3.6402(3), 3.8705(4)	21
[[Ca <sub>5</sub> (1,3-bdc) <sub>5</sub> (H <sub>2</sub> O) <sub>9</sub> ].8H <sub>2</sub> O] <sub>n</sub> *	8,8,9	3.659	35
[[Ca(H <sub>2</sub> O)] <sub>2</sub> (L)(μ-H <sub>2</sub> O)] <sub>n</sub>	8	3.71	36
[[Ca(NH <sub>2</sub> -NH-CO <sub>2</sub> ) <sub>2</sub> ].H <sub>2</sub> O] <sub>n</sub>	8	3.70, 3.87	37
[Ca(gly) <sub>2</sub> .H <sub>2</sub> O] <sub>n</sub>	8	3.749	22
[Ca(N-MeIm)(4-nba) <sub>2</sub> ]	6	3.8585(7), 5.531(1)	This work
[Ca(H <sub>2</sub> O)(dnSa)] <sub>n</sub>	7	3.8665(8), 4.1067(5)	38
[Ca(H <sub>2</sub> O) <sub>2</sub> (4-aba) <sub>2</sub> ]] <sub>n</sub>	8	3.9047(5)	39
[Ca(H <sub>2</sub> O)(DMF)(benz) <sub>2</sub> ]] <sub>n</sub>	8	3.956	40
[Ca <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (Oac) <sub>3</sub> (NO <sub>3</sub> )] <sub>n</sub>	8	3.9953(8)	41
[Ca(H <sub>2</sub> O) <sub>2</sub> (3-aba) <sub>2</sub> ]] <sub>n</sub>	8	4.0034(5)	42
[[Ca(H <sub>2</sub> O) <sub>4</sub> ][Ca(L <sup>1</sup> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> .7H <sub>2</sub> O] <sub>n</sub>	7	4.008(1)	43
[Ca(leu) <sub>2</sub> .3H <sub>2</sub> O] <sub>n</sub>	8	4.020	22
[Ca(H <sub>2</sub> O) <sub>2</sub> (4-CNbenz) <sub>2</sub> ]] <sub>n</sub>	8	4.023(15)	20
{Ca(H <sub>2</sub> O)[(O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CO <sub>2</sub> H] <sub>n</sub>	8	4.0290(7)	23
[[Ca(H <sub>2</sub> O) <sub>2</sub> (Nic) <sub>2</sub> ].(H <sub>2</sub> O) <sub>3</sub> ]] <sub>n</sub>	7	4.055	44
[Ca(H <sub>2</sub> O) <sub>2</sub> (C <sub>8</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>2</sub> ]] <sub>n</sub>	8	4.0651(3)	45
[Ca(H <sub>2</sub> O) <sub>2</sub> (2-OPA) <sub>2</sub> ]] <sub>n</sub>	8	4.1022	46
[Ca(H <sub>2</sub> O) <sub>3</sub> (2-aba) <sub>2</sub> ]] <sub>n</sub>	7	4.699(1)	47
[[Ca(Hpdc)(H <sub>2</sub> O) <sub>4</sub> ].H <sub>2</sub> O] <sub>n</sub>	8	4.751(1)	48
[Ca(Sa) <sub>2</sub> (Phen)] <sub>n</sub>	6	4.831(1)	49
[Ca(val) <sub>2</sub> (H <sub>2</sub> O)] <sub>n</sub>	7	6.073	22
[[Ca(PY-Threonato) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub> ]] <sub>n</sub>	8	6.404	50
[[Ca(H <sub>2</sub> O) <sub>4</sub> (Hpdc)].2H <sub>2</sub> O] <sub>n</sub>	7	6.867(2)	48
[Ca(H <sub>2</sub> O) <sub>2</sub> (C <sub>9</sub> H <sub>8</sub> NO <sub>4</sub> ) <sub>2</sub> ].2.5H <sub>2</sub> O] <sub>n</sub>	6	7.669	51

$[\text{Ca}(\text{H}_2\text{O})_3(\text{C}_9\text{H}_{11}\text{N}_6\text{O}_5)_2]_n$	10	7.701	52
$[[\text{Ca}(\text{H}_2\text{O})_4(\text{AIP})_2](\text{H}_2\text{O})]_n$	8	9.816(1)	19

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Abbreviations used: C.N. = coordination number; \* three unique Ca(II) ions; 4-fba = 4-fluorobenzoate; benz = benzoate; 1,4-bdc = 1,4 benzenedicarboxylate; 1,3-bdc = 1,3-benzenedicarboxylate; L = 4-(2-nitrophenyl)-3,6-dioxaoctane dioate; (NH<sub>2</sub>-NH-CO<sub>2</sub>) = hydrazine carboxylate; gly = glycinate; dnSa = 3,5 dinitrosalicylato; 4-aba = 4-amino benzoate; DMF = N,N- dimethylformamide; OAc = acetate; 3-aba = 3-aminobenzoate; L<sup>1</sup> = 2,2',2''-nitriлотriбенzoate; leu =rac-leucinate; 4-CNbenz = 4-cyanobenzoate; (O<sub>2</sub>C)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H = 1,2,4-benzenetricarboxylate; Nic = nicotinate; C<sub>8</sub>H<sub>5</sub>O<sub>3</sub> = 2-formylbenzoate; 2-OPA = 2-oxo-1,2-dihydropyridine-1-acetate; 2-aba = 2-aminobenzoate; Hpdc = 3,5-pyrazoledicarboxylate ; Sa = salicylato; Phen = 1,10-phenanthroline; val =rac-valinate; PY = N-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl); C<sub>9</sub>H<sub>8</sub>NO<sub>4</sub>= 2-(pyridinium-1-yl)butanedioate C<sub>9</sub>H<sub>11</sub>N<sub>6</sub>O<sub>5</sub> = Bis[N-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidine-2-yl) glycyglycinate; AIP = 5-aminoisophthalate;

## Figure Captions

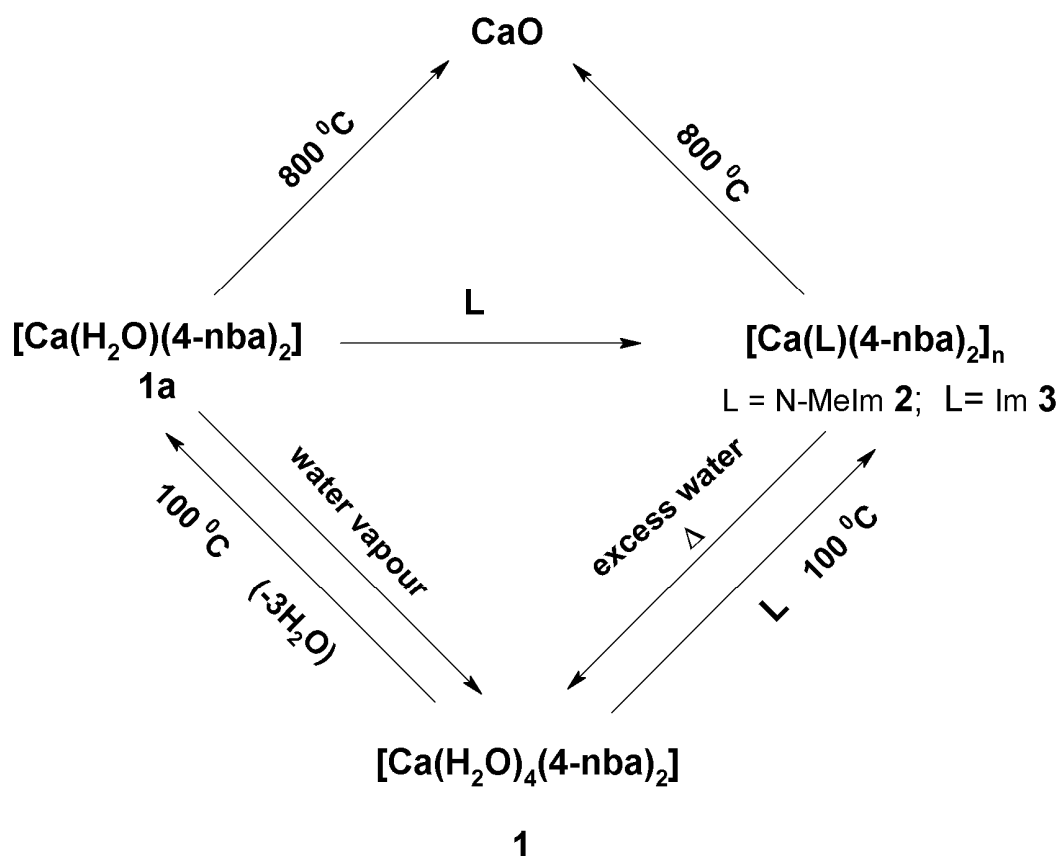
Fig. 1 IR spectra of compound **1**, **1a**, **2** and **3**

Fig. 2. The coordination sphere of Ca(II) in **2** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. (top). The  $\mu_2\text{-}\eta^1\text{:}\eta^1$  (O5,O6) and  $\mu_3\text{-}\eta^2\text{:}\eta^1$  (O1,O1,O2) bridging binding modes of the 4-nitrobenzoate ligands in **2** (bottom). Symmetry code: i)  $-x+1, -y+1, -z+1$  ii)  $-x+2, -y+1, -z+1$  iii)  $x-1, y, z$

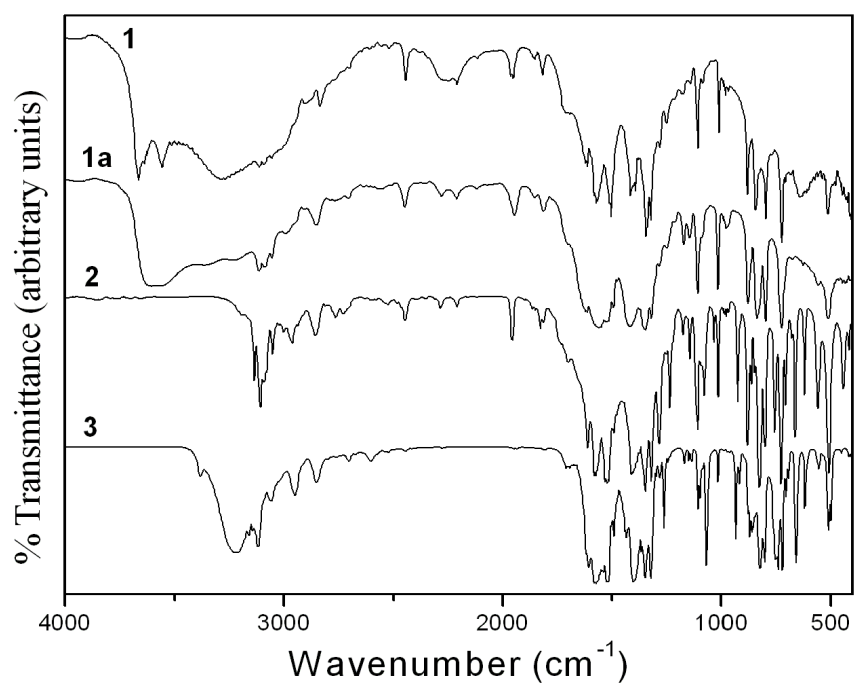
Fig. 3 A view of the bridging bidentate coordination ( $\mu_2\text{-}\eta^1\text{:}\eta^1$ ) of 4-nba through O5 and O6 leading to a one-dimensional polymeric Ca(II) chain extending along *a* with Ca...Ca separation of 5.531(1) Å. The monoatomic bridging mode of O1 in the second 4-nba ligand results in the linking of two infinite chains. In the chains each Ca(II) is bonded to five O atoms and one N atom. For clarity only the carboxylate groups are shown.

Fig. 4 TG-DSC thermogram of compound **2**

Fig. 5 TG-DSC thermogram of compound **3**



Scheme 1

Fig. 1 IR spectra of compound **1**, **1a**, **2** and **3**



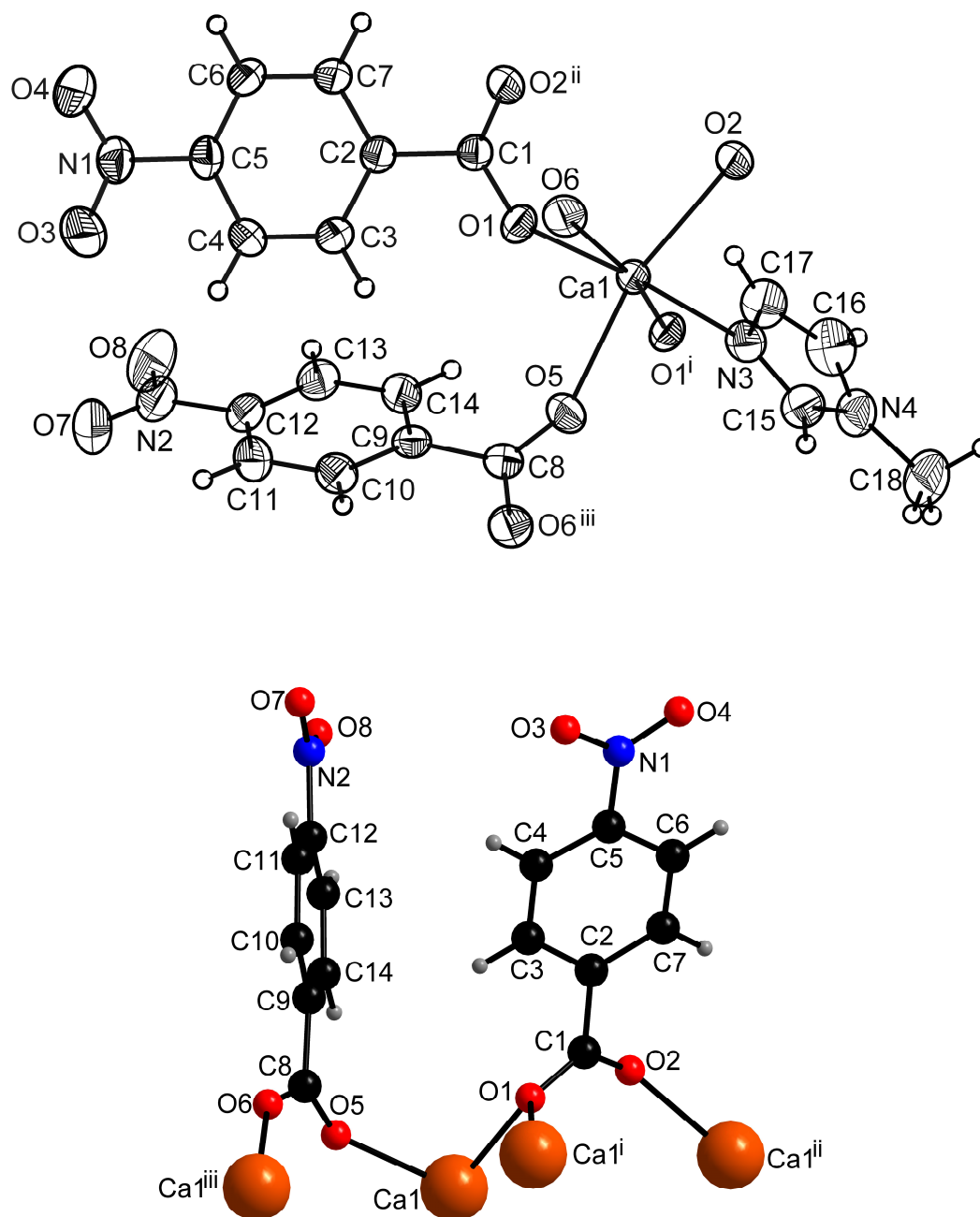


Fig.2. The coordination sphere of Ca(II) in **2** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. (top). The  $\mu_2\text{-}\eta^1\text{:}\eta^1$  (O5,O6) and  $\mu_3\text{-}\eta^2\text{:}\eta^1$  (O1,O1,O2) binding modes of the 4-nitrobenzoate ligands in **2** (bottom). Symmetry code: i)  $-x+1, -y+1, -z+1$  ii)  $-x+2, -y+1, -z+1$  iii)  $x-1, y, z$

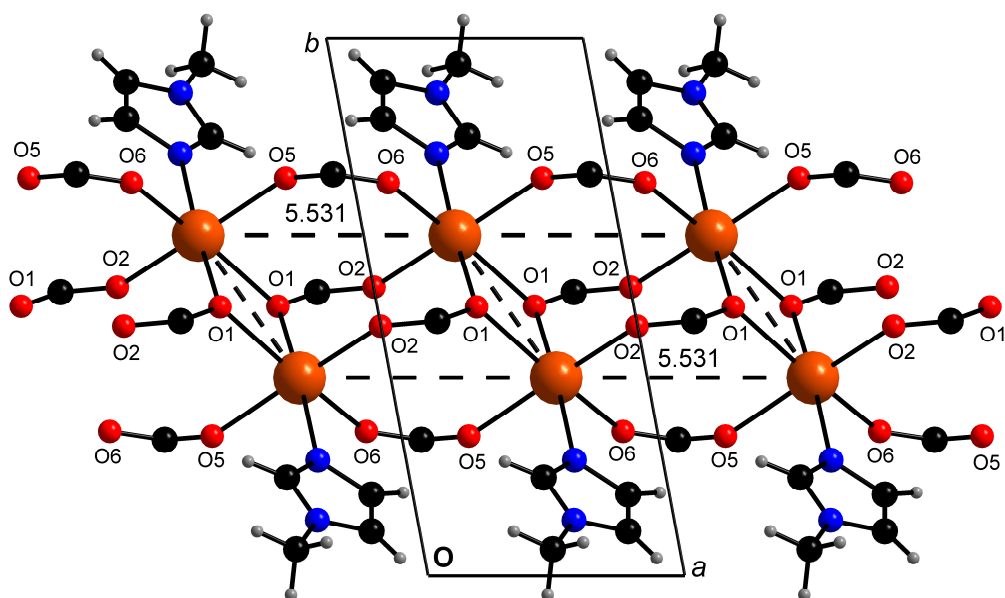


Fig. 3 A view of the bridging bidentate coordination ( $\mu_2\text{-}\eta^1:\eta^1$ ) of 4-nba through O5 and O6 leading to a one-dimensional polymeric Ca(II) chain extending along *a* with Ca $\cdots$ Ca separation of 5.531(1) Å. The monoatomic bridging mode of O1 in the second 4-nba ligand results in the linking of two infinite chains. In the chains each Ca(II) is bonded to five O atoms and one N atom. For clarity only the carboxylate groups are shown.

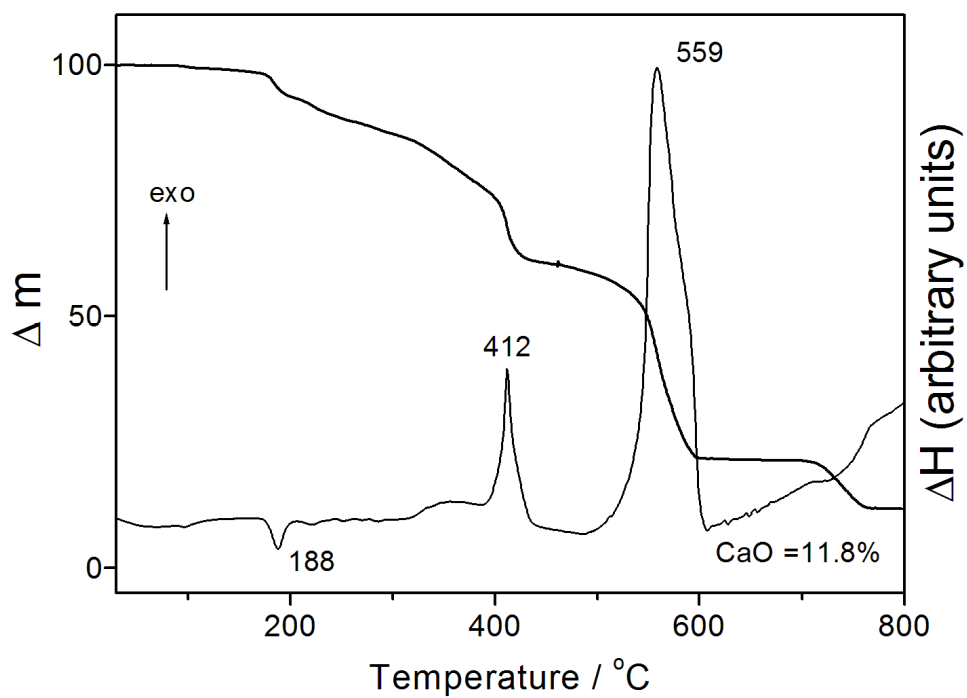


Fig. 4 TG-DSC thermogram of compound 2

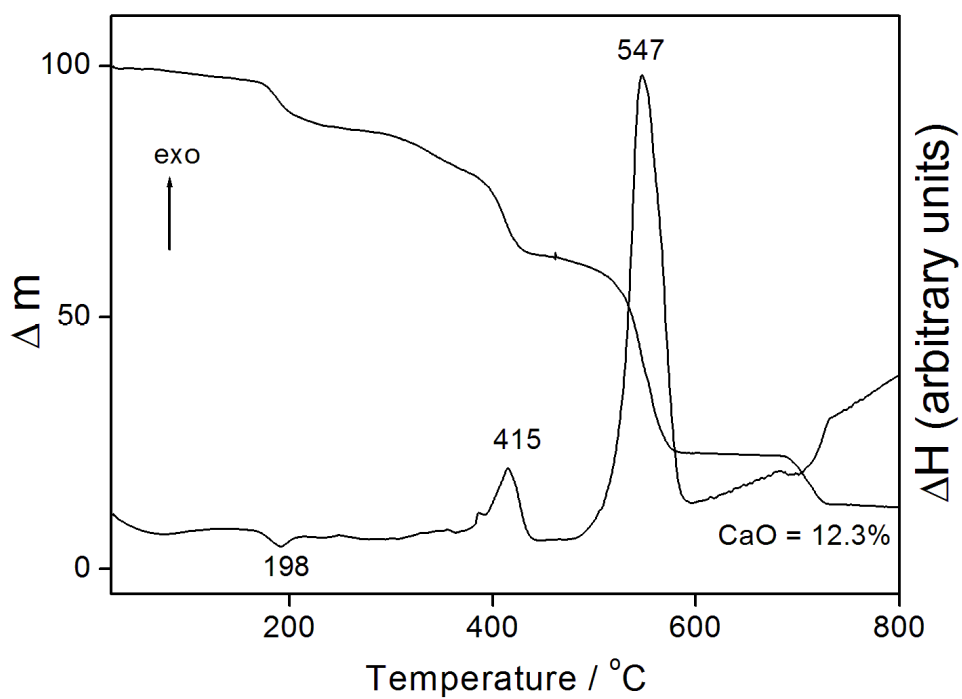


Fig. 5 TG-DSC thermogram of compound 3