

## Synthesis, spectroscopy, thermal and X-structure studies of a seven coordinated hydrated Ca(II)-*para*-nitrobenzoate complex showing mono and bidentate carboxylate ligation<sup>ψ</sup>

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The reaction of  $\text{CaCO}_3$  with 4-nitrobenzoic acid (4-nbaH) results in the formation of a seven coordinated Ca(II) complex  $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$  **1**, (4-nba being 4-nitrobenzoate). The compound has been characterized by elemental analysis, IR and UV-Vis spectra and its structure determined. The complex can be dehydrated to the corresponding anhydrous Ca(II)-bis-4-nitrobenzoate  $\text{Ca}(4\text{-nba})_2$  **2**, and the anhydrous complex thus formed can be rehydrated as evidenced by IR spectra. The structure of **1** exhibits both monodentate and bidentate carboxylate ligation of the 4-nitrobenzoate ligand. The coordination by the O atom from four water molecules completes the heptacoordination around Ca(II). The free O atoms of the monodentate 4-nba and one of the coordinated O atom of the bidentate 4-nba in **1** are linked via H-bonding to one of the coordinated waters of a neighbouring Ca(II) resulting in the formation of pseudo dimers. The dimers thus formed are further linked with the aid of H-bonds, along *a* as well as *b* resulting in the formation of an intricate supramolecular network.

The chemistry of metal-carboxylates is an area of continuing research investigations for several years, in view of the diverse applications of carboxylates, which include their use as reagents in organic synthesis, model compounds in bioinorganic chemistry and precursors for oxide materials<sup>1-5</sup>. An important aspect of the structural chemistry of metal-carboxylates is the versatile ligational behaviour of the carboxylate ligand, which can function as a monodentate, or bidentate or bridging type of ligand<sup>6</sup>. This property, combined with the fact that many metal-carboxylates are hydrated and contain both coordinated as well as crystal water molecules that can participate in H-bonding interactions<sup>7-8</sup>, are useful components for the development of supramolecular assemblies based on carboxylate ligands. Benzene substituted carboxylic acids are suitable reagents for the construction of metal-carboxylate supramolecular assemblies due to their ready availability in pure form. The advantage of using benzene based systems is that donor groups like  $-\text{COOH}$ ,  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{SH}$ , etc. can be anchored onto a rigid six-membered benzene ring and the resulting supramolecular structures will depend on the positioning of the donor

groups on the ring. The donor groups on the six-membered ring can also participate in weak H-bonding interactions in addition to the formation of a metal-ligand bond. Further, the positioning of the different donor moieties with respect to each other on the benzene ring can be changed and this offers the possibility to investigate the effect of the substituent on the structure. In view of this, metal complexes derived from substituted benzene carboxylic acids have been investigated by several research groups, as evidenced by the impressive array of interesting metal-organic supramolecular architectures constructed from these types of ligands<sup>9-14</sup>.

Recent reports on the chemistry of aminobenzoic acids with the biologically relevant alkali-earth metals have shown that these compounds exhibit a rich and variable supramolecular chemistry<sup>15-16</sup>. In contrast, there are very few reports on alkali-earth nitrobenzoate complexes<sup>17</sup>. Although the electron withdrawing nitro group lacks the donor characteristics of the amino functionality, it can participate in H-bonding interactions by forming H-acceptor bonds, which can then lead to novel supramolecular architectures<sup>18,19</sup>. A survey of the reported structures of 4-nitrobenzoate (4-nba) complexes indicates that 4-nba is a versatile ligand

<sup>ψ</sup>Dedicated to Prof. W Weis Weiler

and can function as a monodentate<sup>18-25</sup>, bidentate<sup>26-28</sup> or bridging ligand<sup>29-31</sup>. While some examples of metal carboxylates showing more than one mode of binding are reported<sup>6,32-34</sup>, there is no report of a mononuclear 4-nba compound, which exhibits mono and bidentate carboxylate ligation. Herein, we describe the first example of a 4-nba complex showing this behaviour.

## Materials and Methods

Doubly distilled water was used as the solvent. All the chemicals used were of reagent grade and used as received. The starting materials and reaction products were stable in air and hence prepared under normal laboratory conditions.

IR spectra were recorded on a Shimadzu (IR Prestige-21) FTIR spectrometer in the range 4000-400  $\text{cm}^{-1}$ . The samples for the IR were prepared as KBr diluted pellets 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. Single crystal X-ray diffraction study was performed at the single crystal X-ray facility at School of Chemistry, University of Hyderabad. Isothermal weight loss studies were performed in an electric furnace fitted with a temperature controller. TG-DTA measurements were performed in a Netzsch STA 409 simultaneous thermal analyzer using a heating rate of 4°C/min in flowing air.

### Preparation of $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ **1**

#### Method 1

A mixture of calcium carbonate (1.00 g) and 4-nitrobenzoic acid (4-nbaH) (3.34 g) was taken in water (50 mL) and heated on a steam bath. The insoluble starting materials slowly started dissolving accompanied with brisk effervescence. The heating of the reaction mixture was stopped when there was no more evolution of  $\text{CO}_2$ . At this stage, the reaction mixture was almost clear and the pH was close to neutral. The hot solution was filtered and left undisturbed for 3-4 days. The colourless crystalline blocks that separated were filtered, washed thoroughly with ether and dried *in vacuo*. Yield: 3.109 g (70%). The crystals obtained in this method were suitable for X-ray studies.

#### Method 2

The sodium salt of 4-nba was first generated *in situ* by reacting 4-nbaH (3.34 g, 20 mmol) with  $\text{NaHCO}_3$  (1.68 g, 20 mmol) in water. Into this, an aqueous

solution of anhydrous  $\text{CaCl}_2$  (1.11 g) was added and the reaction mixture was filtered and left aside for crystallization. The crystals that separated after a few days were isolated as above [86% (3.820 g)]. The IR spectrum of the product obtained in this method was identical to that of the spectrum of the product obtained using  $\text{CaCO}_3$  as the Ca source.

Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{CaN}_2\text{O}_{12}$  (444.24): Ca, 9.01; 4-nbaH, 74.32; C, 37.78; H, 63; N, 6.3 Found: C, 37.93; H, 3.58, N, 6.24;. IR (KBr  $\text{cm}^{-1}$ ): 3667(s), 3559(s), 3512-2570(bs), 2442(w), 2247(w), 2208(w), 1954(w), 1815(w), 1620(s), 1572(s), 1504(s), 1416(s), 1391(s), 1344(s), 1321(s), 1281(m), 1248(m), 1169(m), 1140(w), 1107(s), 1011(m), 982(m), 881(s), 845(s), 799(s), 727(s), 683(m), 644(s), 515(s). UV-vis: 274 nm ( $\epsilon = 23775 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ).

### Preparation of $\text{Ca}(4\text{-nba})_2$ **2**

A powdered sample of  $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$  **1** (0.488 g) was heated in a temperature controlled furnace at 250°C for ~20 min. This resulted in the formation of the anhydrous compound **2**. The observed mass loss of 16.4% is in very good agreement with the expected value (16.2%) for the loss of four moles of water. IR (KBr  $\text{cm}^{-1}$ ): 3109(s), 3084(m), 2845(w), 2766(w), 2739(w), 2702(w), 2519(w), 2446(m), 2278(w), 2214(w), 1950(m), 1850(m), 1811(m), 1705(m), 1620(s), 1585(s), 1518(s), 1422(s), 1391(s), 1350(s), 1319(s), 1248(m), 1169(m), 1144(m), 1107(s), 1090(m), 1015(s), 984(w), 968(w), 864(s), 827(s), 802(s), 727(s), 708(s) 627(w), 559(m), 511(s), 440(m).

### Rehydration studies

A powdered sample of **2** (0.451 g) was equilibrated over water in a desiccator. This resulted in the formation of **1** in near quantitative yield in a day. The IR spectrum of the rehydrated product is identical to that of **1**.

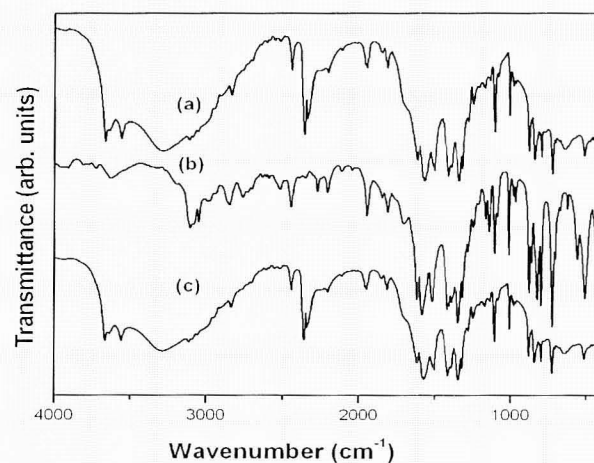
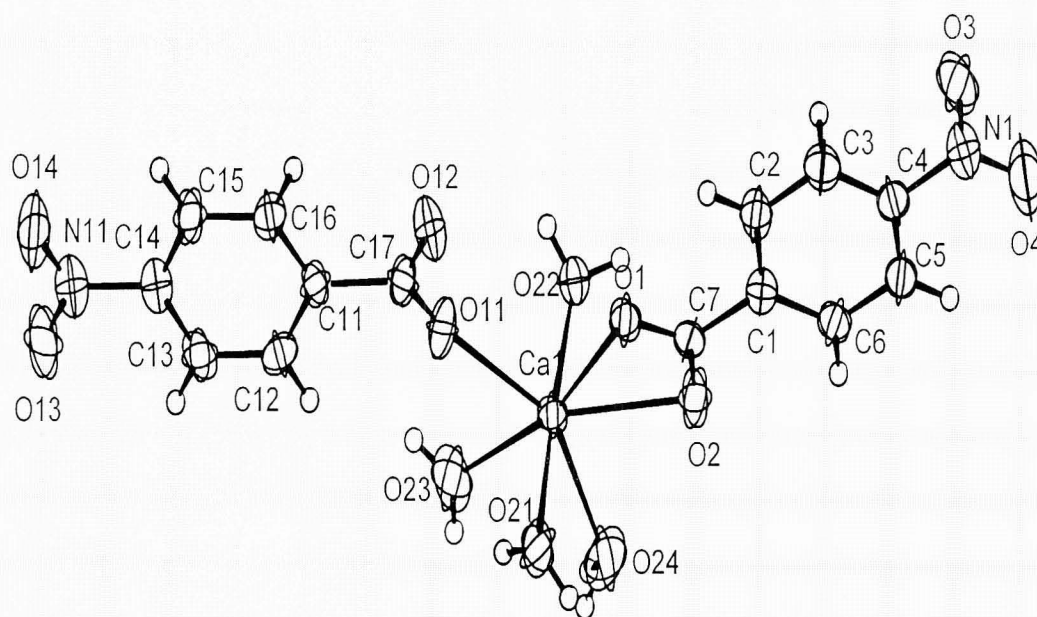
### X-ray crystallography

Intensity data for **1** were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The data integration and reduction were processed with SAINT software<sup>35</sup>. An empirical absorption correction was applied to the collected reflections with SADABS<sup>36</sup>. The structure was solved with direct methods using SHELXS-97<sup>37</sup> and refinement was done against  $F^2$  using SHELXL-97<sup>37</sup>. All non-hydrogen atoms were refined anisotropically.

Table 1 — Crystal data and structure refinement for  $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2] \mathbf{1}$ 

Empirical formula	$\text{C}_{14}\text{H}_{16}\text{CaI}\text{N}_2\text{O}_{12}$
Formula weight	444.24 $\text{g mol}^{-1}$
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	$a = 13.4766(8)$ Å $b = 9.9758(6)$ Å $\beta = 104.9820(10)^\circ$ $c = 14.3936(9)$ Å $\beta = 104.9820(10)^\circ$
Volume	1869.3(2) Å <sup>3</sup>
Z	4
Density (calculated)	1.579 $\text{mg/m}^3$
Absorption coefficient	0.404 $\text{mm}^{-1}$
$F(000)$	920
Crystal size	0.41×0.40×0.40 $\text{mm}^3$
Theta range for data collection	1.56 to 26.01°
Index ranges	$-16 \leq h \leq 16$ , $-12 \leq k \leq 12$ , $-17 \leq l \leq 17$
Reflections collected	18934
Independent reflections	3681 [ $R(\text{int}) = 0.0252$ ]
Completeness to $\theta = 26.01^\circ$	99.9%
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3681/0/263
Goodness-of-fit on $F^2$	1.064
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0351$ , $wR2 = 0.0951$
$R$ indices (all data)	$R1 = 0.0387$ , $wR2 = 0.0978$
Extinction coefficient	0.0111(11)
Largest diff. peak and hole	0.355 and $-0.281 \text{ e.Å}^{-3}$

Aromatic hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms. The H atoms attached to O24 could not be located, while the hydrogen atoms of all the other coordinated water molecules were located in the difference map. The O-H bond lengths were set to ideal values (0.840 Å) and afterwards refined isotropic using a riding model. The technical details of data acquisition and some selected crystal refinement results for **1** are summarized in Table 1.

Fig 1 — IR spectra of: (a)  $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2] \mathbf{1}$ ; (b) **1** heated at 250°C; and (c) rehydrated product.Fig. 2 — The asymmetric unit of **1**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as circles of arbitrary radius.

## Results and Discussion

The aqueous reaction of  $\text{CaCO}_3$  with 4-nbaH resulted in the formation of the seven coordinated  $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$  **1**, which can also be crystallized from an aqueous solution containing  $\text{CaCl}_2$  and sodium 4-nitrobenzoate generated *in situ*. Crystals of **1** were characterized by elemental analysis, IR, UV-Vis spectra, thermogravimetry, weight loss studies and single crystal X-ray structure studies. Treatment of **1** with dil HCl resulted in the formation of the insoluble 4-nbaH. The insoluble 4-nitrobenzoic acid (4-nbaH) obtained on acid treatment of complex **1** was weighed and analyzed as described earlier<sup>17</sup>. The filtrate obtained from this procedure was analyzed titrimetrically for Ca(II) content following a standard procedure. Heating the complex **1** at around 800°C resulted in the formation of the oxide product as evidenced by weight loss. IR spectrum of the residue was featureless indicating complete removal of organic compounds. The formula of the complex **1** was arrived at based on these data.

IR spectrum of **1** exhibits several sharp bands in the mid-infrared region, clearly indicating the presence of the organic moiety. The strong signal in the region 3670-2570  $\text{cm}^{-1}$  centered at 3285  $\text{cm}^{-1}$ , can be assigned to the O-H stretching vibration. The signals for the carboxylate and the nitro functionalities were observed as expected<sup>38</sup>. For the anhydrous complex **2**, no band due to -OH vibration is observed, while the signals due to the organic ligand are seen **2** on exposure to moisture resulted in the formation of **1** and the IR spectrum of the rehydrated product is identical to that of the pristine material (Fig. 1). Complex **1** absorbs strongly at 274 nm in the UV region, which can be assigned to the intramolecular charge transfer transition of the aromatic acid and the observed absorption maximum is comparable to the value observed for other nitrobenzoate complexes<sup>17-19</sup>.

**1** crystallizes in the monoclinic space group  $P2_1/c$  and all atoms are located in general positions. The central metal is seven coordinated and linked to the O atoms of the four water ligands. One carboxylate O atom from a monodentate 4-nba and two carboxylate O atoms from a bidentate 4-nba ligand complete the heptacoordination around Ca(II) (Fig. 2). Interestingly, in the related 4-aminobenzoate (4-aba) complex  $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-aba})_2]$ <sup>15</sup>, the metal is eight coordinated with the 4-aba ligand, and is coordinated in bidentate mode with one of the bidentate O atoms

functioning as a bridge to the next Ca. The Ca-O distances for the bidentate 4-nba ligand at 2.4846(13) and 2.5202(12) Å are nearly equal indicating a symmetric bidentate mode while the Ca-O distance for the monodentate 4-nba is shorter at 2.3418(12) Å. The observed Ca-O (water) scatter in a small range from 2.3162(14) to 2.4323(15) Å and all Ca-O bond distances in **1** are in good agreement with those observed in Ca(II) complexes<sup>39-41</sup>. Selected bond lengths and bond angles are collected in Table 2.

Each molecule of **1** is linked to five other molecules with the aid of O-H...O interactions

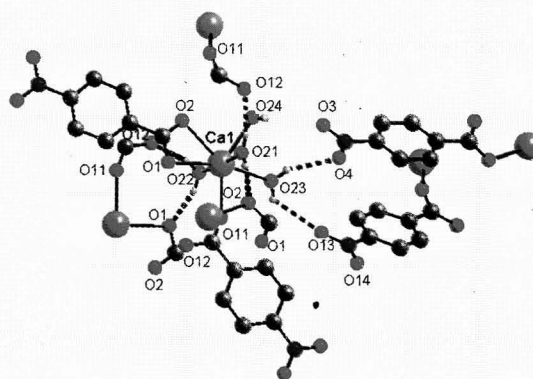


Fig. 3 — H-bonding situation around compound **1** showing the linking of each Ca complex with five other complexes via intermolecular O-H...O interactions. H atoms attached to C are not shown for clarity. Black=C, Pink=H, Blue=N, Orange=O=Brown=Ca

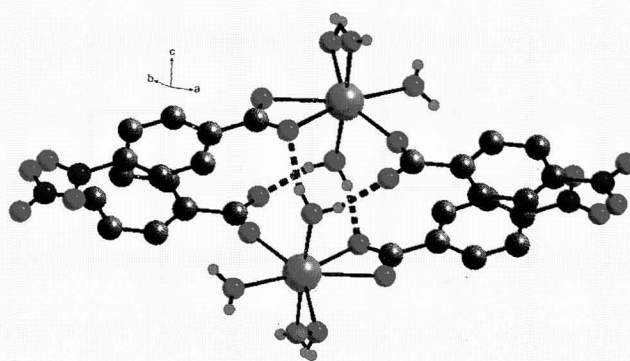


Fig. 4 — Linking of two adjacent molecules of **1** with the aid of O22-H4O...O1, O22-H3O...O12 interactions resulting in the formation of pseudo dimers. Black=C, Pink=H, Blue=N, Orange=O=Brown=Ca

Table 2 — Selected bond distances and bond angles for  $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2] \mathbf{1}$ 

<i>Bond lengths</i>			
Ca(1)-O(21)	2.3162(14)	C(2)-C(3)	1.384(2)
Ca(1)-O(22)	2.3257(12)	C(3)-C(4)	1.373(3)
Ca(1)-O(11)	2.3418(12)	C(4)-C(5)	1.375(3)
Ca(1)-O(23)	2.4130(14)	C(5)-C(6)	1.379(2)
Ca(1)-O(24)	2.4323(15)	O(11)-C(17)	1.247(2)
Ca(1)-O(2)	2.4846(13)	O(12)-C(17)	1.254(2)
Ca(1)-O(1)	2.5202(12)	O(13)-N(11)	1.216(2)
Ca(1)-C(7)	2.8564(16)	O(14)-N(11)	1.223(2)
O(1)-C(7)	1.256(2)	N(11)-C(14)	1.473(2)
O(2)-C(7)	1.249(2)	C(11)-C(12)	1.386(2)
O(3)-N(1)	1.214(2)	C(11)-C(16)	1.389(2)
O(4)-N(1)	1.211(2)	C(11)-C(17)	1.515(2)
N(1)-C(4)	1.472(2)	C(12)-C(13)	1.383(2)
C(1)-C(6)	1.385(2)	C(13)-C(14)	1.375(3)
C(1)-C(2)	1.386(2)	C(14)-C(15)	1.374(2)
C(1)-C(7)	1.508(2)	C(15)-C(16)	1.379(2)
<i>Bond angles</i>			
O(21)-Ca(1)-O(22)	177.09(5)	C(6)-C(1)-C(2)	119.53(15)
O(21)-Ca(1)-O(11)	92.14(5)	C(6)-C(1)-C(7)	120.12(15)
O(22)-Ca(1)-O(11)	89.89(5)	C(2)-C(1)-C(7)	120.34(14)
O(21)-Ca(1)-O(23)	94.80(6)	C(3)-C(2)-C(1)	120.64(16)
O(22)-Ca(1)-O(23)	87.68(6)	C(4)-C(3)-C(2)	117.97(16)
O(11)-Ca(1)-O(23)	76.89(5)	C(3)-C(4)-C(5)	123.00(16)
O(21)-Ca(1)-O(24)	81.27(7)	C(3)-C(4)-N(1)	118.64(16)
O(22)-Ca(1)-O(24)	98.09(7)	C(5)-C(4)-N(1)	118.35(16)
O(11)-Ca(1)-O(24)	147.64(6)	C(4)-C(5)-C(6)	118.19(16)
O(23)-Ca(1)-O(24)	72.19(6)	C(5)-C(6)-C(1)	120.67(16)
O(21)-Ca(1)-O(2)	95.14(5)	O(2)-C(7)-O(1)	121.79(15)
O(22)-Ca(1)-O(2)	81.95(5)	O(2)-C(7)-C(1)	119.55(14)
O(11)-Ca(1)-O(2)	136.46(5)	O(1)-C(7)-C(1)	118.66(14)
O(23)-Ca(1)-O(2)	144.57(5)	O(2)-C(7)-Ca(1)	60.20(8)
O(24)-Ca(1)-O(2)	75.86(5)	O(1)-C(7)-Ca(1)	61.85(8)
O(21)-Ca(1)-O(1)	85.38(5)	C(1)-C(7)-Ca(1)	174.52(11)
O(22)-Ca(1)-O(1)	92.68(4)	C(17)-O(11)-Ca(1)	154.42(12)
O(11)-Ca(1)-O(1)	86.24(4)	O(13)-N(11)-O(14)	123.26(17)
O(23)-Ca(1)-O(1)	163.13(5)	O(13)-N(11)-C(14)	118.37(17)
O(24)-Ca(1)-O(1)	124.33(5)	O(14)-N(11)-C(14)	118.36(16)
O(2)-Ca(1)-O(1)	51.84(4)	C(12)-C(11)-C(16)	119.22(15)
O(21)-Ca(1)-C(7)	91.67(5)	C(12)-C(11)-C(17)	120.91(15)
O(22)-Ca(1)-C(7)	85.65(5)	C(16)-C(11)-C(17)	119.86(14)
O(11)-Ca(1)-C(7)	111.27(5)	C(13)-C(12)-C(11)	120.64(16)
O(23)-Ca(1)-C(7)	169.41(5)	C(14)-C(13)-C(12)	118.31(16)
O(24)-Ca(1)-C(7)	100.62(5)	C(15)-C(14)-C(13)	122.68(16)
O(2)-Ca(1)-C(7)	25.85(4)	C(15)-C(14)-N(11)	118.55(16)
O(1)-Ca(1)-C(7)	26.06(4)	C(13)-C(14)-N(11)	118.76(16)
C(7)-O(1)-Ca(1)	92.09(10)	C(14)-C(15)-C(16)	118.24(16)
C(7)-O(2)-Ca(1)	93.95(10)	C(15)-C(16)-C(11)	120.89(15)
O(4)-N(1)-O(3)	122.40(17)	O(11)-C(17)-O(12)	125.63(15)
O(4)-N(1)-C(4)	118.42(17)	O(11)-C(17)-C(11)	117.74(15)
O(3)-N(1)-C(4)	119.18(16)	O(12)-C(17)-C(11)	116.62(14)

ranging from 1.880 to 2.511 Å (Fig. 3), and all these O...H contacts are shorter than the sum of their van der Waals radii<sup>42</sup>. The geometric parameters of these interactions are summarized in Table 3. A careful analysis of the structure reveals that **1** is involved in H-bonding interactions with three of the four waters

O21, O22 and O23 functioning as H donors while the carboxylate and nitro oxygens function as H-acceptors. The free uncoordinated O atom of the monodentate 4-nba ligand (O12) and one of the coordinated O atom of the bidentate 4-nba (O1) in **1** are linked to the coordinated water O22 of a

Table 3 — Hydrogen-bonding geometry (Å) for [Ca(H<sub>2</sub>O)<sub>4</sub>(4-nba)<sub>2</sub>] **1**

D-H...A	<i>d</i> (D-H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<DHA	Symmetry code
O21-H10...O12	0.840	1.933	2.745	162.29	[-x, y+1/2, -z+1/2]
O21-H20...O2	0.840	1.866	2.680	162.73	[-x, y-1/2, -z+1/2]
O22-H30...O12	0.840	1.880	2.695	163.18	[-x, -y+2, -z]
O22-H40...O1	0.840	1.882	2.700	164.04	[-x, -y+2, -z]
O23-H50...O4	0.840	2.282	3.043	150.80	[x+1, -y+5/2, z+1/2]
O23-H60...O13	0.840	2.511	3.104	128.47	[-x+1, y+1/2, -z+1/2]

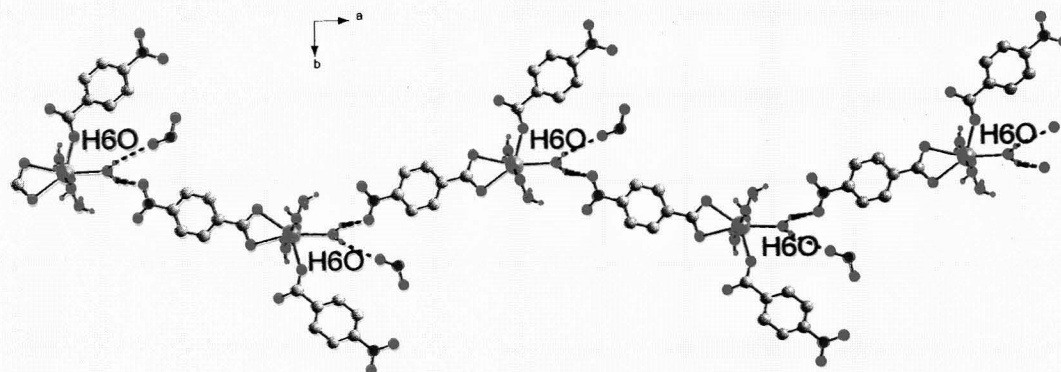
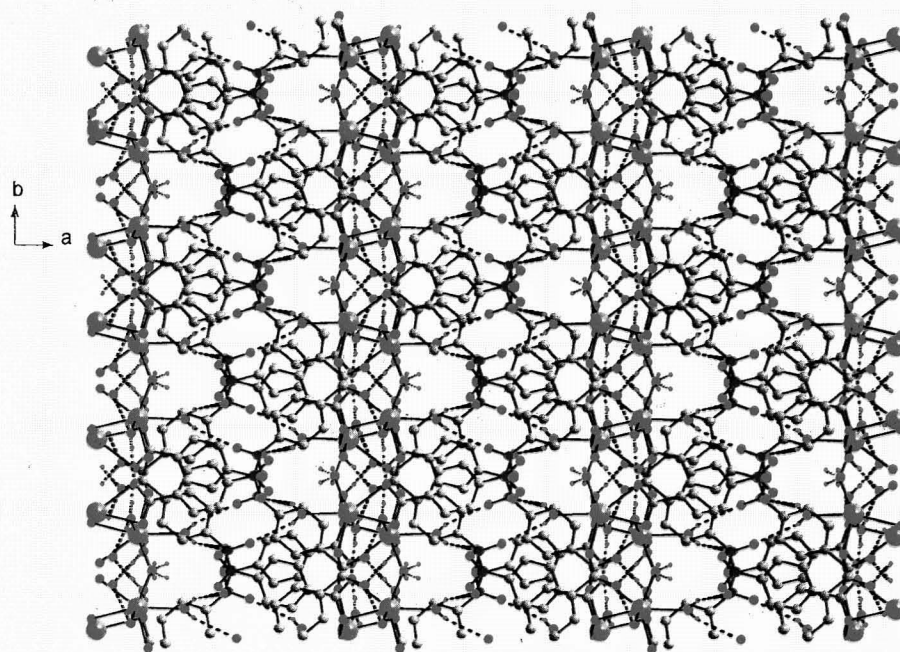


Fig. 5 — Mixed organic-inorganic zigzag H-bonded chain formed by hydrogen acceptors bonds of the nitro group (O23-H50...O4 and O23-H60...O13) with coordinated water (O23). Black=C, Pink=H, Blue=N, Orange=O=Brown=Ca

Fig. 6 — Three-dimensional H-bonded network showing O-H...O interactions in the crystal lattice viewed along *c*-axis. H atoms attached to C are omitted for clarity. Black=C, Pink=H, Blue=N, Orange=O=Brown=Ca

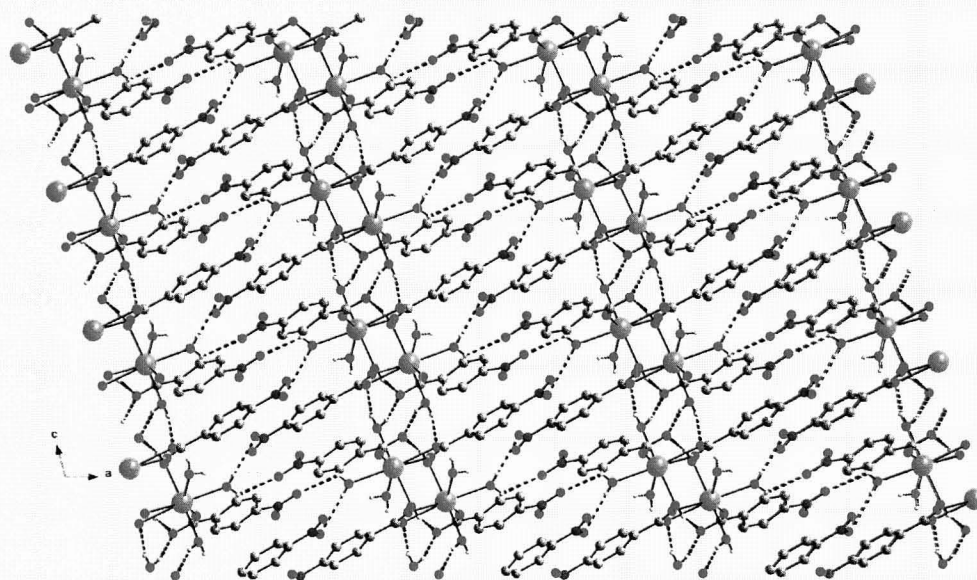


Fig 7 — A view of the extended supramolecular architecture of **1** stabilized by  $\pi$ - $\pi$  stacking interactions along *c*. Black=C, Pink=H, Blue=N, Orange=O=Brown=Ca

neighbouring Ca(II) with the aid of short H-bonds at around 1.88 Å (Fig. 4). The same contacts are observed between the second Ca(II) and the first due to the linking of the carboxylate O atoms with the coordinated water O22 of the first Ca(II) in a head to tail fashion, leading to the formation of H-bonded dimers. The pseudo dimers, thus formed, are further linked along *a* with the aid of H-acceptor bonds formed by the nitro oxygens O4 and O13 in two different complex molecules on either side of **1** with the coordinated water O23 of **1** resulting in the formation of a mixed organic-inorganic zigzag H-bonded chain along *a* (Fig. 5). The H-donor bonds of the third water O21 further extend the network along *b* completing the supramolecular architecture of **1** (Fig. 6). An analysis of the ring interactions reveals that the structure of **1** is further stabilized by  $\pi$ - $\pi$  stacking interactions (Fig. 7). The DTA thermogram of **1** exhibits three signals at 113°C (endo), 266°C (exo) and 427°C(exo) corresponding to removal of three moles of water, phase change and decomposition process, respectively. Based on TG-DTA studies, isothermal weight loss studies were performed in a temperature-controlled oven at various steps in the temperature range 100-260°C. Initially, it was observed that heating the compound at 100°C on a water bath resulted in mass loss corresponding to

three moles of water. The IR spectrum of **1** recorded, after further heating it to 150°C is very similar to that of **1** and the presence of water can be evidenced by the strong O-H signal. However, the profile of this signal is different as compared to **1**. No further mass loss was observed, on heating (~15 min) the complex **1** at several temperatures till 240°C. When **1** was heated at 250°C, a mass loss of 16.4% equivalent to the removal of four moles of water was observed, resulting in the formation of the anhydrous compound [Ca(4-nba)<sub>2</sub>] clearly indicating that the last water molecule is held tightly and its removal requires higher temperature. It is likely that the coordinated water O22, which is involved in the formation of dimers is held strongly and this is probably responsible for the high temperature required for its removal. Equilibration of **2** over water results in the formation of **1** as evidenced by IR spectra. This phenomenon of de- and rehydration has also been observed for hydrated 4-nitro as well as 4-aminobenzoate complexes of Mg(II) in previous work<sup>17-19,43</sup>.

### Conclusions

In the present work, we have described the synthesis, thermal behaviour, de- and rehydration characteristics and supramolecular structure of a

seven-coordinated Ca(II) complex, which exhibits both mono and bidentate carboxylate ligation.

### Supplementary Material

Crystallographic data (excluding structure factors) for the reported structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 615915 (1). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

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### References

- Mehrotra R C & Bohra R, *Metal carboxylates* (Academic Press, London) 1983; Mehrotra R C & Singh A., *Prog Inorg Chem*, 46 (1997) 239.
- Cannon R D & White R P, *Prog Inorg Chem*, 36 (1988) 195.
- Waller B J & Lipscomb J D, *Chem Rev*, 96 (1996) 2625.
- Pfeiffer H, Lima E & Bosch P, *Chem Mater*, 18 (2006) 2642.
- Rane K S & Vernekar V M S, *Bull Mater Sci*, 24 (2001) 39.
- Cotton F A, Wilkinson G, Murillo C A & Bochmann M, *Advanced Inorganic Chemistry* 6<sup>th</sup> Edn (John Wiley & sons, Inc) 1999, 487.
- Desiraju G R & Steiner T, *The Weak Hydrogen Bond in Structural Chemistry & Biology* (Oxford University Press, Oxford) 1999.
- Frontiers in Crystal Engineering*, edited by E R T Tiekink & J J Vittal (John Wiley & Sons Publications, Chichester England) 2006.
- Murugavel R, Baheti K & Anantharaman G, *Inorg Chem*, 40 (2001) 6870; Murugavel R, Krishnamurthy D, Sathiyendiran M, *J Chem Soc, Dalton Trans*, (2002) 34.
- Y Li, Hao N, Lu Y, Wang E, Kang Z Q & Hu C, *Inorg Chem*, 42 (2003) 3119.
- Konar S, Mukherjee P S, Zangrando E, Drew M G B, Diaz C, Ribas J & Chaudhuri N R, *Inorg Chim Acta*, 358 (2005) 29.
- Plater M J, Foreman M R St J, Howie A, Skakle J M S & Slawin A M Z, *Inorg Chim Acta*, 315 (2001) 126.
- Kim J, Chen B, Reineke T M, Li H, Eddaoudi M, Mole D B, O'Keefe M & Yaghi O M, *J Am Chem Soc*, 123 (2001) 8239.
- Reineke T M, Eddaoudi M, O'Keefe M & Yaghi O M, *Angew Chem Int Ed*, 38 (1999) 2590.
- Murugavel R, Karambelkar V V & Anantharaman G, *Indian J Chem*, 39A (2000) 843; Murugavel R & Banerjee S, *Inorg Chem Comm* 6 (2003) 810; Murugavel R, Karambelkar V V, Anantharaman G & Walawalkar M G, *Inorg Chem*, 39 (2000) 1381.
- Wiesbrock F, Schier A & Schmidbaur H, *Z Naturforsch*, 57b (2002) 251.
- Srinivasan B R & Sawant S C, *Thermochim Acta*, 402 (2003) 45.
- Srinivasan B R, Sawant S C & Das S K, *Indian J Chem*, 43A (2004) 1066.
- Srinivasan B R, Sawant J V & Raghavaiah P, *J Chem Sci* (communicated).
- Klinga M, *Cryst Struct Commun*, 10 (1981) 521.
- Hokelek T & Necefoglu H, *Acta Crystallogr*, 54C (1998) 1242.
- Hokelek T, Budak K & Necefoglu H, *Acta Crystallogr*, 53C (1997) 1049.
- Mandal S K & Chakravarty A R, *Indian J Chem*, 29A (1990) 1169.
- Tahir M N, Ulku D, Movsumov E M & Hokelek T, *Acta Crystallogr*, 53C, (1997) 176.
- Xu T G & Xu D J, *Acta Crystallogr*, E60 (2004) m27: m1131; m1462.
- Rodesiler P F, Griffith E A H, Charles N G & Amma E L, *Acta Crystallogr*, 41C (1985) 673.
- Usabaliev B T, Amirasanove I R, Nadzhafov G N, Movsumov E M, Musaev O N & Mamedov Kh S, *Koord Khim*, 7 (1981) 440.
- Nacefoglu H, Clegg W & Scott A J, *Acta Crystallogr*, E57 (2001) m-472.
- Das B K & Chakravarty A R, *Inorg Chem*, 30 (1991) 4978.
- Jaber F, Charbonnier F & Faure R, *Eur J Solid State Inorg Chem*, 32 (1995) 25.
- Tahir M N, Ulku D & Muvsumov E M, *Acta Crystallogr*, 52C (1996) 593.
- Martin J D & Hess R F, *Chem Commun*, (1996) 2419.
- Bernabé A G, Lahuerta P, Ubeda M A, Granda S G & Pertierra P, *Inorg Chim Acta*, 229 (1995) 203.
- Htwe T, Muppidi V K, Pradeep C P, Zacharias P S & Pal S, *J Coord Chem*, 59 (2006) 671.
- Bruker (1999), *SAINT+*, 6.02ed (Bruker AXS Inc., Madison, Wisconsin, USA), 1999.
- Bruker (1997), *SADABS, Empirical Absorption Correction Program* (Bruker AXS Inc., Madison, Wisconsin, USA) 1997.
- Sheldrick G M, *SHELXS-97; SHELXL-97, Programs for Crystal Structural Solution and Refinement* (University of Göttingen, Germany) 1997.
- Silverstein R M, Bassler G C & Morrill T C, *Spectrometric Identification of Organic Compounds*, 5<sup>th</sup> Edn (Wiley, New York) 1991.
- Einspahr H & Bugg C E, *Acta Crystallogr*, B37 (1981) 1044.
- Karipides A, White C & Peiffer K, *Acta Crystallogr*, C48 (1992) 1015.
- Yano S, Numata M, Kato M, Motoo S & Nishimura T, *Acta Crystallogr*, E57 (2001) m488.
- Bondi A, *J Phys Chem*, 68 (1964) 441.
- Srinivasan B R, Sawant S C & Dhuri S N, *Indian J Chem*, 41A (2002) 290.