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## Solid state synthesis and characterization of a triple chain calcium(II) coordination polymer showing two different bridging 4-nitrobenzoate coordination modes

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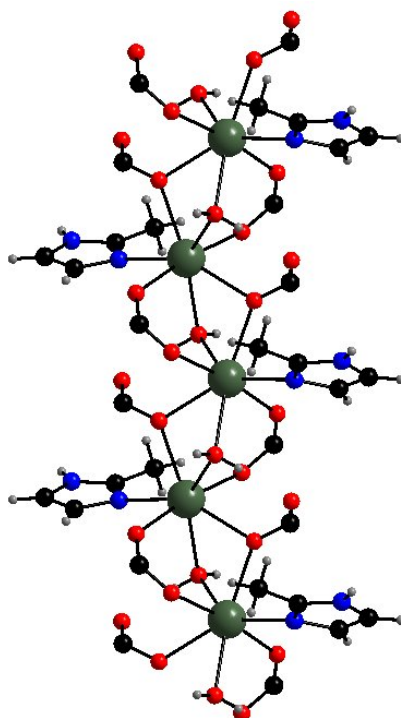
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### Graphical Abstract

In the coordination polymer  $[\text{Ca}(\text{L}^2)(\text{H}_2\text{O})(4\text{-nba})_2]_n$  ( $\text{L}^2 = 2\text{-methylimidazole}$ ;  $4\text{-nba} = 4\text{-nitrobenzoate}$ ) the aqua and the 4-nba ligands exhibit bridging binding modes leading to the formation of a triple chain coordination polymer.



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2 calcium(II) coordination polymer showing two different  
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13  
14 Abstract. The solid state reaction of  $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-nba})(\eta^2\text{-4-nba})]$  1 (4-nba = 4-  
15 nitrobenzoate) with 2-methylimidazole ( $\text{L}^2$ ) at  $100^\circ\text{C}$  results in the formation of a  
16 Ca(II) coordination polymer  $[\text{Ca}(\text{H}_2\text{O})(\text{L}^2)(4\text{-nba})_2]_n$  2. Compound 2 was  
17 characterized by elemental analysis, spectral and thermal methods, and its structure  
18 determined. The coordination polymer 2 crystallizes in the centrosymmetric  
19 monoclinic space group  $\text{P}2_1/\text{n}$  with all atoms situated in general positions and its  
20 structure consists of a central Ca(II), a monodentate 2-methylimidazole, a bridging  
21 water ligand ( $\mu_2\text{-H}_2\text{O}$ ), a bidentate bridging ( $\mu_2\text{-}\eta^1\text{:}\eta^1$ ) 4-nba ligand and a  
22 monoatomic bridging ( $\mu_2\text{-}\eta^2$ ) 4-nba ligand. Each seven-fold coordinated Ca(II) in the  
23 title compound is bonded to a nitrogen atom of a terminal 2-methylimidazole ( $\text{L}^2$ )  
24 ligand, two symmetry related water molecules and four symmetry related 4-nba  
25 ligands, resulting in a distorted pentagonal bipyramidal  $\{\text{CaO}_6\text{N}\}$  polyhedron. Due to  
26 the bridging nature of the aqua and 4-nba ligands  $[(2\text{-methylimidazole})\text{calcium(II)}]$   
27 units in 2 are linked into a one-dimensional coordination polymer consisting of three  
28 chains, all of which propagate along b-axis. In the triple chain coordination polymer a  
29  $\text{Ca}\cdots\text{Ca}$  separation of  $3.8432(3)$  Å is observed between neighbouring Ca(II) ions. The  
30 oxygen atoms of the carboxylate and nitro functionalities of the 4-nba ligand and the

31 coordinated water are involved in O-H $\cdots$ O, N-H $\cdots$ O and C-H $\cdots$ O interactions.A

32 comparative study of nine alkaline-earth 4-nitrobenzoate compounds is described.

33

34 Keywords. 4-nitrobenzoate; 2-methylimidazole; coordination polymer; pentagonal

35 bipyramid; monoatomic bridging; triple chain.

36

## 37 1. Introduction

38

39 In recent years metal-organic frameworks (MOFs) or coordination polymers have  
40 attracted much attention because of their topology and potential applications in  
41 catalysis, adsorption (gas storage), separation, luminescence, magnetism, drug  
42 delivery etc [1-9]. Ligands containing carboxylic acid functional groups are attractive  
43 candidates for the construction of coordination polymers as metals can be linked into  
44 an extended chain with the aid of bridging binding modes of the carboxylate ligand  
45 [10, 11]. Depending on the electronic and steric requirements of the central metal, the  
46 flexibility, binding modes and hydrogen bonding characteristics of the carboxylate  
47 ligand, the presence of additional bridging or terminal ligands, coordination polymers  
48 of differing dimensionalities (D) namely one (1D)-, two (2D)- and three (3D)-  
49 dimensional can be constructed.

50 Compared to the extensive chemistry of coordination polymers based on transition  
51 metals, the coordination chemistry of group 1 and 2 metal compounds with organic  
52 ligands is a relatively less explored area. Recently there is a growing interest in the  
53 chemistry of the coordination compounds of s-block elements as alkali and / or  
54 alkaline-earth metal cations are preferred to transition or lanthanide metal ions  
55 because most of the s-block cations have the advantage of being non-toxic, cheap and  
56 soluble in aqueous media. The recent work of Fromm [12] provides an overview on  
57 different ligand and polymer types of the s-block compounds. In the past decade  
58 several MOFs of alkaline earth metals have been synthesized, structurally  
59 characterized and their properties investigated [13-48].

60 For the preparation of coordination polymers different synthetic methodologies have  
61 been reported. These include the aqueous reaction of basic metal sources like metal  
62 carbonate or hydroxide with the carboxylic acid under ambient conditions [13-26],

63 reaction of aqueous metal chloride or nitrate with the carboxylic acid in the presence  
64 of a mild base [27-41], the hydrothermal reaction of metal sources with carboxylic  
65 acids in autoclaves under autogeneous pressures [42-48]. Based on a review of the  
66 synthetic methods of s-block coordination compounds, it has been noted that  
67 microwave and solid state synthesis are scarce for the preparation of alkaline-earth  
68 metal-organic frameworks unlike the solution or hydrothermal methods of synthesis,  
69 which have been more widely used [12].

70 Recently we reported [49] that the zero-dimensional compound  $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-}$   
71  $\text{nba})(\eta^2\text{-4-nba})]$  (4-nba = 4-nitrobenzoate) 1 can be readily transformed into a one-  
72 dimensional Ca(II) coordination polymer  $[\text{Ca}(\text{L}^1)(4\text{-nba})_2]_n$  by heating it in the  
73 presence of N-methylimidazole ( $\text{L}^1$ ) (Scheme 1) demonstrating that thermal reactions  
74 can be employed as an useful alternative method for the preparation of new  
75 coordination polymers. The loss of coordinated water molecules during the thermal  
76 reaction leads to a reorganization of the coordination sphere around Ca(II) resulting in  
77 the formation of a polymeric chain compound. In the present work, we have  
78 investigated the solid state reaction of compound 1 with 2-methylimidazole ( $\text{L}^2$ )  
79 which is an isomer of  $\text{L}^1$  (Scheme 1). It is interesting to note that the reaction of 1  
80 with  $\text{L}^2$  at 100°C results in the formation of a new mixed ligand one-dimensional  
81 Ca(II) coordination polymer 2 consisting of three chains.

82

## 83 2. Experimental

### 84 2.1. Materials and methods

85 All the chemicals used in this study were of reagent grade and were used as received.

86 The starting materials and reaction products are air stable and hence were prepared

87 under normal laboratory conditions. The compounds  $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-nba})(\eta^2\text{-4-nba})]$

88 1 [50] and  $[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]$  1a [49] were prepared as described earlier. Infrared (IR)  
89 spectra were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the  
90 range  $4000\text{-}400\text{ cm}^{-1}$ . The samples for the IR spectra were diluted with KBr in the  
91 solid state and the signals referenced to polystyrene bands. UV-visible diffuse-  
92 reflectance spectra were obtained using a Shimadzu UV-2450 double beam  
93 spectrophotometer.  $\text{BaSO}_4$  powder was used as reference (100% reflectance).  
94 Absorption data were calculated from the reflectance data using the Kubelka–Munk  
95 function ( $a / S = (1-R)^2 / 2R$  where  $a$  is the absorption coefficient,  $R$  the reflectance  
96 and  $S$  the scattering coefficient).  $^1\text{H}$  NMR spectrum was recorded in  $\text{DMSO-d}_6$  on a  
97 Bruker 400 MHz FT-NMR spectrometer. Luminescence spectra were recorded at RT  
98 using a Perkin-Elmer LS 55 Luminescence spectrophotometer. TG-DSC  
99 measurements were performed in flowing air, in  $\text{Al}_2\text{O}_3$  crucibles on a STA-409PC  
100 simultaneous thermal analyzer from Netzsch. A heating rate of  $10\text{ K min}^{-1}$  was  
101 employed for all measurements. The insoluble 4-nbaH obtained on acid treatment of  
102 the complexes was weighed as described earlier [51] and metal analysis was  
103 performed titrimetrically following a standard procedure. Isothermal weight loss  
104 studies were performed in an electric furnace.

105

## 106 2.2 Preparation of $[\text{Ca}(\text{H}_2\text{O})(\text{L}^2)(4\text{-nba})_2]_n$ 2

107 A powdered sample of compound 1 (0.444 g, 1 mmol) was mixed well with 2-  
108 methylimidazole ( $\text{L}^2$ ) (0.082 g, 1 mmol) and the solid mixture was heated on a steam  
109 bath for ~30 min. The hot reaction mixture was cooled, washed well with ether and  
110 dried in air to obtain compound 2 as a yellow powder in quantitative yield. Crystals  
111 suitable for structure determination were prepared by recrystallizing the powdered  
112 sample from hot water (~10 ml) containing  $\text{L}^2$  (0.246 g, 3 mmol). The crystalline

113 needles of 2 were washed with cold water followed by alcohol and then dried in air.  
114 The infrared spectrum and the DSC thermogram of the crystalline product are  
115 identical with that of the yellow powder. 2 can also be prepared by first heating a  
116 powdered sample of 1 on a steam bath for ~20 min to obtain the monohydrate  
117  $[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]$ . The N-donor ligand ( $\text{L}^2$ ) was mixed with this freshly prepared  
118 monohydrate and left at 100°C for 15 min to obtain 2.

119 Analytical data: Calc. for  $\text{CaC}_{18}\text{H}_{16}\text{N}_4\text{O}_9$  (2): Ca 8.48; 4-nbaH 70.75; CaO 11.87; C  
120 45.76; H 3.41; N 11.86. Found: Ca, 8.45; 4-nbaH, 70.30, CaO, 11.81; C, 45.73; H,  
121 3.63; N, 11.8%.

122 IR data: 3536 ( $\nu_{\text{O-H}}$ ), 3264 ( $\nu_{\text{N-H}}$ ), 3117, 2204, 1944, 1622, 1591, 1570, 1514, 1487,  
123 1412, 1346, 1323, 1280, 1169, 1148, 1103, 1011, 997, 876, 854, 827, 795, 787, 752,  
124 721, 673, 600, 517, 440  $\text{cm}^{-1}$ .

125  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  (in ppm) : 2.25 (s, 3H); 6.83 (d, 2H); 7.14 (d, 2H); 8.14 (q,  
126 2H); 11.52 (s, H)

127 DSC data (in °C): 172 (endo) 410 (exo) 559 (exo)

128 UV-Vis (Diffused reflectance): 251, 330 nm

129

### 130 2.3 X-ray crystal structure determination

131 Intensity data for 2 was collected on a STOE Image Plate Diffraction System using  
132 graphite-monochromated Mo- $K\alpha$  radiation. The structure was solved with direct  
133 methods using SHELXS-97 [52] and refinement was done against F2 using SHELXL-  
134 97 [52]. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens  
135 were introduced at their calculated positions and included in the refinement riding on  
136 their respective parent atoms. The H atoms of the coordinated water molecule were located  
137 in the difference Fourier map and refined with fixed isotropic displacement parameters. The

138 technical details of data acquisition and some selected refinement results are summarized in  
139 [table 1](#).

140

### 141 3. Results and discussion

#### 142 3.1 Synthesis and spectroscopy

143 The solid state reaction of an intimate mixture of the tetraaqua compound  
144  $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$  **1** and 2-methylimidazole ( $\text{L}^2$ ) at  $100^\circ\text{C}$  resulted in the formation  
145 of the mixed ligand Ca(II) compound  $[\text{Ca}(\text{L}^2)(\text{H}_2\text{O})(4\text{-nba})_2]$  **2** in quantitative yield  
146 ([Scheme 2](#)). Compound **2** was formulated based on the elemental analysis and the  
147 mass loss leading to the formation of CaO on pyrolysis. The use of excess  $\text{L}^2$  in the  
148 thermal reaction did not result in the formation of new products containing additional  
149 N-donor ligands. The mixed ligand compound **2** can also be synthesized in a two step  
150 process. The first step involves the synthesis of a monohydrate compound  
151  $[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]$  **1a** by heating **1** at  $100^\circ\text{C}$ . The reaction of  $\text{L}^2$  with **1a** at  $100^\circ\text{C}$   
152 afforded the new compound **2**, which is insoluble in all common solvents like water,  
153  $\text{CH}_3\text{CN}$ ,  $\text{CH}_2\text{Cl}_2$ , DMF etc. The solid is partially soluble in DMSO and this property  
154 was used to study its NMR spectrum, which exhibits the characteristic signals of the  
155 organic moieties 4-nba and  $\text{L}^2$ .

156

157 The thermal reaction of **1** was investigated with other N-donor ligands like pyridine  
158 (pKa 5.1), benzimidazole (pKa 5.4) and 4-picoline (pKa 6.02). However from these  
159 reactions no new product containing N-donor ligand could be obtained. In all these  
160 cases the product obtained consisted of a mixture of  $[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]$  and unreacted  
161 N-donor ligand. The unreacted ligand could be quantitatively recovered by washing  
162 the mixture with ether. The non-incorporation of N-donor ligand can be attributed to



163 the less basic nature of benzimidazole and the pyridine ligands as compared to <sup>1</sup>L  
164 (pKa 7.1) or L<sup>2</sup> (pKa 7.75). The N-donor ligands L<sup>1</sup> and L<sup>2</sup> are isomers and differ in  
165 terms of the positioning of the methyl substituent. The ligand L<sup>2</sup> employed in this  
166 work resulted in the formation of a final product containing a mole of water for each  
167 mole of Ca, unlike imidazole or N-methylimidazole (L<sup>1</sup>) which yielded anhydrous  
168 compounds having molar composition of Ca:4-nba:L<sup>1</sup> 1:2:1 [49]. Crystals of 2  
169 suitable for structure determination were prepared by recrystallising compound 1 from  
170 an aqueous solution containing L<sup>2</sup>. The crystalline nature of 2 (Fig. 1) can be  
171 evidenced from the sharp signals in its powder diffractogram. A comparison of the  
172 powder pattern of the bulk sample with that of the theoretically calculated pattern  
173 from the single crystal data (vide infra) reveals the phase purity of the mixed ligand  
174 product 2. The presence of water in 2 is inferred from the strong signal in its infrared  
175 spectrum at 3536 cm<sup>-1</sup>. The signal at 3264 cm<sup>-1</sup> can be assigned to the N-H (L<sup>2</sup>)  
176 vibration (Supplementary Fig. 1) of the N-donor ligand. It is to be noted that the  
177 profile of the infrared spectra in the region 3500 to 2800 cm<sup>-1</sup> of compound 2 is quite  
178 different as compared to that of the tetraaqua compound 1 or the monohydrate  
179 [Ca(H<sub>2</sub>O)(4-nba)<sub>2</sub>] 1a. Compound 2 exhibits several signals in the mid IR region  
180 indicating the presence of the organic moieties. The strong signals at 1514 and 1346  
181 cm<sup>-1</sup> can be assigned to the asymmetric and symmetric stretching vibrations of the –  
182 NO<sub>2</sub> group of 4-nba while the bands at 1591 and 1570 cm<sup>-1</sup> are assignable to the  
183 asymmetric vibration of the carboxylate group. The signal at 1411 cm<sup>-1</sup> is assigned for  
184 the symmetric vibration of the –COO group. However based only on the infrared  
185 data, the exact nature of the binding of the 4-nba ligand cannot be unambiguously  
186 determined. In view of the insolubility of 2 in all common solvents the diffused  
187 reflectance spectrum was recorded in the UV-Vis region. The observed signals at 251

188 and 330 nm in the spectrum can be attributed to the intraligand charge transfer bands  
 189 of the 4-nba ligand based on a comparison of the reflectance spectra of compounds 2  
 190 and 1 (Fig. 2). The luminescence studies of alkaline-earth metal complexes are of  
 191 considerable importance since the divalent cations Mg and Ca are the most abundant  
 192 in living cells and play vital roles in many cellular processes [1]. Two emission  
 193 maxima are observed at around 450 and 490 nm for compound 2. Interestingly both 4-  
 194 nbaH and  $L^2$  exhibit emission signals around 450 nm. A scrutiny of the emission  
 195 spectra reveals that the emission of the Ca(II) compound 2 is reduced as compared to  
 196 that of the free ligands (Fig. 3) A reduction in the emission intensity has been  
 197 recently reported for the 1D coordination polymer  $[Ca(SA)_2(phen)]_n$  (SA= salicylate;  
 198 phen = 1,10-phenanthroline) [53].

199

### 200 3.2. Crystal structure description of 2

201 Compound 2 crystallizes in the centrosymmetric monoclinic space group  $P2_1/n$  with  
 202 all atoms situated in general positions. The structure reveals that 2 is a coordination  
 203 polymer and can be formulated as  $[Ca(H_2O)(L^2)(4-nba)_2]_n$ . The structure of catena-  
 204 poly[[ $(2\text{-methylimidazole})\text{calcium(II)}(\mu_2\text{-aqua})(\mu_2\text{-}\eta^1:\eta^1\text{-4-nitrobenzoato})(\mu_2\text{-}\eta^2\text{-4-}$   
 205  $\text{nitrobenzoato})$ ] 2 consists of a central Ca(II) ion, a terminal 2-MeIm ligand, a  
 206 bridging aqua ligand and two crystallographically independent bridging 4-nba ligands  
 207 (Fig. 4). In the crystal structure, each Ca(II) is bonded to a nitrogen atom of a terminal  
 208 2-methylimidazole ligand, two oxygen atoms from two symmetry related aqua ligands  
 209 and four oxygen atoms from four symmetry related 4-nba ligands resulting in a  
 210 distorted  $\{CaO_6N\}$  pentagonal bipyramidal polyhedron around Ca (Fig. 4). The  
 211 geometric parameters of the 4-nba anions and 2-MeIm are in the normal range. The  
 212 O-Ca-O and O-Ca-N angles range from  $65.73(3)$  to  $172.63(5)^\circ$ . The Ca-O distances in

213 2 range from 2.3100(11)-2.5654(11) Å (Table 2) and are in agreement with literature  
214 values [49, 50, 53]. A Ca-N bond distance of 2.5024(13) Å is observed. The oxidation  
215 state of the central metal in compound 2 based on the bond valence sum was found to  
216 be 2.139 [54]. The bond valence sum for the precursor calcium compound  
217 [Ca(H<sub>2</sub>O)<sub>4</sub>(4-nba)<sub>2</sub>] 1, the mixed ligand compound [Ca(H<sub>2</sub>O)<sub>3</sub>(Im)(4-nba)<sub>2</sub>].Im and  
218 the 1-D ladder polymer [Ca(L<sup>1</sup>)(4-nba)<sub>2</sub>]<sub>n</sub> are 2.187, 2.27 and 2.177 respectively. It is  
219 interesting to note that the bond valence sums are very close to the expected value of  
220 2 for the bivalent metal and the estimated bond valence sums for the coordination  
221 polymers 2 and [Ca(L<sup>1</sup>)(4-nba)<sub>2</sub>]<sub>n</sub> are slightly less than those observed for the zero-  
222 dimensional calcium compounds.

223

224 The coordinated water (O41) functions as  $\mu_2$ -bridging ligand with the O41 atom  
225 linked to two symmetry related Ca(II) ions resulting in the formation of an infinite  
226 chain extending along b axis (Supplementary Fig. 2). It is interesting to note that both  
227 4-nitrobenzoates in each formula unit are coordinated to the central Ca(II) in different  
228 bridging modes. One of the two unique 4-nba anions in each formula unit is  
229 coordinated to two different Ca(II) ions through one of the carboxylate oxygen atoms  
230 (O1), which functions as a monoatomic bridge ( $\mu_2\text{-}\eta^2$ ) resulting in an extended chain  
231 along b axis (Supplementary Fig. 3). The second independent 4-nba ligand functions  
232 as a bridging bidentate ligand ( $\mu_2\text{-}\eta^1\text{:}\eta^1$ ) and is linked to two symmetry related Ca(II)  
233 ions via O11 and O12 oxygen atoms. An infinite chain extending along b axis is  
234 formed due to this binding mode of 4-nba. Due to the bridging nature of the aqua and  
235 4-nba ligands [(2-methylimidazole)calcium(II)] units in 2 are linked into a one-  
236 dimensional coordination polymer consisting of three chains, all of which propagate  
237 along b-axis (Fig. 5). In the triple chain coordination polymer a Ca $\cdots$ Ca separation of

238 3.8432(3) Å is observed between neighbouring Ca(II) ions. This value is comparable  
239 with the Ca···Ca distance of 3.8585(7) Å reported for the related compound [Ca(L<sup>1</sup>)(4-  
240 nba)<sub>2</sub>]<sub>n</sub> [49] and in several other Ca(II) coordination polymers.

241

242 A scrutiny of the structure reveals that the oxygen atoms of the carboxylate and nitro  
243 functionalities of the 4-nba ligand and the coordinated water are involved in O-H···O,  
244 N-H···O and C-H···O interactions. A total of six H-bonding interactions with H···O  
245 distances ranging from 2.002 – 2.600 Å (Table 3) are observed. These can be  
246 classified as intra- and interchain interactions. The C24-H24A···O11, O41-H41B···O2  
247 and O41-H41B···O1 interactions occur within the triple chain 1-D polymer, while the  
248 N22-H22···O2, O41-H41A···O13 and C5-H5···O3 interactions serve to link adjacent  
249 polymeric chains (Fig. 5).

250

### 251 3.3 Comparative study of alkaline-earth 4-nitrobenzoates

252 The coordination polymer [Ca(H<sub>2</sub>O)(L<sup>2</sup>)(4-nba)<sub>2</sub>]<sub>n</sub> 2 described in this work and the  
253 reported compounds [Ca(H<sub>2</sub>O)<sub>4</sub>(η<sup>1</sup>-4-nba)(η<sup>2</sup>-4-nba)] 1 [50], [Ca(H<sub>2</sub>O)<sub>3</sub>(Im)(η<sup>1</sup>-4-  
254 nba)<sub>2</sub>]·Im [55], and [Ca(L<sup>1</sup>)(4-nba)<sub>2</sub>]<sub>n</sub> [49] constitute a group of Ca(II) compounds  
255 with a 1:2 mole ratio of Ca:4-nba and exhibit different binding modes of the 4-nba  
256 ligand. In addition to these 4-nitrobenzoates of Ca(II), five other 4-nba compounds  
257 containing Mg, Sr and Ba have been structurally characterized [55-58]. The  
258 availability of structural features of several compounds (Table 4) permits a  
259 comparative study of the structural chemistry of alkaline-earth 4-nitrobenzoates, the  
260 details of which are described below. All the structurally characterized alkaline-earth  
261 4-nitrobenzoates listed in Table 4, exhibit a metal:4-nba ratio of 1:2 and crystallize in  
262 centrosymmetric space groups. The nuclearity of the compounds ranges from

263 monomer (5 compounds) to dimer (one compound) and polymer (three compounds).  
264 The coordination number of the central metal varies from 6 to 9, with the Mg(II)  
265 compounds showing hexacoordination. The Sr and Ba compounds exhibit nine  
266 coordination while both hexa and hepta coordination are observed in the Ca(II)  
267 compounds. In addition to functioning as charge balancing anions for the bivalent  
268 metal in all the compounds, 4-nba is bonded to the central metal as a monodentate  
269 ( $\eta^1$ ) or bidentate or ( $\eta^2$ ) or as a bridging ( $\mu$ -) ligand (Scheme 3). In  $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-}$   
270  $\text{nba})_2 \cdot 2\text{H}_2\text{O}$  the 4-nba anions are not coordinated to the central metal, while in  
271  $[\text{Sr}(\text{H}_2\text{O})_7(4\text{-nba})](4\text{-nba}) \cdot 2\text{H}_2\text{O}$  one unique 4-nba remains uncoordinated with the  
272 other 4-nba functioning as a chelating bidentate ligand. The bridging bidentate  
273 binding mode ( $\mu_2\text{-}\eta^1:\eta^1$ ) is observed in the mixed ligand dimeric Mg(II) compound as  
274 well as in the three coordination polymers. The monoatomic bridging binding mode  
275 ( $\mu_2\text{-}\eta^2$ ) and the tridentate bridging coordination modes ( $\mu_3\text{-}\eta^2:\eta^1$ ) are observed in the  
276 Ca(II) coordination polymers. Interestingly in the four different Ca(II)-4-  
277 nitrobenzoates a total of five different coordination modes of the 4-nba ligand are  
278 observed. All the compounds exhibit several H-bonding interactions resulting in  
279 different H-bonded networks.

280

### 281 3.4 Thermal studies

282 The TG-DSC thermogram of compound 2 is depicted in Fig.6. The DSC curve of  
283 compound 2 exhibits three thermal events. The first endothermic process at 172 °C can  
284 be assigned to the loss of a neutral water ligand. The observed mass loss of 10.52% is  
285 much more than the loss expected for the loss of a mole of water. The drop in the TG  
286 curve indicates that the loss of water results in the loss of the neutral N-donor ligand.  
287 The isothermal weight loss studies at this temperature showed a mass loss of 13%

288 which is much more than the loss expected for a mole of water and much less than  
289 loss due to either  $L^2$  or a combination of two neutral ligands in 2. The exothermic  
290 events at 410 and 559 °C correspond to the degradation of the 4-nba ligand as  
291 evidenced by the rapid drop in the TG curve. The assignment of the endothermic  
292 signal at 410 °C for the decomposition of 4-nba gains more credence as a similar  
293 behaviour has been observed for the related Ca(II) compounds 1 and 1a [49]. The TG  
294 curve above 750 °C is parallel to the temperature axis and observed residue of 11.58%  
295 is in very good agreement with the expected value of 11.87% for the formation of  
296 CaO. The formation of CaO as the final residue has been confirmed based on the X-  
297 ray powder pattern of the residue (Supplementary Fig. 4) as well as isothermal weight  
298 loss studies.

299

#### 300 4. Conclusions

301 In summary, we have shown that the zero-dimensional mononuclear tetraaqua Ca(II)  
302 compound 1 can be transformed into a phase pure Ca(II) coordination polymer  
303  $[Ca(H_2O)(L^2)(4-nba)_2]_n$  2 by heating it in the presence of 2-methylimidazole (Im).  
304 The key step in this solid state transformation is the formation of an intermediate  
305 monohydrate compound followed by incorporation of the N-donor ligand into the  
306 coordination sphere of Ca(II) resulting in the formation of a triple stranded  
307 coordination polymer. A comparative study of the structural features of nine 4-  
308 nitrobenzoate compounds of alkaline-earth metals reveals five different binding  
309 modes of the 4-nba ligand all of which are observed in the structurally characterized  
310 compounds  $[Ca(H_2O)_4(4-nba)_2]_n$  1  $[Ca(H_2O)_3(Im)(4-nba)_2]_n$ .Im,  $[Ca(L^1)(4-nba)_2]_n$  and  
311  $[Ca(H_2O)(L^2)(4-nba)_2]_n$  2.

312

313 .

314

315 Appendix A. Supplementary Data

316

317 CCDC 688701 contains the supplementary crystallographic data for the structure

318 reported in this paper. These data can be obtained free of charge via

319 <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge

320 Crystallographic Data Centre 12 Union Road, Cambridge CB2 1EZ, UK. (fax: (+44)

321 1223-336-033 or email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Additional figures related to the

322 crystal structure of 2, comparative infrared spectra compounds 1, 1a and 2 and X-ray

323 powder pattern of residue of compound 2 are available. Supplementary data

324 associated with this article can be found in the online version, at doi:\*\*

325

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484 Table 1 — Crystal data and structure refinement for  $[\text{Ca}(\text{H}_2\text{O})(\text{L}^2)(4\text{-nba})_2]_n \cdot 2$ 

Empirical formula	$\text{C}_{18}\text{H}_{16}\text{CaN}_4\text{O}_9$
Formula weight	472.43 g mol <sup>-1</sup>
Temperature	220(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 15.5486(13)$ Å $\alpha = 90^\circ$ $b = 7.0358(4)$ Å $\beta = 98.789(10)^\circ$ $c = 18.4282(15)$ Å $\gamma = 90^\circ$
Volume	1992.3(3) Å <sup>3</sup>
Z	4
Density (calculated)	1.575 mg/m <sup>3</sup>
Absorption coefficient	0.377 mm <sup>-1</sup>
F(000)	976
Crystal size	0.4 × 0.3 × 0.2 mm <sup>3</sup>
Theta range for data	2.65 to 28.09°
Collection	
Index ranges	-20 ≤ h ≤ 20, -8 ≤ k ≤ 9, -24 ≤ l ≤ 24
Reflections collected	18549
Independent reflections	4768 [R(int) = 0.0334]
Completeness to theta = 28.09°	98.0 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4768 / 0 / 291
Goodness-of-fit on F <sup>2</sup>	1.055
Final R indices [I > 2σ(I)]	R1 = 0.0399, wR2 = 0.1069
R indices (all data)	R1 = 0.0484, wR2 = 0.1123
Extinction coefficient	0.027(3)
Largest diff. peak and hole	0.337 and -0.386 e.Å <sup>-3</sup>

485

486

487 Table 2 Selected bond lengths and bond angle ( $\text{\AA}$ ,  $^\circ$ ) for  $[\text{Ca}(\text{H}_2\text{O})(\text{L}^2)(4\text{-nba})_2]_n \cdot 2$   
 488

Ca(1)-O(11)	2.3100(11)	Ca(1)-O(41)	2.4978(11)
Ca(1)-O(12) <sup>i</sup>	2.3119(11)	Ca(1)-N(21)	2.5024(13)
Ca(1)-O(1) <sup>ii</sup>	2.4205(11)	Ca(1)-O(41) <sup>ii</sup>	2.5654(11)
Ca(1)-O(1)	2.4912(11)	Ca(1)-Ca(1) <sup>ii</sup>	3.8432(3)
O(11)-Ca(1)-O(12) <sup>i</sup>	172.63(5)	O(12) <sup>i</sup> -Ca(1)-N(21)	83.69(5)
O(11)-Ca(1)-O(12) <sup>ii</sup>	87.00(4)	O(1) <sup>ii</sup> -Ca(1)-N(21)	77.74(4)
O(12)-Ca(1)-O(1) <sup>ii</sup>	100.11(4)	O(1)-Ca(1)-N(21)	146.38(4)
O(11)-Ca(1)-O(1)	79.52(4)	O(41)-Ca(1)-N(21)	80.64(4)
O(12) <sup>i</sup> -Ca(1)-O(1)	93.94(4)	O(11)-Ca(1)-O(41) <sup>ii</sup>	95.97(4)
O(1) <sup>ii</sup> -Ca(1)-O(1)	135.28(3)	O(12) <sup>i</sup> -Ca(1)-O(41) <sup>ii</sup>	85.31(4)
O(11)-Ca(1)-O(41)	85.80(4)	O(1) <sup>ii</sup> -Ca(1)-O(41) <sup>ii</sup>	65.73(3)
O(12) <sup>i</sup> -Ca(1)-O(41)	88.42(4)	O(1)-Ca(1)-O(41) <sup>ii</sup>	73.50(4)
O(1) <sup>ii</sup> -Ca(1)-O(41)	155.67(4)	O(41)-Ca(1)-O(41) <sup>ii</sup>	138.19(3)
O(1)-Ca(1)-O(41)	65.76(3)	N(21)-Ca(1)-O(41) <sup>ii</sup>	139.17(4)
O(11)-Ca(1)-N(21)	99.84(5)		

489 Symmetry transformations used to generate equivalent atoms:

490 i)  $-x+1/2, y-1/2, -z+3/2$ ; ii)  $-x+1/2, y+1/2, -z+3/2$

491 Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for  $[\text{Ca}(\text{H}_2\text{O})(\text{L}^2)(4\text{-nba})_2]_n \cdot 2$   
 492

D-H $\cdots$ A	d(D-H)	d(H $\cdots$ A)	D(D $\cdots$ A)	<DHA	Symmetry code
Intrachain interactions					
C24-H24A $\cdots$ O11	0.940	2.411	3.347	162	
O41-H41B $\cdots$ O2	0.820	2.002	2.642	170	$[-x+1/2, y-1/2, -z+3/2]$
O41-H41B $\cdots$ O1	0.820	2.600	3.026	114	$[-x+1/2, y-1/2, -z+3/2]$
Interchain interactions					
N22-H22 $\cdots$ O2	0.870	2.012	2.873	170	$[x-1/2, -y+3/2, z-1/2]$
O41-H41A $\cdots$ O13	0.820	2.160	2.972	171	$[-x+1, -y+1, -z+1]$
C5-H5 $\cdots$ O3	0.940	2.532	3.398	153	$[-x+3/2, y+1/2, -z+3/2]$

493

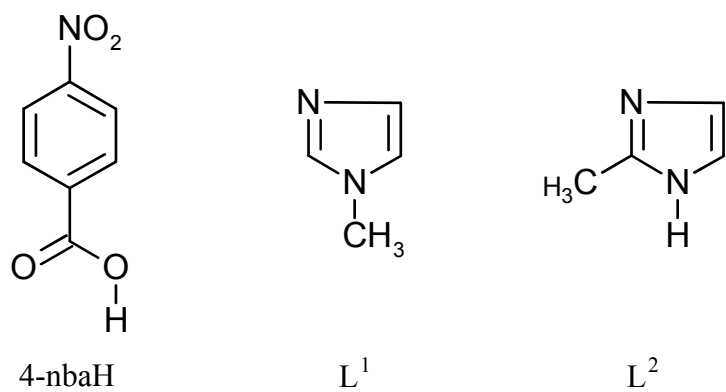
494

495

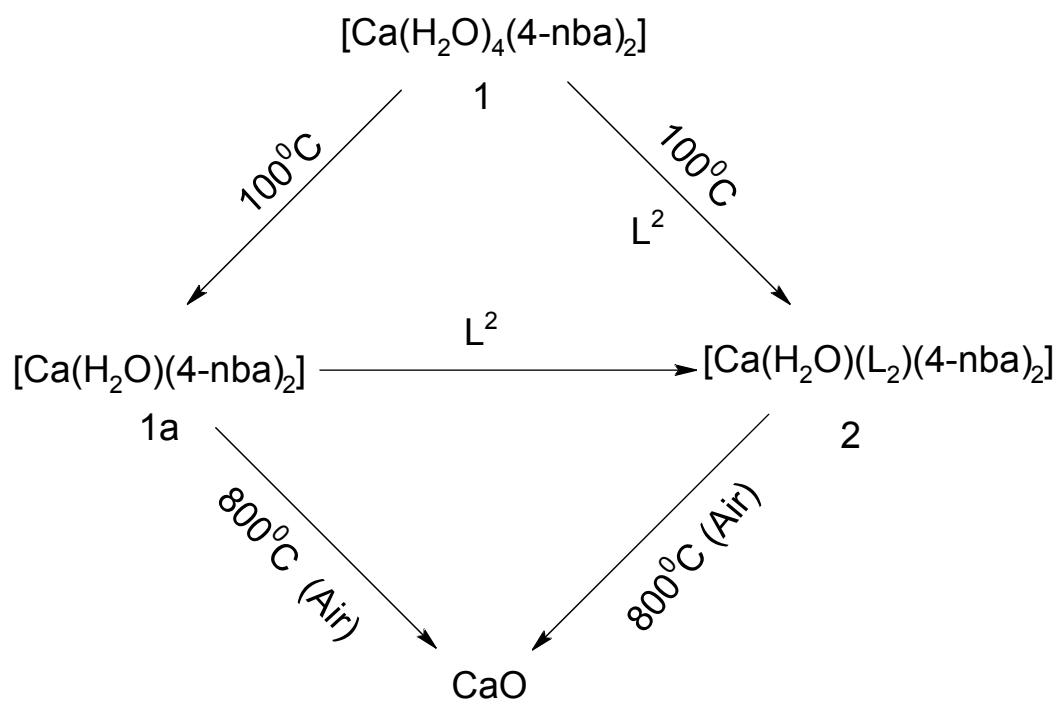
Table 4 Structural features of 4-nitrobenzoates of alkaline-earth metals

Compound	C.N.	Space Group	Nuclearity	Binding mode of 4-nba	H-bonding
[Mg(H <sub>2</sub> O) <sub>6</sub> ](4-nba) <sub>2</sub> .2H <sub>2</sub> O	6	P $\bar{1}$	monomer	Uncoordinated	O-H $\cdots$ O
[Mg(H <sub>2</sub> O) <sub>2</sub> (Im) <sub>2</sub> (4-nba) <sub>2</sub> ]	6	P $\bar{1}$	monomer	$\eta^1$	O-H $\cdots$ O, N-H $\cdots$ O
[Mg(H <sub>2</sub> O)(L <sup>1</sup> ) <sub>2</sub> (4-nba) <sub>2</sub> ] <sub>2</sub>	6	P $\bar{1}$	Dimer	$\eta^1, \mu_2\text{-}\eta^1:\eta^1$	O-H $\cdots$ O
[Ca(H <sub>2</sub> O) <sub>4</sub> (4-nba) <sub>2</sub> ] <sub>n</sub>	7	P2 <sub>1</sub> /c	monomer	$\eta^1, \eta^2$	O-H $\cdots$ O, C-H $\cdots$ O
[Ca(H <sub>2</sub> O) <sub>3</sub> (Im)(4-nba) <sub>2</sub> ].Im	6	P2 <sub>1</sub> /c	monomer	$\eta^1$	O-H $\cdots$ O, N-H $\cdots$ O O-H $\cdots$ N
[Ca(L <sup>1</sup> )(4-nba) <sub>2</sub> ] <sub>n</sub>	6	P $\bar{1}$	Polymer	$\mu_2\text{-}\eta^1:\eta^1, \mu_3\text{-}\eta^2:\eta^1$	C-H $\cdots$ O
[Ca(H <sub>2</sub> O)(L <sup>2</sup> )(4-nba) <sub>2</sub> ] <sub>n</sub>	7	P2 <sub>1</sub> /n	Polymer	$\mu_2\text{-}\eta^1:\eta^1, \mu_2\text{-}\eta^2$	O-H $\cdots$ O, C-H $\cdots$ O N-H $\cdots$ O
[Sr(H <sub>2</sub> O) <sub>7</sub> (4-nba)](4-nba).2H <sub>2</sub> O	9	P2 <sub>1</sub> /c	monomer	$\eta^2$ , uncoordinated	O-H $\cdots$ O, C-H $\cdots$ O
[Ba(H <sub>2</sub> O) <sub>5</sub> (4-nba) <sub>2</sub> ] <sub>n</sub>	9	P2 <sub>1</sub> /c	Polymer	$\eta^2, \mu_2\text{-}\eta^1:\eta^1$	O-H $\cdots$ O, C-H $\cdots$ O

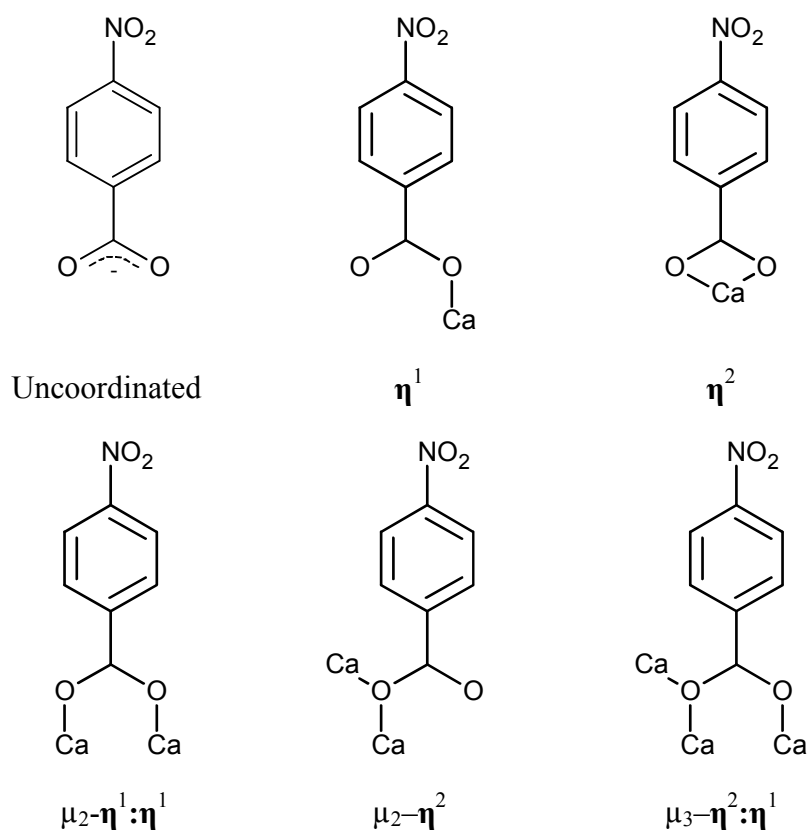
Abbreviations: C.N. = coordination number; 4-nba = 4-nitrobenzoate; Im=imidazole; L<sup>1</sup>=N-methylimidazole  
L<sup>2</sup>=2-methylimidazole



Scheme 1



Scheme 2



Scheme 3. Structurally characterized binding modes of 4-nba ligand in alkaline-earth 4-nitrobenzoates

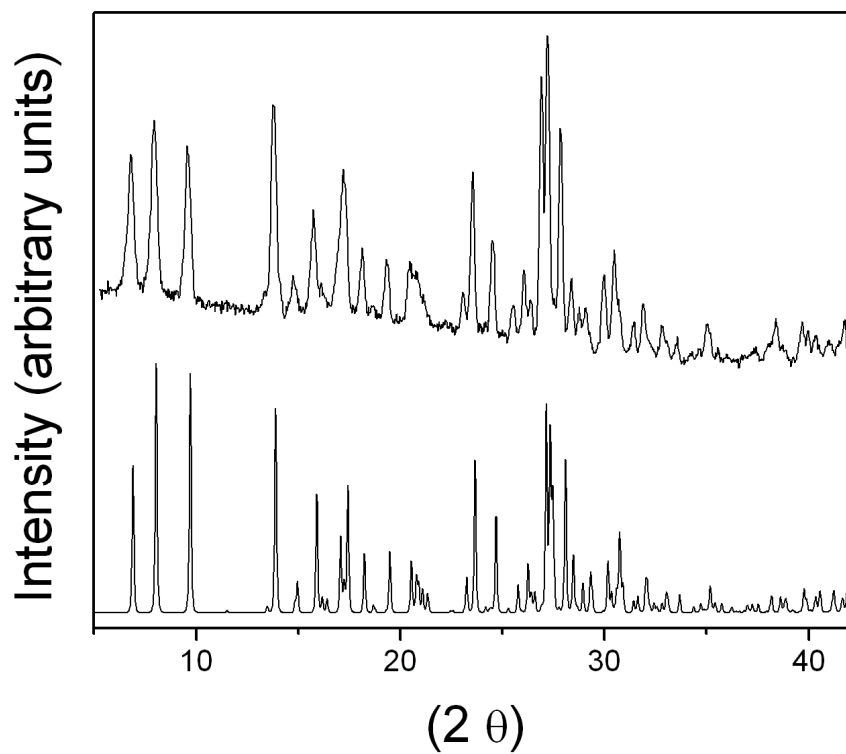


Fig. 1 X-ray powder pattern of a bulk sample of  $[\text{Ca}(\text{H}_2\text{O})(\text{L}^2)(4\text{-nba})_2]_n \cdot 2$  (top); theoretical pattern calculated from single crystal data (bottom).



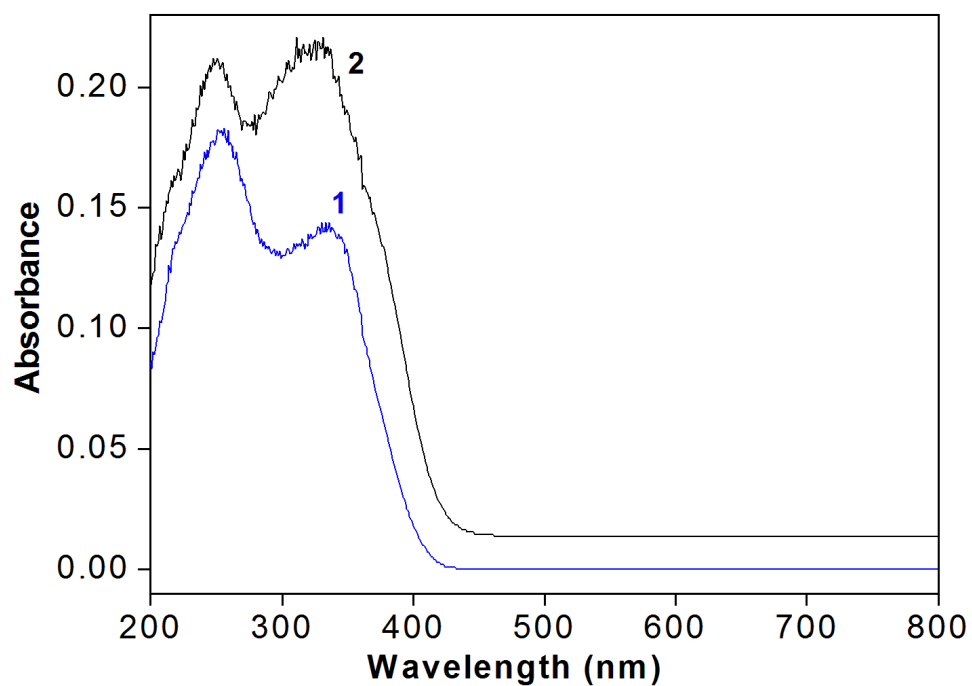


Fig. 2. Diffuse reflectance spectra of 1 and 2.

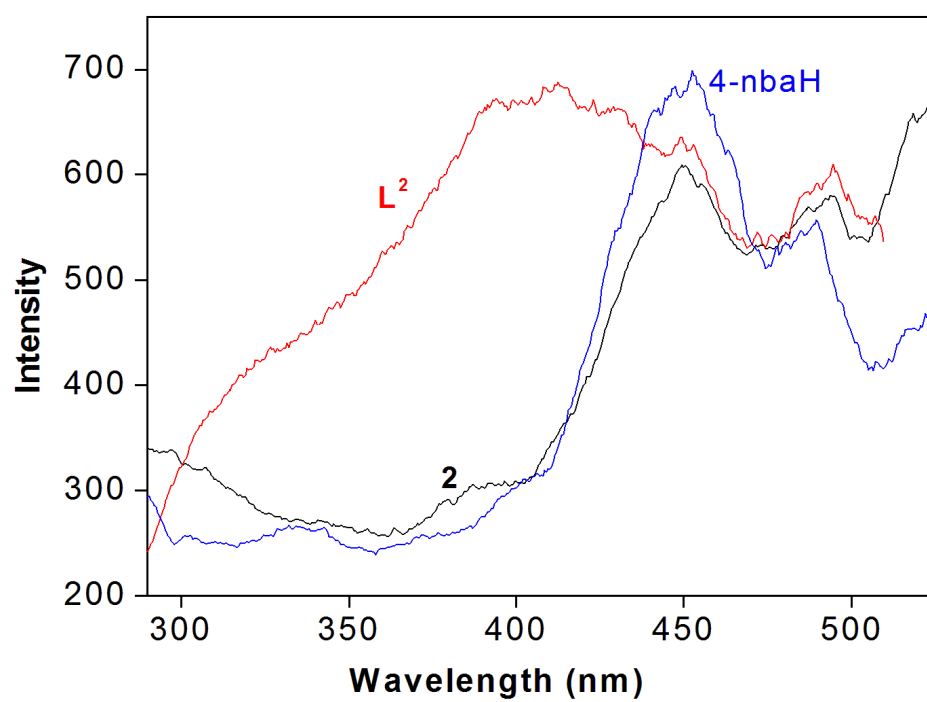


Fig. 3. Luminescence spectra of 2 and free the ligands

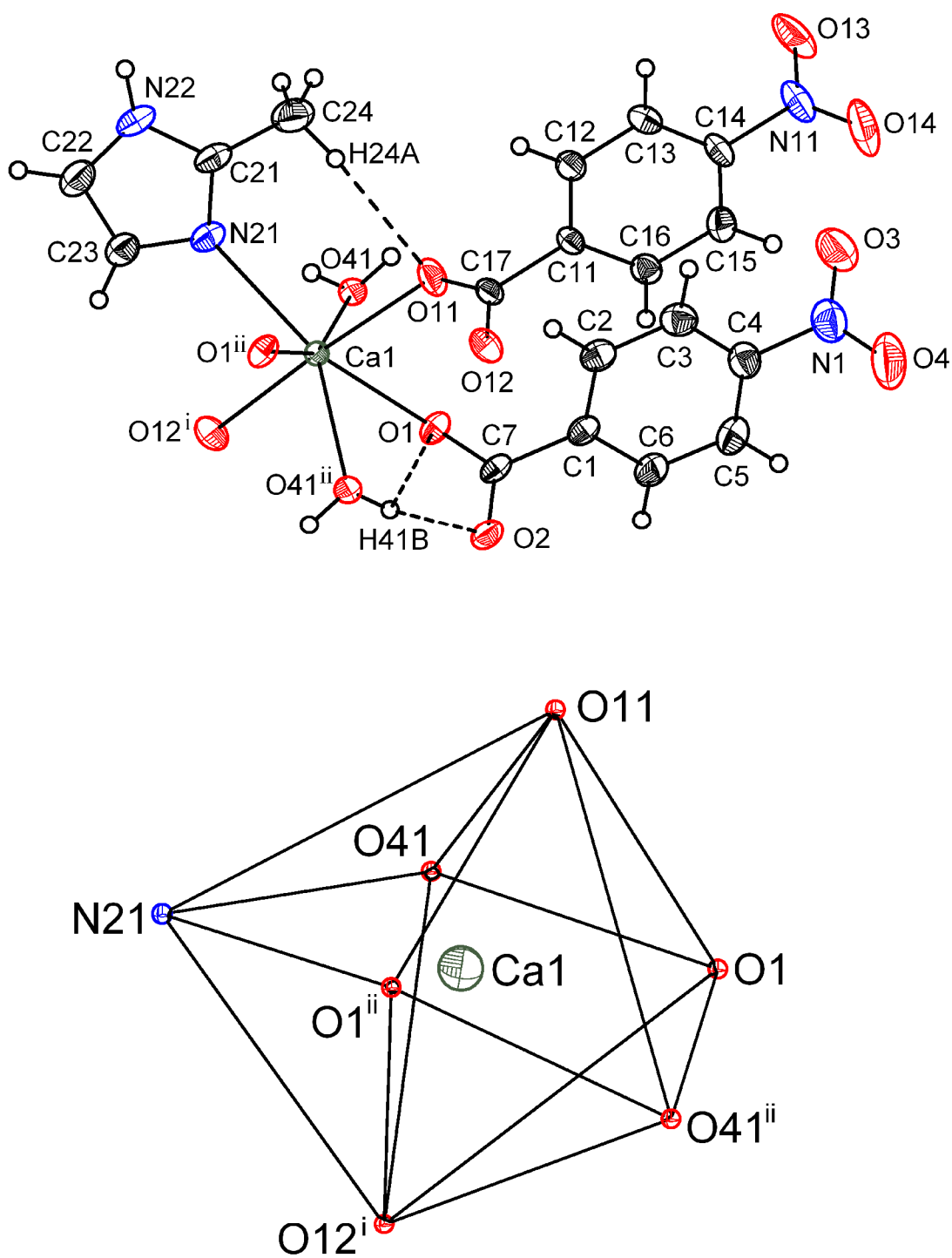


Fig. 4. A view of the coordination sphere of Ca(II) in  $[\text{Ca}(\text{H}_2\text{O})(\text{L}^2)(4\text{-nba})_2]_n \mathbf{2}$ , showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as circles of arbitrary radius (top). Intramolecular H-bonding is shown by the broken lines. The distorted pentagonal bipyramidal coordination polyhedron around Ca(II) in  $\mathbf{2}$  (bottom). Symmetry code: i)  $-x+1/2, y-1/2, -z+3/2$ ; ii)  $-x+1/2, y+1/2, -z+3/2$

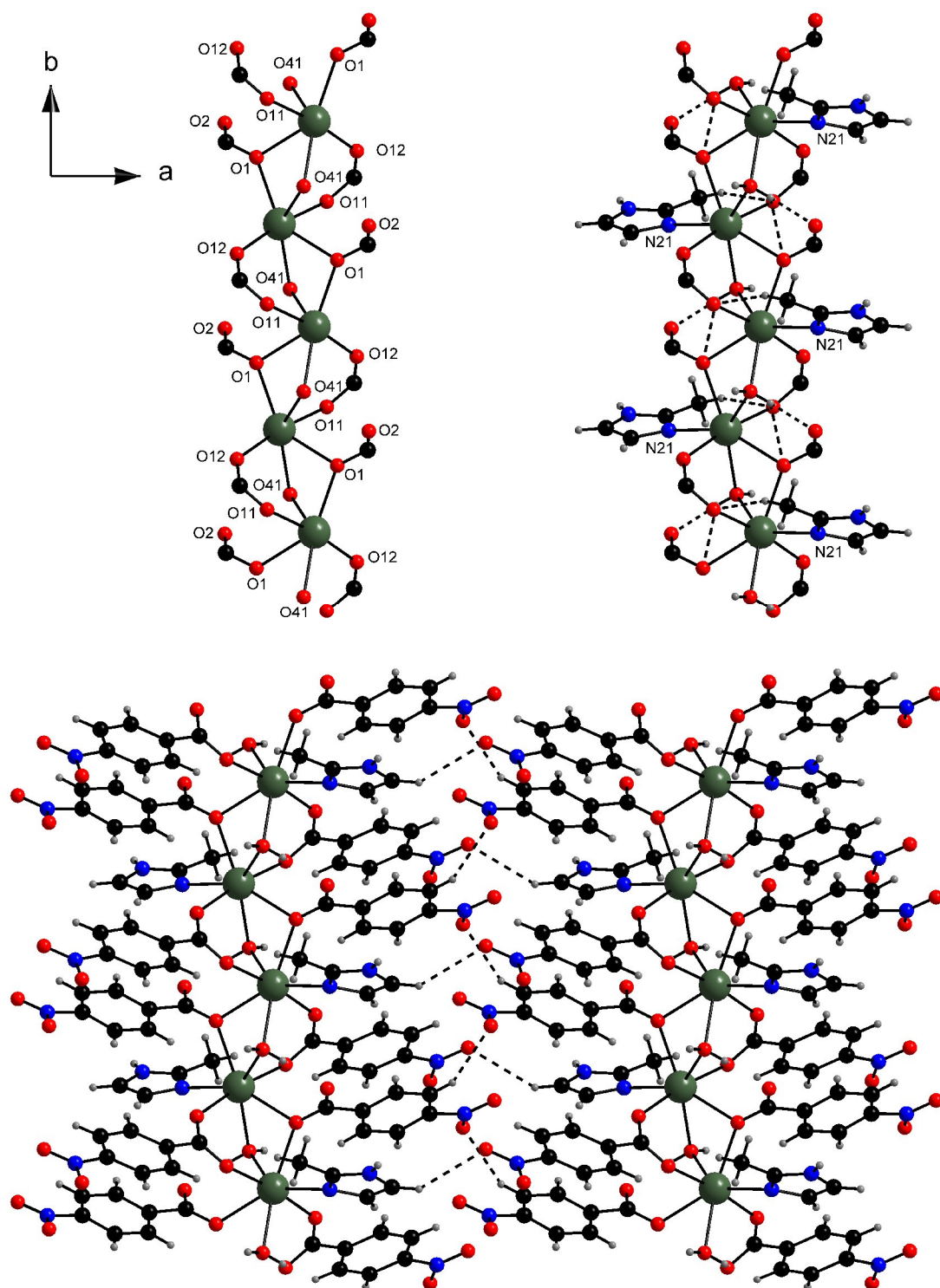


Fig. 5. A part of the triple chain extending along *b* axis due to the bridging binding modes of the aqua (O41) and the crystallographically independent  $\mu_2\text{-}\eta^2$  (O1) and  $\mu_2\text{-}\eta^1\text{:}\eta^1$  (O11, O12) 4-nba ligands in **2**. For clarity, only the -COO groups of 4-nba and the O atom of water are shown (top right). The H-atoms of the bridging water and the terminal  $L^2$  ligand (N21) are included in the triple chain to show the intrachain H-bonding interactions in broken lines (top left). A view along *c* axis is shown for the crystallographic packing of **2**. Two adjacent polymeric chains of **2** in the *ab* crystallographic plane are linked by weak C-H $\cdots$ O bonds shown in broken lines (bottom).