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A calcium(II) coordination polymer based on a tricyclic dicalcium-bis(2-nitrobenzoate) building block

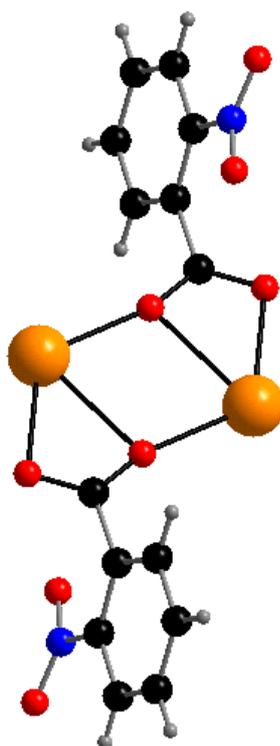
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Graphical Abstract. A pair of $\mu_{-2-\eta^2:\eta^1}$ carboxylate ligands bridge two symmetry related Ca(II) ions leading to the formation of a tricyclic dicalcium-bis(2-nitrobenzoate) unit which constitutes the building block of the coordination polymer.



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12 Abstract. The reaction of CaCO_3 with 2-nitrobenzoic acid (2-nbaH) results in the
13 formation of a coordination polymer $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$ 1 (2-nba = 2-nitrobenzoate),
14 which can be dehydrated to $[\text{Ca}(2\text{-nba})_2]$ 2. Compound 2 can be rehydrated to 1 on
15 exposure to water vapour. Compounds 1 and 2 were characterized by elemental
16 analysis, IR and UV-Vis spectra, TG-DSC thermograms, and the structure of 1 was
17 determined. 1 crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with all
18 atoms situated in general positions. The central Ca(II) is eight coordinated and is
19 linked to two oxygen atoms of two aqua ligands and six oxygen atoms of four
20 different 2-nba ligands resulting in a distorted triangular dodecahedral coordination
21 polyhedron. The crystal structure of 1 consists of a central Ca(II), two terminal aqua
22 ligands and two crystallographically independent 2-nba anions, both of which
23 function as $\mu_2\text{-}\eta^2:\eta^1$ bridging ligands. Each unique 2-nba ligand is linked to a Ca(II)
24 in a bidentate fashion via the carboxylate oxygen atoms and is further linked to a
25 symmetry related Ca(II) via one of the oxygens. A pair of such $\mu_2\text{-}\eta^2:\eta^1$ 2-nba ligands
26 are bridged to two symmetry related Ca(II) ions resulting in the formation of a
27 tricyclic dicalcium-bis(2-nitrobenzoate) moiety, which constitutes the basic building
28 block of the polymer. In the crystal structure of 1 pairs of two crystallographically
29 independent $\mu_2\text{-}\eta^2:\eta^1$ 2-nba ligands link pairs of $\{\text{Ca}(\text{H}_2\text{O})_2\}^{2+}$ units into a 1-D

30 polymeric chain extending along a axis. The oxygen atoms of the coordinated water,
31 and the carboxylate and nitro groups of the 2-nba are involved in O-H \cdots O and C-H \cdots O
32 interactions. The importance of the number of coordinated waters in the structural
33 chemistry of polymeric calcium carboxylates is discussed based on a comparative
34 study of forty six calcium coordination polymers.

35

36 Keywords. coordination polymer; triangular dodecahedron; μ_2 - η^2 : η^1 binding mode;
37 dicalcium-bis(2-nitrobenzoate).

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41 1. Introduction

42 The structural chemistry of the alkaline-earth metals especially calcium is an area of
43 considerable research interest for the past several years in view of the biological
44 relevance [1-3]. The structural features of major interest are the interactions of
45 alkaline-earth metals with O-donor ligands [4] like water, carbonate, sulfate,
46 phosphate and especially carboxylate [5, 6]. In recent years there is a growing interest
47 on the synthesis and structural aspects of alkaline-earth carboxylates in order to
48 comprehend the interactions of alkaline-earths with biologically relevant carboxylic
49 acids [7-12] and also to prepare new lightweight s-block based coordination
50 polymeric materials [13-16]. In view of their ready availability combined with the
51 non-toxic and water soluble nature, the chemistry of the s-block elements is
52 investigated by several researchers. Recent developments in the chemistry of s-block
53 coordination polymers has been reviewed by Fromm [17] and this work describes an
54 overview on different ligand and polymer types of the s-block compounds.

55

56 An analysis of the Cambridge Structural Database (CSD) and Protein Data Bank
57 (PDB) crystal structure databases has been performed by different research groups to
58 identify geometrical features of a general nature that can be useful to understand the
59 structural chemistry of calcium. In a pioneering study of the crystal structures of
60 calcium-carboxylates, Einspahr and Bugg [18] reported that the Ca ion in all calcium-
61 carboxylates lies near the plane of the carboxylate group and usually binds to several
62 carboxylate groups. The most commonly observed number of carboxylates bound to
63 each Ca was three and the carboxylate groups so bound may be crystallographically
64 independent or symmetry related. It was also noted that the carboxylate groups
65 coordinate to more than one Ca ion the most common number being two Ca ions. A

66 very recent study based on the analysis of the crystal structures of 131 Ca-
67 carboxylates has shown that the coordination number of calcium in these compounds
68 ranges from three to ten, with octacoordination being the most favored [19]. Due to
69 the larger ionic radius of 0.99 Å for the divalent Ca, the carboxylate ligand adopts a
70 bridging binding mode resulting in the formation of an extended chain structure in
71 many calcium-carboxylates. This property of the carboxylate ligand can be evidenced
72 by the structural characterization of several calcium based coordination polymers [7-
73 12, 15-47]. The heptacoordinated Ca compound $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-nba})(\eta^2\text{-4-nba})]$ (4-
74 nba is 4-nitrobenzoate) reported by us in an earlier work [48] differs from several
75 polymeric Ca-carboxylates of aromatic acids in that the 4-nba ligand is not involved
76 in bridging coordination. Instead the 4-nba ligand binds to Ca in a monodentate (η^1)
77 and bidentate (η^2) fashion accompanied by several O-H \cdots O interactions involving the
78 oxygen atoms of the nitro and carboxylate moieties of 4-nba and the coordinated
79 water. In view of this, it was of interest to investigate the chemistry of Ca with the
80 other isomeric nitrobenzoic acids to understand the role of the nitro substituent in the
81 structural chemistry of calcium-nitrobenzoates. It is interesting to note that the
82 disposition of the $-\text{NO}_2$ substituent ortho to the $-\text{COOH}$ group in 2-nitrobenzoic acid
83 (2-nbaH) results in the formation of a polymeric compound in which the carboxylate
84 moiety of 2-nba (2-nitrobenzoate) functions as a $\mu_2\text{-}\eta^2\text{:}\eta^1$ bridging ligand. The results
85 of these investigations are described in this paper.

86

87 2. Experimental

88 2.1 Materials and Methods

89

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

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

92 under normal laboratory conditions. Infrared (IR) spectra were recorded on a
93 Shimadzu (IR prestige -21) FT-IR spectrometer in the range 4000-400 cm⁻¹. Samples
94 for IR spectra were diluted with solid KBr and the signals referenced to polystyrene
95 bands. UV-visible diffuse-reflectance spectra were obtained using a Shimadzu UV-
96 2450 double beam spectrophotometer. BaSO₄ powder was used as reference (100%
97 reflectance). Absorption data were calculated from the reflectance data using the
98 Kubelka–Munk function ($a / S = (1-R)^2 / 2R$ where a is the absorption coefficient, R
99 the reflectance and S the scattering coefficient). TG-DSC measurements were
100 performed in Al₂O₃ crucibles on a STA-409PC simultaneous thermal analyzer from
101 Netzsch in flowing air. A heating rate of 10 K min⁻¹ was employed for all
102 measurements. Metal analysis was performed as described earlier [48, 49].
103 Isothermal weight loss studies were performed in an electric furnace fitted with a
104 temperature controller. Single crystal X-ray diffraction study was performed at the
105 National single crystal X-ray facility at School of Chemistry, University of
106 Hyderabad.

107

108 2.2 Preparation of [Ca(H₂O)₂(2-nba)₂] 1

109

110 A mixture of calcium carbonate (1.0 g, 10 mmol) and 2-nitrobenzoic acid (2-nbaH)

111 (3.34 g, 20 mmol) was taken in water (50 ml) and heated on a steam bath. The

112 insoluble CaCO₃ slowly started dissolving accompanied with brisk effervescence. The

113 heating of the reaction mixture was stopped when there was no more evolution of

114 CO₂. At this stage, the reaction mixture was almost clear. The hot pale yellow

115 solution was filtered and left undisturbed for 9-10 days. The colourless crystalline

116 blocks that separated were filtered, washed thoroughly with ether and dried. Yield:

117 3.42 g (84%). The crystals obtained in this method were suitable for X-ray studies. 1

118 can also be prepared starting from CaCl_2 as the Ca source. The sodium salt of 2-nba
119 was first generated in situ by reacting 2-nbaH (1.67 g, 10 mmol) with NaHCO_3 (0.84
120 g, 10 mmol) in water. Into this, an aqueous solution of CaCl_2 (1.11 g, 5 mmol) was
121 added and the reaction mixture was filtered and left aside for crystallization. The
122 crystals that separated after a few days were isolated in 71 % yield. The IR spectrum
123 and the DSC thermogram of the product obtained in this method were identical to that
124 of the product obtained using CaCO_3 as the Ca source.

125 Anal. Calc. for $\text{C}_{14}\text{H}_{12}\text{CaN}_2\text{O}_{10}$ (1): Ca, 9.82; C, 41.18; H, 2.96; N 6.86; CaO 13.71.

126 Found: Ca, 9.80; C, 41.10; H, 2.98; N, 6.58; CaO, 13.70%.

127 IR (in cm^{-1}): 3649, 3591, 3350, 3078, 2864, 2425, 2000, 1967, 1859, 1626, 1568,
128 1526, 1485, 1423, 1350, 1306, 1265, 1144, 1076, 968, 870, 851, 795, 789, 746, 702,
129 650, 430.

130 UV-Vis (in nm): 250, 350

131 DSC (in $^{\circ}\text{C}$): 144 (Endo), 322 (Exo), 354 (Exo), 545 (Exo).

132

133 2.3 Preparation of anhydrous bis(2-nitrobenzoato)calcium(II) 2

134 A powdered sample of 1 (0.325 g) was heated at 150°C for 15 min. This resulted in
135 the formation of the anhydrous compound 2. The observed mass loss of 8.80% is in
136 agreement with the expected value (8.81%) for the loss of two moles of water.

137 Anal. Found (Calcd) for $\text{C}_{14}\text{H}_8\text{CaN}_2\text{O}_8$ (376.34): Ca, 10.5 (10.64); 2-nbaH, 88.15
138 (88.28); C, 44.53 (44.64); H, 2.1 (2.13); N 7.40 (7.44); CaO 13.70 (14.88)

139 IR (in cm^{-1}): 3074, 2866, 1585, 1566, 1524, 1517, 1485, 1415, 1350, 1308, 1265,
140 1153, 1078, 961, 864, 847, 785, 737, 700, 648, 432

141 DSC (in $^{\circ}\text{C}$): 322 (Exo), 354 (Exo), 545 (Exo)

142

143 2.4 Rehydration studies

144 The anhydrous compound 2 was prepared from 1 as mentioned above. Equilibration
145 of a powdered sample of 2 over water vapor resulted in the formation of the starting
146 material 1 in near quantitative yield in about a day. The IR spectrum and the DSC
147 thermogram of the rehydrated compound are identical to that of 1.

148

149 2.5 X-ray crystallography

150 Intensity data for 1 were collected on a Bruker Smart Apex CCD diffractometer using
151 graphite-monochromated Mo-K α radiation. The data integration and reduction were
152 carried out using SAINT [50] software. An empirical absorption correction was
153 applied to the collected reflections with SADABS [50]. The structure was solved with
154 direct methods using SHELXS-97 [51] and refinement was done against F^2 using
155 SHELXL-97 [51]. All non-hydrogen atoms were refined anisotropically. Aromatic
156 hydrogens were introduced on calculated positions and included in the refinement
157 riding on their respective parent atoms. The hydrogen atoms of the coordinated water
158 molecules were located in the difference map but were not stable on subsequent
159 refinements and hence were fixed at calculated positions by using DFIX command
160 and later refined isotropically using a riding model. The technical details of data
161 acquisition and selected crystal refinement results for 1 are summarized in Table 1.

162

163 3. Results and Discussion

164 3.1 Synthesis and spectroscopy

165 During the course of our studies of metal carboxylates [52, 53] we have shown that
166 crystalline hydrates of metal-nitrobenzoates can be conveniently prepared in good
167 yields under ambient conditions by an aqueous reaction of alkali-metal carbonate with

168 4-nbaH or by the reaction of in situ generated sodium salt of 4-nbaH with a metal
169 halide. The generality of these reactions for the synthesis of hydrated metal-
170 carboxylates can be evidenced by the synthesis of 4-nba compounds of alkaline-earths
171 [48-49, 54-56] as well as transition metals [57-59], the synthesis of a polymeric Ba
172 compound [60] containing 2-nba as well as the Ca compound described herein. In the
173 present work, the direct reaction of CaCO_3 with 2-nbaH in water resulted in the
174 formation of a crystalline hydrate 1 containing $\text{Ca}:2\text{-nba}:\text{H}_2\text{O}$ in a 1:2:2 mole ratio.
175 Compound 1 could also be prepared by reacting an aqueous solution of CaCl_2 with in
176 situ generated sodium salt of 2-nbaH. The composition of 1 was arrived at based on
177 elemental analysis and weight loss studies. Compound 1 can be dehydrated to the
178 anhydrous bis(2-nitrobenzoato)calcium(II) 2 by heating at 150°C (Scheme 1). The
179 temperature for the dehydration reaction was chosen based on the thermal property
180 (vide infra) of 1. Equilibration of the anhydrous compound 2 in an atmosphere of
181 water vapor resulted in the regeneration of compound 1. This was confirmed by a
182 comparison of the IR spectrum and the TG-DSC thermogram of the rehydrated
183 product with that of 1. Both 1 and 2 are decomposed to CaO by heating in a furnace at
184 800°C .

185

186 The UV-Visible diffuse reflectance spectrum of compound 1 which absorbs strongly
187 at around 350 nm is very similar to that of the free acid (Fig. 1) and this can be
188 assigned to the intramolecular charge transfer transition of the aromatic 2-
189 nitrobenzoate. In addition 1 also exhibits a signal at around 250 nm unlike the free
190 acid and the diffused reflectance spectrum of the anhydrous compound 2 is very
191 similar to that of 1. An additional signal The IR spectra of 1 and 2 exhibit several
192 sharp bands in the mid-infrared region, clearly indicating the presence of the organic

193 moiety. The strong signals at 3649 and 3591 cm^{-1} in 1 indicates the presence of water
194 and can be assigned to the O-H stretching vibration. The IR spectrum of 2 is devoid
195 of bands above 3074 cm^{-1} , which is indicative of the anhydrous nature of 2. Below
196 3074 cm^{-1} , the IR spectrum is very similar to that of 1. Although the IR spectra 1 and
197 2 exhibit the absorptions due to the vibrations of the carboxylate and nitro groups, no
198 definite conclusions can be drawn on the exact nature of the binding of the 2-nba
199 ligand based only on infrared data.

200

201 3.2 Thermal studies

202 The TG-DSC thermogram of 1 (Fig.2) exhibits an endothermic event at 144 $^{\circ}\text{C}$
203 accompanied by a mass loss of 8.5% assignable for the removal of two molecules of
204 water. Above this temperature, the thermogram exhibits only exothermic processes
205 with signals at 322, 354 and 544 $^{\circ}\text{C}$. The first two closely related exotherms can be
206 attributed to the decomposition of 2-nitrobenzoate. In view of the absence of mass
207 spectral data of the emitted fragments, we do not wish to comment on the exact nature
208 of the decomposition processes at these high temperatures. However it should be
209 noted that the observed mass of 13.7 % for the residue is in good agreement for the
210 formation of CaO. The formation of the oxide phase can also be evidenced by the
211 featureless infrared spectrum of the residue as well as the powder pattern of the
212 residue. The residue on exposure to atmosphere shows an increase in weight
213 corresponding to the formation of calcium carbonate. The results of the isothermal
214 weight loss studies at 150 $^{\circ}\text{C}$ and at 800 $^{\circ}\text{C}$ in a furnace add more credence to the TG-
215 DSC data. The TG-DSC thermogram of the anhydrous compound 2 is devoid of the
216 first endothermic signal observed for the dehydration of 1. A comparison of the TG-
217 DSC thermograms of 1 and 2 (Fig. 2) shows the identical nature of the TG-DSC

218 curves of 2 to that of 1 above 150 °C. The observed residual mass of 14.58 % is in
219 accordance with that for the formation of CaO.

220

221 3.3. Description of crystal structure of 1

222 Compound 1 crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ and all atoms
223 are located in general positions. The crystal structure consists of a Ca(II) ion, two
224 coordinated water molecules and two crystallographically independent 2-nba ligands.
225 The central metal is eight coordinated and is bonded to two O atoms of the two aqua
226 ligands and six oxygen atoms from four symmetry related 2-nba anions resulting in a
227 distorted triangular dodecahedral $\{CaO_8\}$ coordination polyhedron (Fig. 3). The
228 geometric parameters of the 2-nba ligand are in the normal range and are in agreement
229 with reported values [60]. The observed Ca-O bond distances vary between
230 2.3442(13) to 2.6539(15) Å (Table 2) while the O-Ca-O angles range from 77.32(6) to
231 150.25(5)°. These values are comparable with those reported for other Ca(II)-
232 carboxylates [7-12]. The Ca(II) is linked to the O9 and O10 atoms of the water
233 molecules at 2.3918(18) and 2.4121(17) Å respectively.

234

235 The structure of compound 1 is a one-dimensional (1-D) polymer and hence it is
236 formulated as $[Ca(H_2O)_2(2-nba)_2]_n$. Each formula unit of 1 contains a Ca(II)
237 coordinated to two aqua ligands and two unique 2-nitrobenzoate ligands both of
238 which function as bridging ligands. The first unique $\mu_2-\eta^2:\eta^1$ 2-nba ligand (O1, O2)
239 binds to a Ca(II) in a bidentate fashion with Ca1-O1 and Ca-O2 distances of
240 2.4548(15) and 2.6313(15) Å respectively. The O2 oxygen is further linked to a
241 symmetry related Ca(II) at a distance of 2.3498(14) Å resulting in a Ca \cdots Ca
242 separation of 3.9865(8) Å. A pair of such $\mu_2-\eta^2:\eta^1$ 2-nba ligands are linked to two

243 Ca(II) ions resulting in the formation of a tricyclic dicalcium-dicarboxylate unit (Fig.
 244 4) which constitutes the basic building block of the coordination polymer. This
 245 tricyclic unit is formed due to the simultaneous binding of the 2-nba ligand in a
 246 bidentate as well as a monoatomic bridging mode and thus differs from the well-
 247 known eight membered cyclic dimetal-dicarboxylate unit in several dinuclear
 248 carboxylates where the (-COO)⁻ functions as a $\mu_2\text{-}\eta^1\text{:}\eta^1$ bidentate bridging ligand. The
 249 second independent 2-nba ligand (O5, O6) binds to two symmetry related Ca(II) ions
 250 in an identical fashion ($\mu_2\text{-}\eta^2\text{:}\eta^1$ bridging mode) like the first 2-nba (O1,O2) ligand
 251 resulting in a tricyclic dicalcium-dicarboxylate unit with a Ca \cdots Ca separation of
 252 3.9967(9) Å. It is to be noted that the Ca-O bond lengths formed by this ligand are
 253 different. With this ligand a Ca(II) ion is linked to the O5 and O6 oxygen atoms in a
 254 bidentate manner (Ca1-O5 2.4213(14); Ca1-O6 2.3442(13) Å) and the O6 is further
 255 linked to a second Ca(II) ion at 2.6539(15) Å. In the crystal structure of 1 pairs of the
 256 two crystallographically independent $\mu_2\text{-}\eta^2\text{:}\eta^1$ 2-nba ligands link $\{\text{Ca}(\text{H}_2\text{O})_2\}^{2+}$ units
 257 into a 1-D polymeric chain extending along a axis (Fig. 5). In the infinite chain, each
 258 eight coordinated Ca(II) is bonded to two water molecules and further linked to six
 259 oxygen atoms of four different 2-nba anions with alternating pairs of Ca(II) ions in the
 260 chain bridged by a pair of bridging 2-nba ligands resulting in alternating Ca \cdots Ca
 261 separations of 3.9865(8) and 3.9967(9) Å across the chain (Fig. 5). These values are
 262 in very good agreement with Ca \cdots Ca separations of 3.8585(7) and 3.8432(3) Å
 263 reported for the coordination polymers $[\text{Ca}(\text{L}^1)(4\text{-nba})_2]_n$ (L^1 =N-methylimidazole)
 264 [46] and $[\text{Ca}(\text{L}^2)(\text{H}_2\text{O})(4\text{-nba})_2]_n$ (L^2 is 2-methylimidazole) respectively [47].
 265
 266 A scrutiny of the crystal structure of 1 reveals that each eight coordinated Ca(II)
 267 complex in the polymeric chain is H-bonded to six neighboring complexes with the

268 aid of two varieties of H-bonding interactions comprising of three O-H \cdots O hydrogen
269 bonds and three weak C-H \cdots O interactions. All these O \cdots H contacts are shorter than
270 the sum of their van der Waals radii and their geometric parameters are listed in [Table](#)
271 [3](#). The O9-H9 \cdots O1ⁱ and O10-H10B \cdots O5ⁱⁱ (for symmetry code see [Table 3](#))
272 interactions between the coordinated water molecules and the carboxylate oxygen
273 atoms O1 and O5 occur within the 1-D polymeric chain ([Fig. 5](#)) and thus are
274 intrachain interactions. The oxygen atoms of the nitro group function as H-acceptors
275 and this behavior has been observed in several nitrobenzoates [[46](#), [47](#), [52-60](#)]. The
276 nitro oxygen atoms O4 and O7 in one polymeric chain are hydrogen bonded to the
277 H11 and H10A atoms in an adjacent chain via C11-H11 \cdots O4^v and O10-H10A \cdots O7ⁱⁱⁱ
278 and these can be termed as interchain interactions. Likewise the H-bonding between
279 O9 (water) and O1 (carboxylate) with the H atoms of the aromatic ring serve to link
280 parallel chains resulting in a two-dimensional H-bonded network.

281

282 A comparison of the structure of the recently reported polymeric barium compound
283 [[60](#)] of 2-nba namely [Ba(H₂O)₃(2-nba)₂]_n with that of the title Ca compound [1](#)
284 reveals certain similarities and several differences. Both compounds contain alkaline-
285 earth:2-nba in a 1:2 ratio and are 1-D polymers based on dinuclear units. The alkali-
286 earth metals in both compounds are linked to four different carboxylate ligands.
287 However the compounds are differently hydrated and Ba adopts nine coordination. Of
288 the two crystallographically independent 2-nba ligands in the Ba compound, one
289 ligand binds in a $\mu_2\text{-}\eta^2\text{:}\eta^1$ manner as observed in the Ca compound, while the other 2-
290 nba ligand functions as a monoatomic bridge between two adjacent Ba ions in the
291 chain with one of the nitro oxygen atoms bonded to one Ba resulting in a denticity of
292 three for this second 2-nba ligand. This binding of the carboxylate moiety in can be

293 designated as $\mu_2\text{-}\eta^1:\eta^1$. In the 1-D polymeric chain alternating pairs of bivalent metals
294 are bridged by a pair of 2-nba ligands.

295

296 In order to understand the role of the nitro group in the structural chemistry of Ca-
297 nitrobenzoates, a comparison of the structural features of the title Ca compound 1
298 with the related monomeric Ca compound [48] of 4-nba namely $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-nba})$
299 $(\eta^2\text{-4-nba})]$ is made. In the 4-nba compound containing the nitro group para to the –
300 COO^- functionality, the heptacoordinated Ca(II) is linked to two crystallographically
301 independent 4-nba ligands which coordinate in monodentate and bidentate manner
302 respectively. In our original report [48] on the structural aspects of $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-}$
303 $\text{nba})(\eta^2\text{-4-nba})]$ only the $\text{O-H}\cdots\text{O}$ interactions were described but the weak $\text{C-H}\cdots\text{O}$
304 interactions were not mentioned. A reinvestigation of the structure data reveals that
305 one nitro oxygen atom on each unique 4-nba is involved in a $\text{C-H}\cdots\text{O}$ interaction at
306 distances of 2.61 and 2.45 Å accompanied by CHO angles of 158 and 166°
307 respectively. Hence the $-\text{NO}_2$ group in the 4-nba and 2-nba compounds of Ca, which
308 are differently disposed with respect to the carboxylate in the benzene ring are very
309 similar in terms of their secondary interactions. However there is a noticeable
310 difference between 1 and $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-nba})(\eta^2\text{-4-nba})]$ in terms of the number of
311 coordinated waters, which can account for the observed structural variation in these
312 two compounds.

313

314 3.4. Comparative study of Ca(II) coordination polymers

315 In the 4-nba compound $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-nba})(\eta^2\text{-4-nba})]$ each Ca(II) is linked to four
316 oxygen atoms from water and the monodentate and bidentate coordination of 4-nba
317 results in heptacoordination around Ca. In contrast, the tridenticity of the two

318 crystallographically independent bridging 2-nba ligands in **1** leads to eight
319 coordination around Ca in the diaqua compound $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]$ **1**, a feature
320 observed in several calcium carboxylates [19]. The attainment of a higher
321 coordination number appears to be a key feature in Ca structural chemistry, which is
322 made possible by the bridging carboxylate ligand. It is to be noted that when there are
323 less number of coordinated water molecules in a calcium carboxylate the carboxylate
324 ligand tends to adopt a bridging mode of ligation so as to attain a higher coordination
325 number around Ca. The importance of the number of coordinated waters can be
326 evidenced by a comparative study of calcium carboxylates, several of which are listed
327 in Table 4.

328

329 Polymeric Ca-carboxylates of varying dimensionalities, derived from different
330 carboxylic acids are listed in Table 4. In all the compounds, the coordination number
331 of Ca(II) varies from 6 to 10 with eight coordination being observed in the majority
332 of the compounds. It is interesting to note that in all the coordination polymers
333 excepting the three Ca compounds (entry numbers 44 to 46) derived from the
334 dicarboxylic acids Hpdc (3,5-pyrazoledicarboxylate) and AIP (5-aminoisophthalate)
335 the number of coordinated water molecules is three or less and in all such compounds
336 the carboxylate ligand exhibits a bridging coordination mode leading to a polymeric
337 chain. In the helical chain compound $[[\text{Ca}(\text{H}_2\text{O})_4(\text{AIP})_2](\text{H}_2\text{O})]_n$ which has four water
338 molecules, the entire AIP ligand acts as a bridge between two symmetry related Ca(II)
339 ions with each carboxylate showing a bidentate coordination to one Ca(II). In this
340 case, octacoordination around Ca can be achieved without a bridging carboxylate
341 mode of binding. Likewise in $[[\text{Ca}(\text{H}_2\text{O})_4(\text{Hpdc})].2\text{H}_2\text{O}]_n$ the Hpdc ligand functions
342 as a bridge between two Ca(II) ions with each carboxylate group binding in a

343 monodentate fashion to one Ca. Additionally one of the pyrazole N is also ligated in
344 one of the ligands. It is to be noted that both AIP and Hpdc are ditopic ligands as they
345 contain two carboxylate groups anchored on to a ring and the ditopicity is responsible
346 for the polymeric structure, without making use of a bridging carboxylate mode in
347 these compounds. It is interesting to note that in the 1-D polymer
348 $[[\text{Ca}(\text{H}_2\text{O})_4(\text{Hpdc})]\cdot\text{H}_2\text{O}]_n$ synthesized at a more acidic pH, a bridging carboxylate
349 ligation is observed even though the Ca is coordinated to four water molecules. In this
350 case the pyrazole N ligation is not observed. From [Table 4](#) it is very clear that when
351 the number of coordinated water molecules is three or less than three a bridging
352 carboxylate binding mode is always observed. In Ca(II) compounds derived from
353 mono carboxylic acids, for example $[\text{Ca}(\text{H}_2\text{O})_4(\eta^1\text{-4-nba})(\eta^2\text{-4-nba})]$ (entry no. 47 in
354 [Table 4](#)) seven coordination around Ca can be achieved due to the mono and chelating
355 binding modes of the crystallographically independent 4-nba ligands and hence this
356 compound exhibits a zero-dimensional structure. When the number of water ligands
357 in this compound is reduced by heating then 4-nba adopts a bridging binding mode
358 leading to a polymeric structure as has been shown by us in recent reports [[46](#), [47](#)].
359 Another noteworthy feature is the tendency for a majority of the compounds to
360 crystallize in centrosymmetric space groups.

361

362 4. Conclusions

363 In the present work we have described the synthesis, spectral and thermal properties
364 and structural characterization of a new Ca(II) coordination polymer based on a
365 tricyclic dicalcium-dicarboxylate building block. A comparative study of several Ca
366 polymers shows that when the coordinated water molecules are three or less in
367 number in a Ca-carboxylate, the carboxylate ligand adopts a bridging mode of ligation

368 in order to enhance the coordination number around calcium.

369

370 Supplementary Material

371

372 Crystallographic data (excluding structure factors) for the structure reported in this

373 paper have been deposited with the Cambridge Crystallographic Data Centre as

374 supplementary publication no. CCDC 690437. Copies of the data can be obtained,

375 free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK.

376 (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

377

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379

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383

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533

534 Table 1. Technical details of data acquisition and selected refinement results for 1

535

536	Empirical formula	$C_{14}H_{12}CaN_2O_{10}$
537	Formula weight	408.34 g mol ⁻¹
538	Temperature	293(2) K
539	Wavelength	0.71073 Å
540	Crystal system	Triclinic
541	Space group	$P\bar{1}$
542	Unit cell dimensions	$a = 7.7477(10)$ Å $\alpha = 80.851(2)^\circ$
543		$b = 10.1953(13)$ Å $\beta = 82.233(2)^\circ$
544		$c = 11.2808(15)$ Å $\gamma = 89.333(2)^\circ$
545		
546	Volume	871.6(2) Å ³
547	Z	2
548	Density (calculated)	1.556 mg/m ³
549	Absorption coefficient	0.418 mm ⁻¹
550	F(000)	420
551	Crystal size	0.38 x 0.32 x 0.20 mm ³
552	Theta range for data collection	1.85 to 25.93°.
553	Index ranges	$-9 \leq h \leq 9$, $-11 \leq k \leq 12$, $-13 \leq l \leq 13$
554	Reflections collected	6780
555	Independent reflections	3353 [R(int) = 0.0204]
556	Completeness to theta = 25.93°	98.4 %
557	Refinement method	Full-matrix least-squares on F ²
558	Data / restraints / parameters	3353 / 4 / 260
559	Goodness-of-fit on F ²	1.077
560	Final R indices [I > 2σ(I)]	R1 = 0.0395 wR2 = 0.0863
561	R indices (all data)	R1 = 0.0461 wR2 = 0.0896
562	Extinction coefficient	0.0040(2)
563	Largest diff. peak and hole	0.215 and -0.202 e.Å ⁻³

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Table 2. Selected bond distances (Å) for compound 1

Ca(1)-O(6)	2.3442(13)	Ca(1)-O(5)	2.4213(14)
Ca(1)-O(2) ⁱⁱ	2.3498(14)	Ca(1)-O(1)	2.4548(15)
Ca(1)-O(9)	2.3918(18)	Ca(1)-O(2)	2.6313(15)
Ca(1)-O(10)	2.4121(17)	Ca(1)-O(6) ⁱⁱ	2.6539(15)
Ca(1)-Ca(1) ⁱⁱ	3.9865(8)	Ca(1)-Ca(1) ⁱ	3.9967(9)
O(6)-Ca(1)-O(2) ⁱⁱ	148.82(5)	O(9)-Ca(1)-O(5)	88.40(6)
O(6)-Ca(1)-O(9)	77.32(6)	O(10)-Ca(1)-O(5)	150.25(5)
O(2) ⁱⁱ -Ca(1)-O(9)	82.91(6)	O(6)-Ca(1)-O(1)	80.89(5)
O(6)-Ca(1)-O(10)	84.37(5)	O(2) ⁱⁱ -Ca(1)-O(1)	124.69(5)
O(2) ⁱⁱ -Ca(1)-O(10)	77.70(6)	O(9)-Ca(1)-O(1)	150.53(5)
O(9)-Ca(1)-O(10)	104.97(7)	O(10)-Ca(1)-O(1)	92.27(6)
O(6)-Ca(1)-O(5)	124.91(5)	O(5)-Ca(1)-O(1)	88.01(5)
O(2) ⁱⁱ -Ca(1)-O(5)	77.78(5)	O(5)-Ca(1)-O(1)	128.87(5)

573 Symmetry transformations are used to generate equivalent atoms i) $-x+1, -y+2, -z$;
574 ii) $-x+2, -y+2, -z$

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576

Table 3 Hydrogen-bonding geometry (Å, °) for compound 1

D-H...A	d(D-H)	d(H...A)	D(D...A)	<DHA
Intrachain interactions				
O9-H9...O1 ⁱ	0.817	1.965	2.769	168
O10-H10B...O5 ⁱⁱ	0.832	1.953	2.754	161
Interchain interactions				
O10-H10A...O7 ⁱⁱⁱ	0.823	2.257	2.999	150
C3-H3...O9 ^v	0.930	2.623	3.548	173
C11-H11...O4 ^v	0.929	2.523	3.404	158
C10-H10...O1 ^{vi}	0.929	2.539	3.464	174

577 Symmetry Code: i) $-x+1, -y+2, -z$; ii) $-x+2, -y+2, -z$ iii) $x, y+1, z$;
578 iv) $x, y, 1+z$; v) $1-x, 1-y, 1-z$; vi) $x, -1+y, z$

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581 Table 4. Metal coordination number, number of coordinated waters and binding mode
 582 of carboxylate in some Ca(II) coordination polymers
 583

No.	Compound	C.N.	D	Bridging (RCOO) ⁻ present	Space Group	Ref
1	[Ca(N-MeIm)(4-nba) ₂] _n	6	1-D	Yes	Pī	46
2	[Ca(Phen)(Sa) ₂] _n	6	1-D	Yes	Pnab	19
3	[Ca _{1.5} (DEF)(μ-BDC) _{1.5}] _n	6,7	1-D	Yes	I2/a	15
4	[[Ca(NH ₂ -NHCO ₂) ₂].H ₂ O] _n	8	1-D	Yes	Pī	20
5	[Ca(2-MeIm)(H ₂ O)(4-nba) ₂] _n	7	1-D	Yes	P2 ₁ /n	47
6	[Ca(gly) ₂ (H ₂ O)] _n	8	1-D	Yes	Pī	7
7	[Ca(H ₂ O)(dnSa)] _n	7	1-D	Yes	P2 ₁ /c	21
8	[Ca(H ₂ O)(DMF)(benz) ₂] _n	8	1-D	Yes	P2 ₁ /n	22
9	[Ca(val) ₂ (H ₂ O)] _n	7	1-D	Yes	C2/c	7
10	[Ca(H ₂ O) ₂ (4-aba) ₂] _n	8	1-D	Yes	P2 ₁ 2 ₁ 2 ₁	8
11	[Ca(H ₂ O) ₂ (2-nba) ₂] _n	8	1-D	Yes	Pī	This work
12	[Ca ₂ (H ₂ O) ₂ (OAc) ₃ (NO ₃) ₃] _n	8	1-D	Yes	Pnma	23
13	[Ca(H ₂ O) ₂ (3-aba) ₂] _n	8	1-D	Yes	Pbcn	10
14	[Ca(H ₂ O) ₂ (4-CNbenz) ₂] _n	8	1-D	Yes	P2/n	24
15	[[Ca(H ₂ O) ₂ (Nic) ₂].(H ₂ O) ₃] _n	7	1-D	Yes	C2/c	25
16	[Ca(H ₂ O) ₂ (2-OPA) ₂] _n	8	1-D	Yes	Pna2 ₁	26
17	[Ca(C ₄ H ₄ O ₅) ₂ .2H ₂ O]	8	1-D	Yes	C2/c	42
18	[Ca(leu) ₂ (H ₂ O) ₃] _n	8	1-D	Yes	Pī	7
19	[Ca(H ₂ O) ₃ (bpdc)]	8	1-D	Yes	Ima2	45
20	[Ca(H ₂ O) ₃ (2-aba) ₂] _n	7	1-D	Yes	Pbcn	9
21	[[Ca(H ₂ O) ₃ (4-fba)](4-fba)] _n	8	1-D	Yes	P2 ₁ /c	27
22	[[Ca(H ₂ O) ₃ (benz) ₂] _n	8	1-D	Yes	P2 ₁ /c	28
23	[Ca(H ₂ O) ₂ (C ₈ H ₅ O ₃) ₂] _n	8	1-D	Yes	C2/c	29
24	[[Ca(H ₂ O) ₂ (Py-Thr) ₂].(H ₂ O) ₂] _n	8	1-D	Yes	C2	30
25	[Ca(H ₂ O) ₃ (C ₉ H ₁₁ N ₆ O ₅) ₂] _n	10	1-D	Yes	C2/c	31
26	[Ca(H ₂ O) ₃ (1,4-bdc)] _n	8	1-D	Yes	P2 ₁ /c	32
27	[[Ca(H ₂ O) ₂ (1,3-bdc)] _{2.5} .4 H ₂ O] _n	8	1-D	Yes	C2/c	33
28	[[Ca ₅ (1,3-bdc) ₅ (H ₂ O) ₉].8H ₂ O] _n	8	1-D	Yes	C2/c	34
29	[[Ca(H ₂ O)] ₂ (L)(μ-H ₂ O)] _n	8	1-D	Yes	Pī	35
30	[Ca(μ-DMF)(μ-NDC)] _n	8	2-D	Yes	Pnma	15
31	[Ca(μ-DEF)(μ-TPDC)] _n	8	2-D	Yes	Pnma	15
32	[Ca(μ-DMF)(μ-DADC)] _n	8	2-D	Yes	Pnma	15
33	[Ca(HBTC).2H ₂ O]	8	2-D	Yes	P1	16
34	[Ca(H ₂ O)(tda)] _n	8	2-D	Yes	Pī	40
35	[Ca ₃ (H ₂ O) ₈ (BTA) ₂].3H ₂ O	7,8	2-D	Yes	Pī	41
36	[Ca(H ₂ O)(O ₂ C) ₂ C ₆ H ₃ CO ₂ H)] _n	8	2-D	Yes	Pī	36
37	[[Ca(H ₂ O) ₂ (DTBB)]0.5C ₂ H ₅ OH] _n	8	2-D	Yes	C2/c	10

38	[Ca(H ₂ O)(Hpdc)] _n	7	3-D	Yes	P2 ₁ /c	37
39	[Ca ₂ (A ₃ Br)].5H ₂ O	6	3-D	Yes	Pnma	38
40	[Ca(H ₂ O)(C ₁₀ H ₈ O ₆)]	8	3-D	Yes	P2 ₁ /c	39
41	[Ca(H ₂ O) ₃ (5-OH-BDC)].H ₂ O	8	3-D	Yes	P2 ₁ /c	43
42	[Ca(C ₃ H ₃ O ₄) ₂] _n	8	3-D	Yes	P2 ₁ /c	44
43	[Ca(H ₂ O)(bpdc)]	7	3-D	Yes	P2 ₁	45
44	[[Ca(H ₂ O) ₄ (Hpdc)].H ₂ O] _n	8	1-D	Yes	P2 ₁ /c	37
45	[[Ca(H ₂ O) ₄ (Hpdc)].2H ₂ O] _n	7	1-D	No	P2 ₁ /c	37
46	[[Ca(H ₂ O) ₄ (AIP) ₂](H ₂ O)] _n	8	1-D	No	R-3	12
47	[Ca(H ₂ O) ₄ (η ¹ -4-nba)(η ² -4-nba)]	7	0-D	No	P2 ₁ /c	48

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586 Abbreviations used: C.N. = coordination number; D = Dimensionality of polymer,
587 N-MeIm = N-methylimidazole, 4-nba = 4-nitrobenzoate, Phen = 1,10-phenanthroline;
588 Sa = Salicylato; BDC- Benzene-1,4-dicarboxylate, DEF = N-N diethylformamide;
589 2-MeIm = 2-methylimidazole, gly = glycinate; dnSa = 3,5 dinitrosalicylato;
590 DMF = N,N-dimethylformamide; benz = benzoate; val =rac-valinate; 4-aba = 4-
591 aminobenzoate; 2-nba = 2-nitrobenzoate, OAc = acetate; 3-aba = 3-aminobenzoate; 4-
592 CNbenz = 4-cyanobenzoate; Nic = nicotinate; OPA = 2-oxo-1,2-dihydropyridine-1-
593 acetate; C₄H₄O₅ = Malate; leu =rac-leucinate; bpdc = 4,4'- biphenyldicarboxylic acid,
594 2-aba = 2-aminobenzoate; 4-fba = 4-fluorobenzoate; C₈H₅O₃ = 2-Formylbenzoate;PY-
595 Thr = N-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl) thronato;
596 C₉H₁₁N₆O₅ = Bis[N-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidine-2-yl)
597 glycyglycinate; 1,4-bdc = 1,4 benzenedicarboxylate; 1,3-bdc = 1,3
598 benzenedicarboxylate; L = 4-(2-nitrophenyl)-3,6-dioxaoctane dioate; NDC-
599 Naphthalene 2,6-dicarboxylate; TPDC – 4,5,9,10-Tetrahydropyrene-2,7-
600 dicarboxylate; DADC – 5,10-dihydroanthracene-2,7-dicarboxylate, H₃BTC =
601 benzene-1,3,5-tricarboxylic acid; tda = S(CH₂COO)₂²⁻; BTA = 1,3,5
602 benzenetriacetate; (O₂C)₂C₆H₃CO₂H = trimellitate; DTBB = 2,2'-dithiobis(benzoate);
603 Hpdc = 3,5-pyrazoledicarboxylate, A₃Br = 1,3-biscarboxyethylimidazolium bromide;
604 C₁₀H₈O₆ = Benzene 1,4 dioxylacetate; 5-OH-BDC = 5 hydroxy isophthalate; C₃H₃O₄
605 = Malonate; AIP = 5-Aminoisophthalate;
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609 Captions for Figures

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611 Fig. 1. Diffuse Reflectance spectra of 2-nbaH and $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$ 1

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613 Fig. 2. TG-DSC thermograms of $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$ 1 (solid line) and $[\text{Ca}(2\text{-nba})_2]_n$ 614 2 (dotted lines). (Heating Rate 5 K min^{-1} ; Air atmosphere)

615

616 Fig. 3. A view of the coordination sphere of Ca(II) in $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$ 1, showing

617 the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability

618 level excepting for the H atoms, which are shown as circles of arbitrary radius (top).

619 The coordination polyhedron around Ca(II) in 1 (bottom). Symmetry code: i) $-x+1, -$ 620 $y+2, -z$; ii) $-x+2, -y+2, -z$

621

622 Fig. 4. A view along b showing the tricyclic dicalcium-bis(2-nitrobenzoate) moiety

623 formed by a pair of $\mu_2\text{-}\eta^2\text{:}\eta^1$ 2-nba ligands between two Ca(II) ions.

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625 Fig. 5. A portion of the 1-D polymeric chain in 1 showing the linking of tricyclic

626 dicalcium-bis(2-nitrobenzoate) units into an infinite chain extending along a axis. For

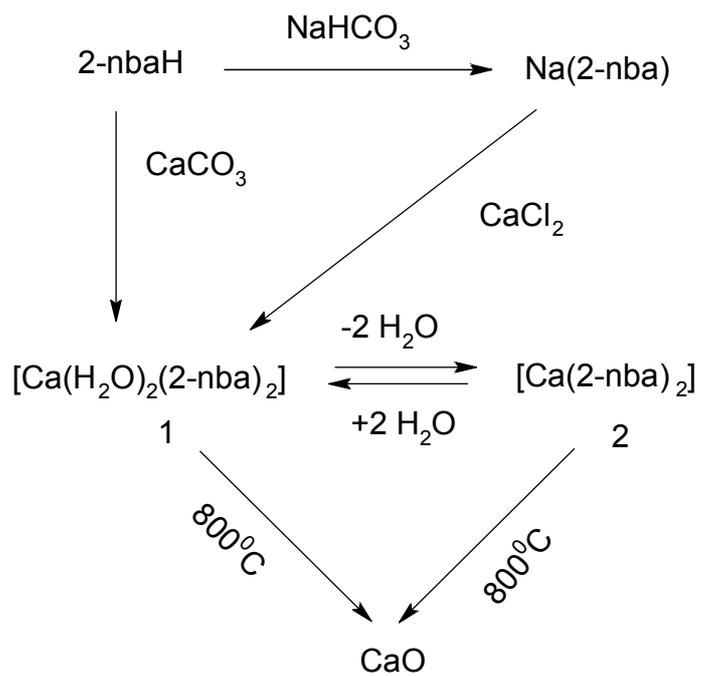
627 clarity the coordinated water molecules and aromatic ring are not shown (top). A

628 wireframe model of the polymeric chain wherein the oxygen atoms O9 and O10 of

629 water are included (middle). The aromatic rings and the H atoms of water are

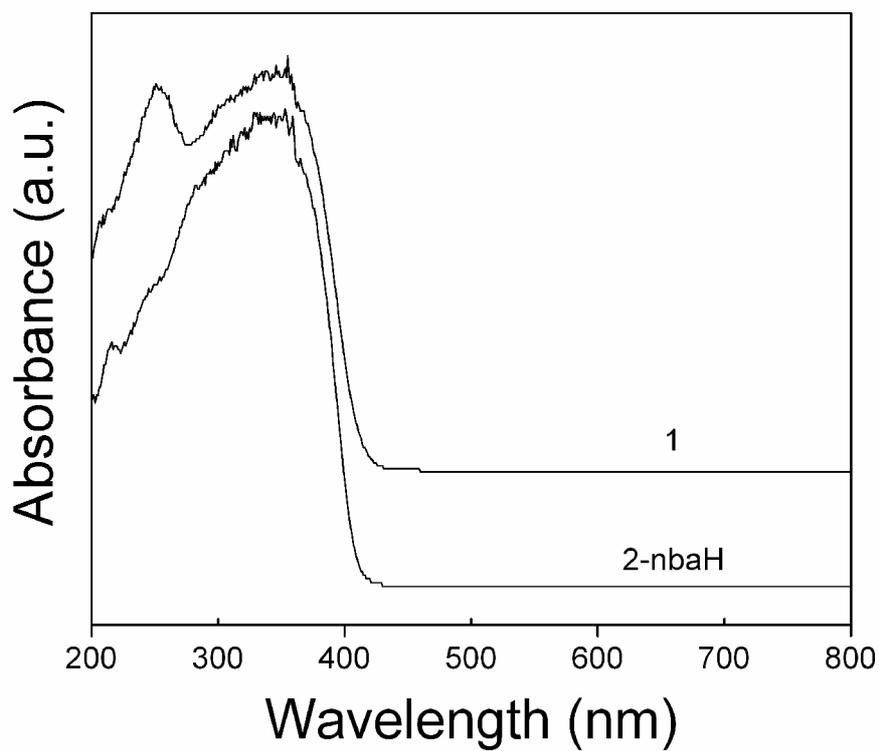
630 included in the polymeric chain to show the intrachain O-H \cdots O bonds in broken lines.

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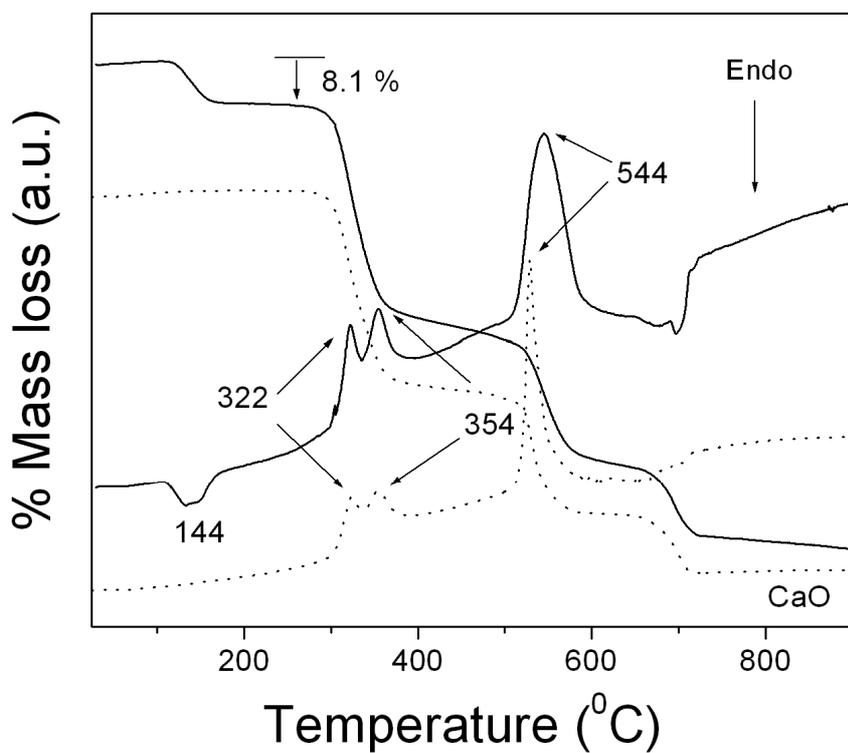
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SCHEME 1



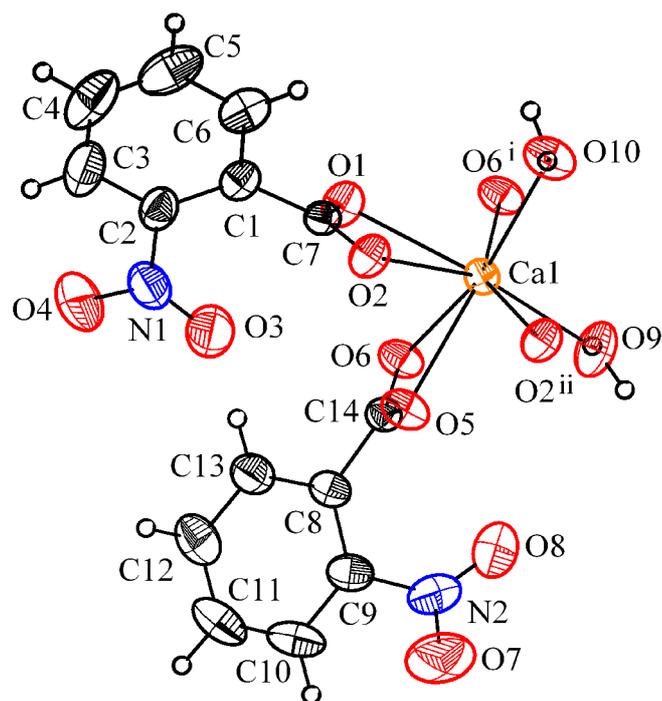
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Fig. 1. Diffuse Reflectance spectra of 2-nbaH and $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$ 1

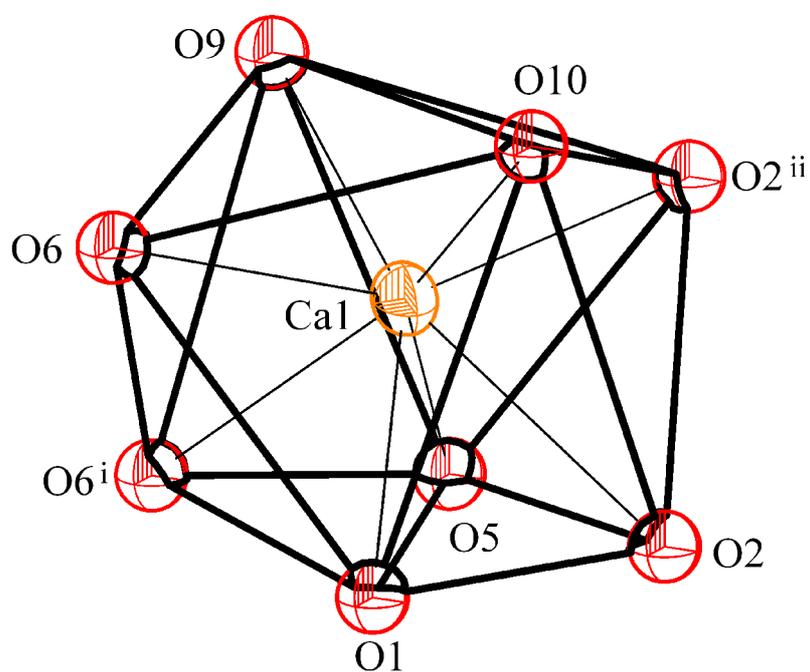


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Fig. 2. TG-DSC thermograms of $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_4]_n$ 1 (solid line) and $[\text{Ca}(2\text{-nba})_4]_n$ 2 (dotted lines). (Heating Rate 5 K min^{-1} ; Air atmosphere)



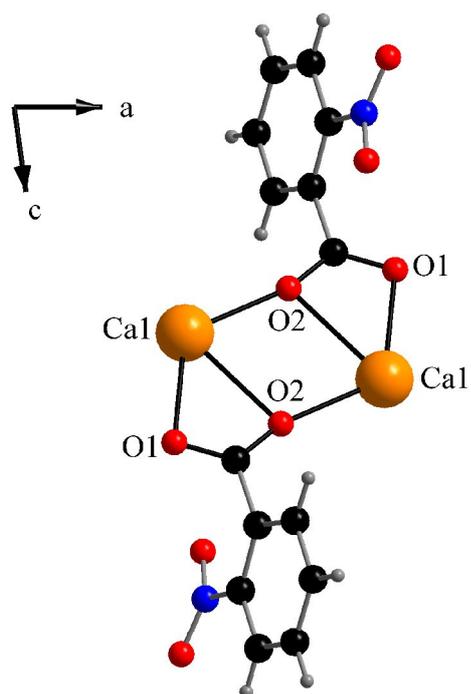
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Fig. 3. A view of the coordination sphere of Ca(II) in 1, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as circles of arbitrary radius (top). The coordination polyhedron around Ca(II) in 1 (bottom). Symmetry code: i) $-x+1, -y+2, -z$; ii) $-x+2, -y+2, -z$

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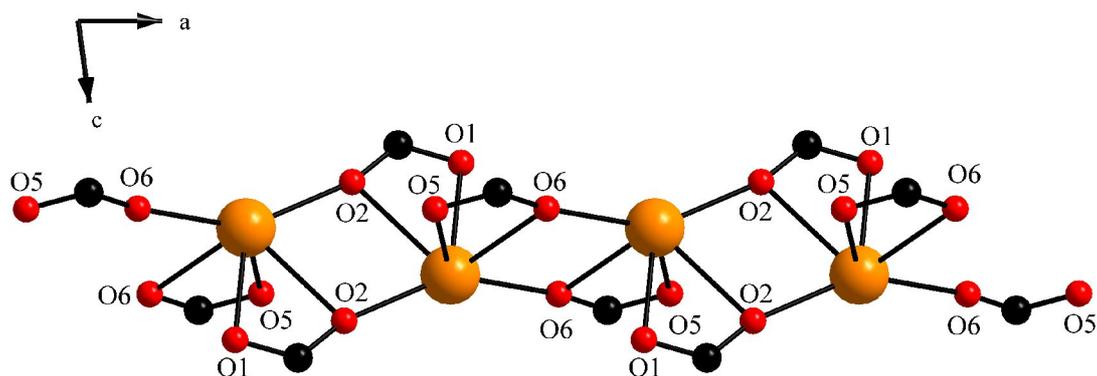
662 Fig. 4. A view along b showing the tricyclic dicalcium-bis(2-nitrobenzoate) unit
663 formed by a pair of $\mu_2\text{-}\eta^2\text{:}\eta^1$ 2-nba ligands between two Ca(II) ions.

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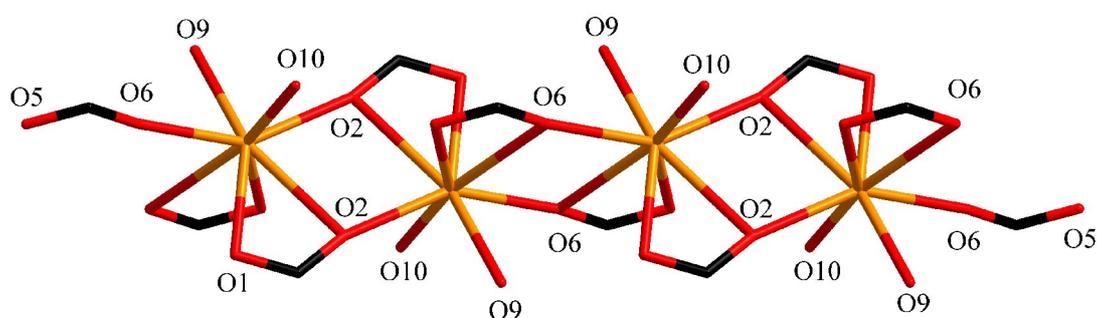
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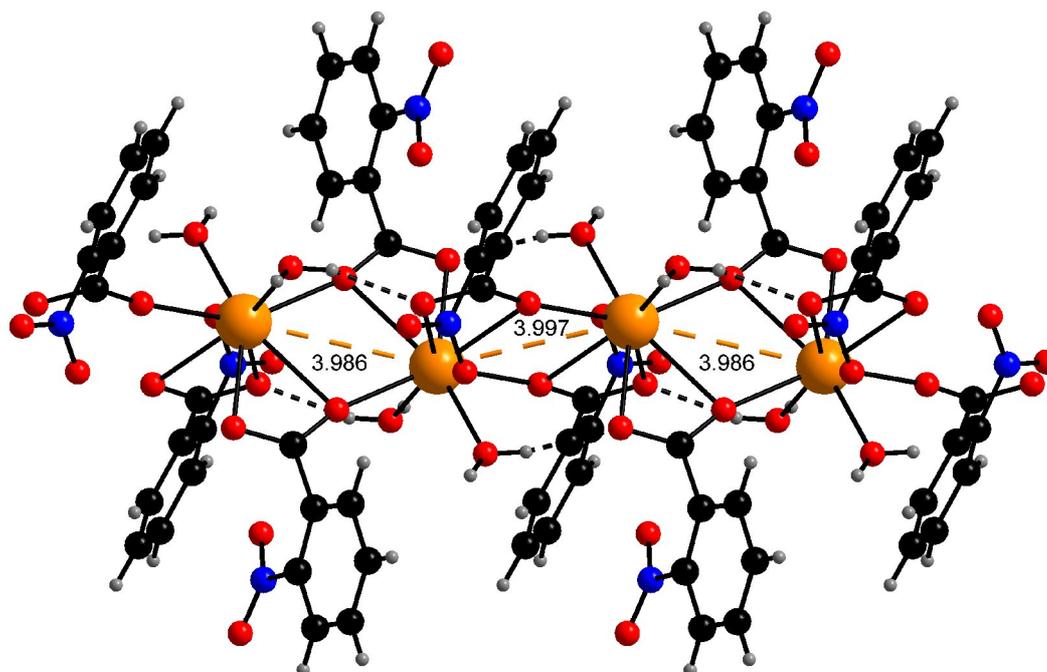
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675 water are included (middle). The aromatic rings and the H atoms of water are
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