



Structural characterization of *catena*-[bis(μ -4-nitrobenzoato)-diaqua-calcium 4,4'-bipyridine] and *catena*-[bis(μ -4-nitrobenzoato)-diaqua-calcium 1H-1,2,4-triazole]

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An attempted incorporation of N-donor ligand in the coordination sphere of Ca in the molecular solid $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (4-nba=4-nitrobenzoate) resulted in the formation of the one-dimensional (1D) coordination polymers *catena*-[bis(μ -4-nitrobenzoato)-diaqua-calcium 4,4'-bipyridine] **1** and *catena*-[bis(μ -4-nitrobenzoato)-diaqua-calcium 1H-1,2,4-triazole] **2** with the N-heterocycle functioning as a solvate. The syntheses, crystal structures and properties of $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot\text{L}$ (L=4,4'-bipyridine **1**; L=1H-1,2,4-triazole **2**) are reported. The central Ca(II) in **1** and **2** exhibits eight-coordination and the aqua ligands are terminal, while 4-nitrobenzoate functions as a μ_2 -bridging ligand. The $\mu_2\text{-}\eta^2\text{:}\eta^1$ tridentate binding mode of the 4-nba ligand results in the formation of an infinite chain of edge-sharing $\{\text{CaO}_8\}$ polyhedra flanked by the 4-nitrobenzoates. The solvate 4,4'-bipyridine in **1** (or 1,2,4-triazole in **2**) links adjacent polymeric chains with the aid of O-H \cdots N hydrogen bonding interactions. A comparative study of $\{\text{CaO}_x\}$ polyhedral linking in structurally characterized calcium coordination polymers based on 4-nitrobenzoate is described.

Keywords: Calcium; 4-Nitrobenzoate, 1,2,4-triazole; 4,4'-Bipyridine, Coordination polymer, Edge-sharing $\{\text{CaO}_8\}$ polyhedra

A recent review article titled “Calcium-based Metal-Organic Frameworks and their potential applications” provides an overview of the recent developments in the area of metal-organic frameworks (MOFs) of Ca¹. A total of one hundred and eighty four structurally characterized compounds of Ca of varying dimensionalities ranging from molecular solids (zero-dimensional) to three-dimensional framework materials are described in the review discussing synthetic methodologies, crystal structures, important properties and related applications. Although most syntheses are performed under solvothermal conditions²⁻¹³, other methodologies like microwave syntheses¹⁴, mechanochemical synthesis¹⁵, ultrasonic irradiation¹⁶ etc. have also been employed for preparation of compounds.

Several papers have appeared in the literature¹⁷⁻³³ which describe the acid base reactions of calcium sources with a carboxylic acid under non-hydrothermal conditions and structural characterization of the product. In many of these compounds the solvent water molecules tend to occupy one or more of the coordination sites of Ca(II) due to the high hydration energy of the Ca centres. In some cases for example L-tartaric acid¹⁷, the reaction can result in a three-

dimensional product while in some cases for example 4-nitrobenzoic acid (4-nbaH), a molecular solid $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ **3**²⁵ is the product of the reaction. In the monomeric compound **3** all the four aqua ligands are terminal, and the unique 4-nba ligands exhibit monodentate (η^1) and bidentate (η^2) binding¹. With 4-nbaH, a water-rich dinuclear compound viz. bis(μ_2 -aqua)-octa-aqua-bis(4-nitrobenzoato)-di-calcium(II) bis(4-nitrobenzoate) octahydrate having formula $[(\text{H}_2\text{O})_4(4\text{-nba})\text{Ca}]_2(\mu_2\text{-H}_2\text{O})_2(4\text{-nba})_2\cdot 8\text{H}_2\text{O}$ has also been structurally characterized³⁰. The role of temperature for product formation was also highlighted in the review on Ca-MOFs¹. High temperature generally favours higher dimensionality and reactions at low temperature or room temperature result in low-dimensional structures.

In earlier work from our laboratory, we have demonstrated that the monomeric tetra(aqua)Ca(II) compound **3** can be transformed into the one-dimensional coordination polymers $[\text{Ca}(\text{L}^1)(4\text{-nba})_2]$ (L¹=N-methylimidazole)³⁴ or $[\text{Ca}(\text{H}_2\text{O})(\text{L}^2)(4\text{-nba})_2]$ (L²=2-methylimidazole)³⁵ by the incorporation of N-donor ligands L¹ or L² accompanied by the complete or partial removal of the aqua ligands. Our attempts to incorporate a bridging N-donor ligand like 4,4'-

bipyridine (or 1,2,4-triazole) resulted in the formation of the new calcium(II) coordination polymers *catena*-[bis(μ -4-nitrobenzoato)-diaqua-calcium 4,4'-bipyridine] **1** and *catena*-[bis(μ -4-nitrobenzoato)-diaqua-calcium 1H-1,2,4-triazole] having formula $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot\text{L}$ (L=4,4'-bipyridine **1**; L=1,2,4-triazole **2**) with the N-heterocycle functioning as a solvate and linking adjacent polymeric chains with the aid of O-H \cdots N hydrogen bonding interactions. The results of these investigations are described herein.

Materials and Methods

All the chemicals used in this study were of reagent grade and used as received. The starting materials and reaction products are air stable and hence were prepared under normal laboratory conditions. The molecular solid $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ **3** was prepared as per a reported procedure²⁵. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range 4000-400 cm^{-1} . UV-visible absorption spectra of aqueous solutions of **1** and **2** were recorded on a Shimadzu UV-2450 double beam spectrophotometer using matched quartz cells. Luminescence spectra of the solid samples were recorded at room temperature using Perkin Elmer LS 55 spectrophotometer. Raman spectra were recorded using 785 nm radiation for excitation on an Agiltron Peak Seeker Pro Raman instrument from 4000 to 200 cm^{-1} . Thermal studies were performed in flowing air, in Al_2O_3 crucibles on a STA-409PC simultaneous thermal analyzer from Netzsch. A heating rate of 10 K min^{-1} was employed for all measurements. Isothermal mass loss studies were performed in a temperature-controlled electric furnace. Microwave reactions were performed in a domestic microwave oven. Elemental analyses (C, H and N) were performed on a Variomicro cube CHNS analyser.

Synthesis of $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot\text{L}$ (4-nba=4-nitrobenzoate; L=4,4'-bipyridine **1**; L=1,2,4-triazole **2**)

Compound **3** (0.889 g, 2 mmol) was dissolved in distilled water (~40 mL) by microwaving it for 1 min on medium power setting. Then 4,4'-bipyridine (0.312 g, 2 mmol) was added and the reaction mixture was microwaved for 2 min. The hot clear reaction mixture was left aside for crystallization. Fine transparent crystals of **1** suitable for structure determination which separated after ~1-3 h were isolated by decanting the filtrate, washed with a little ice cold water followed by ether and air dried

(yield: 73%). Alternatively, **1** can be prepared by dissolution of a mixture of **3** (0.889 g, 2 mmol) and 4,4'-bipyridine (0.312 g, 2 mmol) in water (~40 mL) by heating the reaction mixture on a steam bath for 15-20 min to obtain a clear solution, followed by crystallization. The use of 1,2,4-triazole (1.104 g) instead of 4,4'-bipyridine in the above reaction and microwaving (or heating) the reaction mixture to attain a final volume of 8-10 mL resulted in the formation of crystals of **2** in 70% yield.

(**1**) Anal. (%): Calc. for $\text{C}_{24}\text{H}_{20}\text{CaN}_4\text{O}_{10}$ (564.52 g/mol) **1**: C, 51.06; H, 3.57; N, 9.92; Found: C, 51.01; H, 3.61; N, 9.82. IR data (KBr cm^{-1}): 3500-2700, 1568 (s), 1510 (m), 1491 (m), 1417 (s), 1348 (s), 1319 (m), 1105 (m), 1014(m), 1001 (m), 878 (m), 841 (m), 810 (m), 797 (s), 741(m), 725 (s), 685 (m), 619 (m), 600 (m), 514 (m); Raman data (cm^{-1}): 3074 (w), 1600 (s), 1341 (s), 1298 (m), 1107 (m), 1005 (m), 870 (w), 627 (w); DSC data ($^{\circ}\text{C}$): 98 (endo), 409 (exo), 585 (exo).

(**2**) Anal. (%): Calc. for $\text{C}_{16}\text{H}_{15}\text{CaN}_5\text{O}_{10}$ (477.41 g/mol) **2**: C, 40.25; H, 3.17; N, 14.67; Found: C, 40.00; H, 3.10; N, 14.64. IR data (KBr cm^{-1}): 3593(m), 3500-2700, 1655 (m), 1614 (m), 1568 (s), 1514 (m), 1477 (m), 1416 (s), 1350 (s), 1319 (m), 1283 (m), 1254 (m), 1155 (m), 1103 (m), 1065 (m), 1013 (m), 970 (m), 910 (m), 876 (m), 841 (m), 799 (m), 725 (s), 681 (m), 631 (m), 513 (m); Raman data (cm^{-1}): 3125 (w), 1600 (s), 1429 (m), 1338 (s), 1103 (m), 869 (m), 630 (w); DSC data ($^{\circ}\text{C}$): 117 (endo), 433 (exo).

The structures of **1** and **2** were determined using Bruker Smart Apex X-ray diffractometer. Intensity data were collected at room temperature (RT) using monochromated Mo ($\text{K}\alpha$) ($\lambda = 0.7107 \text{ \AA}$) radiation. The structures were solved with SHELXS and subsequent refinements were performed with SHELXL³⁶. All non-hydrogen atoms were refined anisotropically. H atoms attached to the aromatic ring of the 4-nba ligand and 4,4'-bipyridine were introduced in calculated positions and included in the refinement by riding on their respective parent C atoms. Technical details of data acquisition and selected crystal refinement results are given in Table 1.

Results and Discussion

Synthetic aspects, spectral and thermal characterization

The synthetic methodology for the preparation of **1** (or **2**) is similar to the one employed by us earlier for the incorporation of N-donor ligands like N-methylimidazole or 2-methylimidazole^{34,35} in the

Table 1 — Selected refinement data for compounds **(1)** and **(2)**

Empirical formula	$\text{C}_{24}\text{H}_{20}\text{CaN}_4\text{O}_{10}$ (1)	$\text{C}_{16}\text{H}_{15}\text{CaN}_5\text{O}_{10}$ (2)
Formula weight (g mol^{-1})	564.52	477.41
Temp. (K)	294 (2)	294 (2)
Wavelength (\AA)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
Unit cell dimensions	$a = 7.8508(18) \text{\AA}$ $b = 12.746(3) \text{\AA}$ $c = 14.003(3) \text{\AA}$ $\alpha = 101.316(4)^\circ$ $\beta = 93.348(4)^\circ$ $\gamma = 97.899(3)^\circ$	$a = 20.792(2) \text{\AA}$ $b = 6.719(5) \text{\AA}$ $c = 12.402(3) \text{\AA}$ $\alpha = 90^\circ$ $\beta = 104.29(3)^\circ$ $\gamma = 90^\circ$
Volume (\AA^3)	1355.6(4)	4040.3(7)
Z	2	8
Density (calc.) (mg/m^3)	1.383	1.570
Abs. coeff. (mm^{-1})	0.292	0.377
F(000)	584	1986
Crystal size (mm^3)	$0.36 \times 0.18 \times 0.09$	$0.14 \times 0.11 \times 0.09$
Theta range for data collection ($^\circ$)	1.49 to 25.00	2.00 to 25.00
Completeness to theta	99.2%	99.9%
Index ranges	$-9 \leq h \leq 9, -15 \leq k \leq 15,$ $-16 \leq l \leq 16$	$-24 \leq h \leq 24, -32 \leq k \leq 32,$ $-8 \leq l \leq 8$
Reflections collected	9746	19182
Independent reflections	4750 (R(int) = 0.0314)	3563 (R(int) = 0.0248)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4750 / 0 / 368	3563 / 0 / 311
Goodness-of-fit on F^2	1.093	1.041
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0554, wR2 = 0.1346	R1 = 0.0277, wR2 = 0.0748
R indices (all data)	R1 = 0.0646, wR2 = 0.1405	R1 = 0.0291, wR2 = 0.0763
Largest diff. peak and hole ($\text{e.}\text{\AA}^{-3}$)	0.664 and -0.230	0.200 and -0.236
CCDC No	892774	892773

coordination sphere of Ca in $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ **3**. A solution based synthesis was employed so as to obtain crystalline products suitable for structure determination. In this work, aqueous reactions of the N-heterocycles viz. 4,4'-bipyridine and 1,2,4-triazole were investigated with **3** under microwave irradiation or by heating on a water bath. Both methods afforded the same products as evidenced by the identical infrared, Raman and optical spectra (Supplementary Data, Fig. S1). However, the microwave-assisted synthesis resulted in product formation in good yield within a shorter reaction time. Use of stoichiometric 4,4'-bipyridine afforded **1** while an excess of 1,2,4-triazole (8 moles per Ca) was required to isolate **2**. Compound **1** precipitated immediately from solution if less water was used, while for **2** excess of 1,2,4-triazole and minimum water was necessary in order to avoid the hydrolysis of the product to the tetraquacalcium compound **3**.

The composition of **1** (or **2**) as consisting of Ca:water:4-nba:L (L=N-heterocycle) in 1:2:2:1 ratio was inferred from elemental analytical data, the amount of 4-nbaH obtained by acidification of **1** (or **2**) and the amount of CaCO_3 residue obtained at 600°C by pyrolysis of **1** (or **2**). A comparison of the infrared spectra of **1** (or **2**) with the IR spectrum of the precursor compound **3** revealed change of the profile of the IR spectra in the $-\text{OH}$ region. Additionally, the spectra of the title compounds contain several more bands indicating the formation of new compounds. The Raman spectra of **1** (or **2**) exhibit an intense band at 1341 (or 1338) cm^{-1} which can be assigned for the symmetric stretching vibration of the nitro group. The DTA curve of **1** (Supplementary Data, Fig. S2) exhibits an endothermic event at 98°C , which can be attributed for dehydration. This is further confirmed by heating **1** at 100°C in an oven, wherein a mass loss, of 6.25%, corresponding to the loss of two moles

of water is observed. The formation of an anhydrous compound is confirmed by the absence of the O-H signal at 3600 cm^{-1} in the IR spectrum (Supplementary Data, Fig. S3), which reappears when the anhydrous compound is equilibrated over water showing successful rehydration. The exothermic peaks at 409 and 585 °C in DTA curve can be assigned for decomposition process leading to loss of organic moiety. The DTA curve of **2** (Supplementary Data, Fig. S2) exhibits an endothermic process at 117 °C which can be assigned for the loss of coordinated water, followed by continuous degradation with temperature as indicated by mass loss in TG curve. The second DTA (at 433 °C) event is exothermic in nature and can be assigned for the decomposition of organic ligand. Compound **1** (or **2**) exhibits diminished fluorescence as compared to that of free 4-nbaH (Supplementary Data, Fig. S4). Although the spectral and analytical studies revealed the presence of N-heterocycles in **1** (or **2**) a crystal structure determination confirmed that 4,4'-bipyridine (or 1,2,4-triazole) are not bonded to the Ca(II) unlike in the case of N-methylimidazole or 2-methylimidazole^{34,35}.

Description of crystal structures

Both compounds crystallizing in centrosymmetric space groups are structurally related and exhibit several similarities. The compounds differ in terms of the N-heterocycle namely 4,4'-bipyridine in **1** and 1,2,4-triazole in **2**, the location of two unique Ca(II) ions in **2** and the secondary interactions. The similarities include the eight coordination around the central Ca(II), μ_2 -tridentate binding mode of 4-nba ligand and edge sharing $\{\text{CaO}_8\}$ polyhedral chain architecture, presence of a N-heterocycle in the lattice. The geometric parameters of the anionic 4-nitrobenzoates (4-nba) and the N-heterocycles are in the normal range³⁷ in both the compounds (Supplementary Data, Table S1 and S2).

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with all atoms located in general position. The asymmetric unit consists of (Supplementary Data, Fig. S5) an unique Ca(II), two crystallographically independent 4-nitrobenzoate ligands, two terminal water molecules, and an unique 4,4'-bipyridine molecule in the lattice. The central Ca(II) is eight coordinated and is bonded to two monodentate water molecules (O31, O32), and to six O atoms from four symmetry related 4-nba anions (Fig. 1), resulting in a distorted square antiprismatic $\{\text{CaO}_8\}$ polyhedron

(Supplementary Data, Fig. S5). The surroundings of Ca(II) in **1** is similar to the one reported earlier for $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}$ (dmp=3,5-dimethylpyrazole)³⁸. The Ca-O bond distances (Table 2) vary between 2.3679(17) and 2.722(2) Å, while the O-Ca-O angles scatter in a very broad range from 50.04(5) to 155.45(7)° indicating a distortion of the $\{\text{CaO}_8\}$ coordination polyhedron. The Ca1-O31 and Ca1-O32 bonds are shorter at 2.372(2) and 2.388(2) Å, respectively. However, these bonds of Ca(II) with the terminal aqua ligands are slightly longer as compared to the Ca-carboxylate bond distances Ca1-O2 and Ca1-O12ⁱ (H₂O) at 2.3679(17) and 2.3698(17), respectively. Both the unique 4-nba ligands function as $\mu_2\text{-}\eta^2\text{:}\eta^1$ bridging tridentate ligands (Fig. 1). The carboxylate oxygens O1 and O2 in the first unique 4-nba ligand (O1, O2) bind to Ca(II) at Ca1-O1 and Ca1-O2 distances of 2.4480(19) and 2.7116(19) Å, respectively. The O2 oxygen is further linked to a symmetry related Ca(II)ⁱⁱ at a distance of 2.3679(17) Å resulting in a Ca...Ca separation of 4.059(4) Å. The second unique ligand (O11, O12) also exhibits $\mu_2\text{-}\eta^2\text{:}\eta^1$ binding mode and binds to Ca1 in a similar fashion resulting in a different Ca...Ca separation of 4.049(4) Å (Fig. 1).

To understand the crystal structure of **1**, the binding of only one unique ligand with Ca(II) is first considered (Supplementary Data, Fig. S6). The binding of only one 4-nba ligand (O1, O2) results in the formation of discrete dimers with Ca...Caⁱⁱ separations of 4.059(4) Å. Thus a pair of (O1, O2) ligands bonded to a pair of Ca(II) ions constitutes the basic building unit namely a tricyclic dicalcium-di(4-nitrobenzoate) moiety. Each Ca(II) in the dimer is coordinated to a pair of terminal aqua ligands O31 and O32. Similarly, if we consider the $\mu_2\text{-}\eta^2\text{:}\eta^1$ binding mode of only the (O11, O12) ligand, a similar set of discrete dimers with Ca...Ca separations of 4.059(4) Å are formed and each Ca(II) is bonded to the terminal waters O31 and O32 (Supplementary Data, Fig. S6). The net result of the $\mu_2\text{-}\eta^2\text{:}\eta^1$ tridentate binding modes of the unique 4-nba ligands is linking of pairs of $\{\text{Ca}(\text{H}_2\text{O})_2\}^{2+}$ units into an infinite chain extending along the direction of *a* axis by alternating pairs of the crystallographically unique 4-nba ligands accompanied by alternating Ca...Ca separations of 4.059(4) and 4.049(4) Å, respectively (Fig. 2). A closer scrutiny reveals that the central $\{\text{CaO}_8\}$ polyhedral chain exhibits an edge-sharing architecture, the shared edge being alternating pairs of

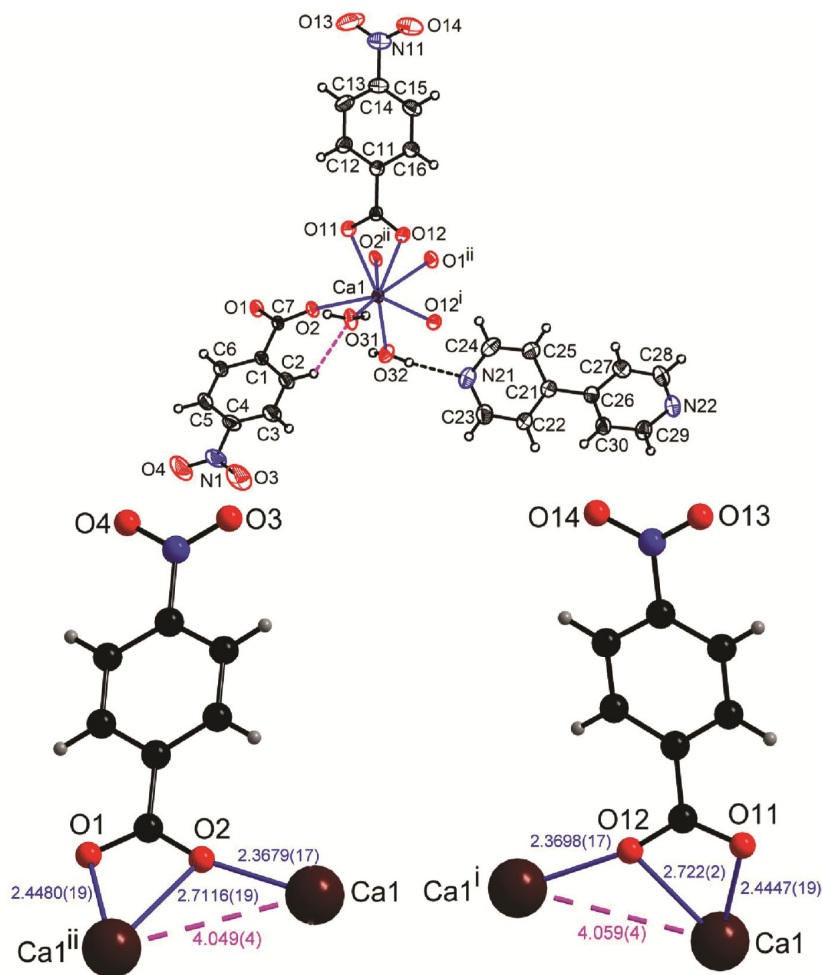


Fig. 1 — The crystal structure of **1** showing the atom labelling scheme and the eight coordination around Ca(II). Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as spheres of arbitrary radii. Intramolecular hydrogen bonding is shown by broken lines (**top**). The $\mu_2\text{-}\eta^2\text{:}\eta^1$ binding modes of the unique 4-nba ligands (**bottom**). Symmetry code: i) $-x+1, -y+1, -z+2$, ii) $-x, -y+1, -z+2$

O2, O2ⁱⁱ and O12, O12ⁱ atoms, respectively (for symmetry code see Table 2). The unique 4-nitrobenzoates flank either side of the $\{\text{CaO}_8\}$ polyhedral chain (Fig. 2).

All of the hydrogen atoms attached to the terminal waters O31 and O32 and the hydrogen atoms H2, H3, H5, H16, H24, H28 and H30 bonded to the carbon atoms of the unique 4-nba or the 4,4'-bipyridine function as hydrogen donors while the oxygen atoms, O1, O3, O4, O11, O13, O31 and O32 and the nitrogen atoms N21 and N22 of 4,4'-bipyridine function as hydrogen acceptors resulting in three varieties of hydrogen bonding interactions (Table 3) viz O-H \cdots N, O-H \cdots O and C-H \cdots O, respectively. Out of the eleven hydrogen bonds listed in Table 3, two are intramolecular. It is interesting to note that the 4,4-bipyridine, which functions as a solvate links

adjacent one-dimensional chains with the aid of O-H \cdots N interactions (Fig. 3).

Compound **2** crystallizes in the monoclinic space group $C2/c$. Its structure (Fig. 4) consists of two unique Ca(II) located on a two-fold axis, two crystallographically independent monodentate water molecules (O31 and O32), two unique 4-nba ligands and a crystallographically independent 1,2,4-triazole in the crystal lattice. As in **1** both the unique 4-nba ligands exhibit μ_2 -bridging tridentate binding mode (Supplementary Data, Fig. S7). The unique Ca(II) ions (Ca1 and Ca2) are eight coordinated. The bonding situation around each unique Ca in **2** is very similar to that observed in **1**. Hence, the unique ligands (O1, O2 and O11, O12), as well as the coordinated water molecules (O31, O32), are labeled as in compound **1**. Due to the special position of the

Table 2 — Selected bond lengths and angles (Å, °) for [Ca(H₂O)₂(4-nba)₂] \cdot L (4-nba=4-nitrobenzoate; L=4,4'-bipyridine **1**; L=1,2,4-triazole **2**)Compound **1**

Ca1-O2	2.3679(17)	Ca1-O11	2.4447(19)	Ca1 \cdots Ca1 ⁱ	4.059(4)
Ca1-O12 ⁱ	2.3698(17)	Ca1-O1 ⁱⁱ	2.4480(19)	Ca1 \cdots Ca1 ⁱⁱ	4.049(4)
Ca1-O31	2.372(2)	Ca1-O2 ⁱⁱ	2.7116(19)		
Ca1-O32	2.388(2)	Ca1-O12	2.722(2)		
O2-Ca1-O12 ⁱ	145.82(7)	O2-Ca1-O1 ⁱⁱ	124.50(6)	O1 ⁱⁱ -Ca1-O2 ⁱⁱ	50.14(5)
O2-Ca1-O31	84.74(7)	O12 ⁱ -Ca1-O1 ⁱⁱ	82.44(6)	O2-Ca1-O12	129.35(6)
O12 ⁱ -Ca1-O31	74.89(7)	O31-Ca1-O1 ⁱⁱ	149.40(7)	O12 ⁱ -Ca1-O12	74.49(7)
O2-Ca1-O32	75.11(7)	O32-Ca1-O1 ⁱⁱ	90.83(8)	O31-Ca1-O12	80.58(7)
O12 ⁱ -Ca1-O32	84.87(7)	O11-Ca1-O1 ⁱⁱ	85.33(7)	O32-Ca1-O12	155.45(7)
O31-Ca1-O32	107.05(9)	O2-Ca1-O2 ⁱⁱ	74.50(7)	O11-Ca1-O12	50.04(5)
O2-Ca1-O11	82.22(6)	O12 ⁱ -Ca1-O2 ⁱⁱ	129.76(6)	O1 ⁱⁱ -Ca1-O12	73.65(6)
O12 ⁱ -Ca1-O11	124.39(6)	O31-Ca1-O2 ⁱⁱ	155.23(7)	O2 ⁱⁱ -Ca1-O12	102.10(6)
O31-Ca1-O11	90.69(8)	O32-Ca1-O2 ⁱⁱ	80.84(7)		
O32-Ca1-O11	149.46(7)	O11-Ca1-O2 ⁱⁱ	73.48(6)		

Symmetry transformations used to generate equivalent atoms: i) -x+1, -y+1, -z+2 ii) -x, -y+1, -z+2

Compound **2**

Ca1-O31	2.3561(11)	Ca1-O1	2.7422(10)	Ca2-O11 ⁱ	2.5238(10)
Ca1-O31 ⁱ	2.3561(11)	Ca1-Ca1 ⁱⁱ	3.8569(4)	Ca2-O11	2.5238(10)
Ca1-O2 ⁱⁱ	2.3664(9)	Ca1-Ca1 ^{iv}	3.8569(4)	Ca2-O12 ⁱ	2.5696(10)
Ca1-O2 ⁱⁱⁱ	2.3664(9)	Ca2-O32 ⁱ	2.3584(11)	Ca2-O12	2.5696(10)
Ca1-O2	2.4655(10)	Ca2-O32	2.3584(11)	Ca2-Ca2 ^{vii}	4.0164(4)
Ca1-O2 ⁱ	2.4655(10)	Ca2-O12 ^v	2.4340(9)	Ca2-Ca2 ^{vi}	4.0164(4)
Ca1-O1 ⁱ	2.7422(10)	Ca2-O12 ^{vi}	2.4340(9)		
O31-Ca1-O31 ⁱ	103.24(6)	O2-Ca1-O1 ⁱ	73.60(3)	O32 ⁱ -Ca2-O11	81.25(4)
O31-Ca1-O2 ⁱⁱ	84.24(4)	O2 ⁱ -Ca1-O1 ⁱ	49.64(3)	O32-Ca2-O11	156.28(4)
O31 ⁱ -Ca1-O2 ⁱⁱ	77.84(4)	O31-Ca1-O1	155.85(4)	O12 ^v -Ca2-O11	79.00(3)
O31-Ca1-O2 ⁱⁱⁱ	77.84(4)	O31 ⁱ -Ca1-O1	83.55(3)	O12 ^{vi} -Ca2-O11	111.62(3)
O31 ⁱ -Ca1-O2 ⁱⁱⁱ	84.24(4)	O2 ⁱⁱ -Ca1-O1	119.91(3)	O11 ⁱ -Ca2-O11	118.09(5)
O2 ⁱⁱ -Ca1-O2 ⁱⁱⁱ	151.00(5)	O2 ⁱⁱⁱ -Ca1-O1	79.87(3)	O32 ⁱ -Ca2-O12 ⁱ	152.28(3)
O31-Ca1-O2	150.75(3)	O2-Ca1-O1	49.64(3)	O32-Ca2-O12 ⁱ	107.47(4)
O31 ⁱ -Ca1-O2	91.35(4)	O2 ⁱ -Ca1-O1	73.60(3)	O12 ^v -Ca2-O12 ⁱ	73.25(3)
O2 ⁱⁱ -Ca1-O2	74.10(3)	O1 ⁱ -Ca1-O1	99.76(4)	O12 ^{vi} -Ca2-O12 ⁱ	124.33(3)
O2 ⁱⁱⁱ -Ca1-O2	129.45(4)	O32 ⁱ -Ca2-O32	84.19(6)	O11 ⁱ -Ca2-O12 ⁱ	51.20(3)
O31-Ca1-O2 ⁱ	91.35(4)	O32 ⁱ -Ca2-O12 ^v	84.26(4)	O11-Ca2-O12 ⁱ	78.75(3)
O31 ⁱ -Ca1-O2 ⁱ	150.74(3)	O32-Ca2-O12 ^v	81.01(4)	O32 ⁱ -Ca2-O12	107.47(4)
O2 ⁱⁱ -Ca1-O2 ⁱ	129.45(4)	O32 ⁱ -Ca2-O12 ^{vi}	81.01(4)	O32-Ca2-O12	152.28(3)
O2 ⁱⁱⁱ -Ca1-O2 ⁱ	74.10(3)	O32-Ca2-O12 ^{vi}	84.26(4)	O12 ^v -Ca2-O12	124.33(3)
O2-Ca1-O2 ⁱ	87.63(5)	O12 ^v -Ca2-O12 ^{vi}	160.11(5)	O12 ^{vi} -Ca2-O12	73.25(3)
O31-Ca1-O1 ⁱ	83.55(4)	O32 ⁱ -Ca2-O11 ⁱ	156.28(4)	O11 ⁱ -Ca2-O12	78.75(3)
O31 ⁱ -Ca1-O1 ⁱ	155.85(4)	O32-Ca2-O11 ⁱ	81.25(4)	O11-Ca2-O12	51.20(3)
O2 ⁱⁱ -Ca1-O1 ⁱ	79.87(3)	O12 ^v -Ca2-O11 ⁱ	111.62(3)	O12 ⁱ -Ca2-O12	73.99(4)
O2 ⁱⁱⁱ -Ca1-O1 ⁱ	119.91(3)	O12 ^{vi} -Ca2-O11 ⁱ	79.00(3)		

Symmetry transformations used to generate equivalent atoms: i) -x+1, y, -z+1/2 ii) -x+1, -y+3, -z iii) x, -y+3, z+1/2 iv) -x+1, -y+3, -z+1 v) x, -y+2, z-1/2 vi) -x+1, -y+2, -z+1

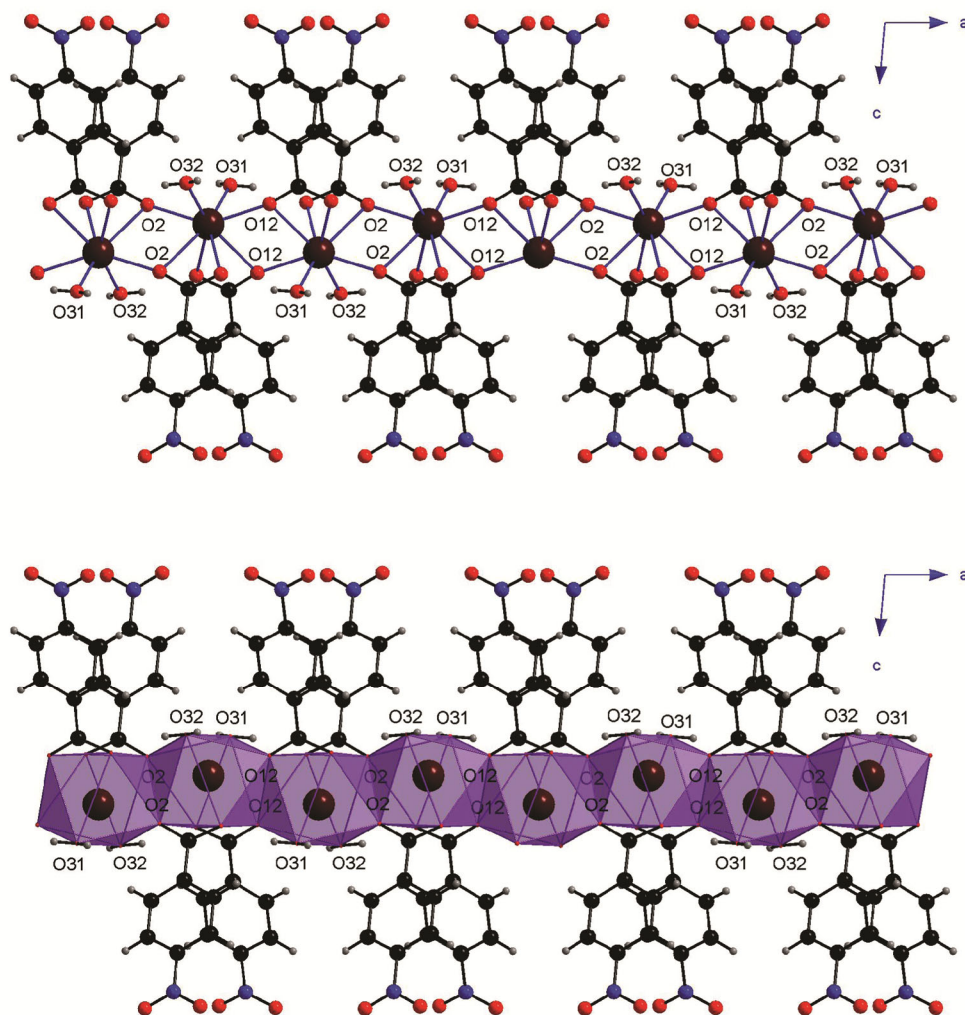


Fig. 2 — (top & bottom) A view along '*b*' showing a portion of an infinite chain extending along *a*-axis due to the $\mu_2\text{-}\eta^2\text{:}\eta^1$ tridentate binding modes of the unique ligands (O1, O2) and (O11, O12) with alternating Ca \cdots Ca separations. Each Ca(II) in the chain is bonded to two monodentate water ligands O31 and O32 (**top**). The central chain of edge-sharing $\{\text{CaO}_8\}$ polyhedra is flanked by the 4-nitrobenzoates. O2 and O12 are the oxygen atoms at the shared edges (**bottom**).

unique Ca(II) ions, Ca1 is bonded to one unique ligand (O1, O2) and one unique water (O31). Similarly, the second unique Ca2 is bonded to (O11, O12) and O32. The two terminal water molecules on Ca1 (or Ca2) can be accounted for by the symmetry generated aqua ligand O31¹ (or O32¹). Thus each Ca(II) is bonded to two oxygen atoms of monodentate water and six O atoms from four symmetry related 4-nba anions, resulting in a distorted square antiprismatic $\{\text{CaO}_8\}$ polyhedron (Fig. S7) as in **1**. Unlike in **1**, the bond distances involving the terminal aqua ligands viz. Ca1-O31 (or the Ca2-O32) are the shortest at 2.3561(11) Å (2.3584(11)). The Ca1-O (Ca2-O) bond distances vary between 2.3561(11) and 2.7422(10) Å (2.3584(11) and 2.5696(10) for Ca2),

while the O-Ca-O angles scatter in a very broad range from 49.64(3) to 155.85(4)° (51.20(3) to 160.11(5) for Ca2) indicating the distortion of the $\{\text{CaO}_8\}$ coordination polyhedra. Both the unique 4-nba ligands behave as $\mu_2\text{-}\eta^2\text{:}\eta^1$ bridging tridentate ligands (Fig. S7) resulting in the formation of a tricyclic dicalcium-di(4-nitrobenzoate) building unit of the coordination polymer. The formation of a one-dimensional polymeric structure can be explained on similar lines as for **1**. Unlike in **1**, two different chains (one for each unique Ca) with both extending along the direction of *c* axis are formed (Supplementary Data, Fig. S8). In view of the special position of Ca1 (or Ca2), each chain exhibits a single Ca \cdots Ca separation of 3.8569(4) Å (or 4.0164(4) Å in the case

Table 3 — Geometric parameters (Å, °) of the hydrogen bonding interactions

D-H...A	d(D-H)	d(H...A)	<DHA	d(D...A)	Symmetry code
Compound 1					
O32-H32B...O11 ⁱⁱ	0.77(4)	2.02(4)	169(4)	2.777(3)	-x, -y+1, -z+2
O32-H32A...N21	0.82(4)	2.01(4)	170(4)	2.828(4)	x, y, z
O31-H31B...N22 ⁱⁱⁱ	0.83(4)	2.00(4)	168(4)	2.816(3)	x-1, y-1, z
O31-H31A...O1 ^{iv}	0.83(4)	1.98(4)	167(3)	2.788(3)	x+1, y, z
C2-H2...O31	0.930(4)	2.629(6)	131.68(19)	3.321(8)	x, y, z
C3-H3...O13	0.929(4)	2.584(5)	157.15(21)	3.459(7)	x, y, z-1
C5-H5...O4	0.929(4)	2.657(8)	167.82(22)	3.571(10)	-x-1, -y, 1-z
C16-H6...O32	0.930(4)	2.625(6)	130.31(19)	3.304(7)	1-x, 1-y, 2-z
C24-H24...O1	0.930(5)	2.601(5)	165.28(25)	3.508(8)	-x, 1-y, 2-z
C28-H28...O11	0.930(4)	2.695(8)	160.36(25)	3.585(11)	1+x, 1+y, z
C30-H30...O3	0.929(4)	2.708(6)	127.38(18)	3.355(8)	1-x, 1-y, 1-z
Compound 2					
O31-H31A...N23 ^{viii}	0.82(2)	1.97(2)	173.0(19)	2.7869(17)	x+1/2, y+1/2, z
O31-H31B...O1 ^{iv}	0.81(2)	2.03(2)	169.7(19)	2.8250(16)	-x+1, -y+3, -z+1
O32-H32A...O3	0.81(3)	2.24(3)	169(2)	3.0338(17)	x, y, z
O32-H32B...N22	0.82(2)	2.01(2)	169.9(19)	2.8228(17)	x, y, z
N21-H21N...O11 ⁱ	0.87(2)	1.89(2)	162.7(19)	2.7271(17)	-x+1, y, -z+1/2
C2-H2...O31	0.930(2)	2.535(1)	162.28(9)	3.433(2)	x, 3-y, -1/2+z
C5-H5...O13	0.929(2)	2.622(2)	166.21(10)	3.531(3)	-1/2+x, 1/2+y, z
C16-H16...O3	0.930(2)	2.599(1)	128.33(10)	3.258(3)	x, 2-y, 1/2+z
C22-H22...O1	0.930(2)	2.498(1)	145.26(12)	3.305(2)	1/2-x, -1/2+y, 1/2-z

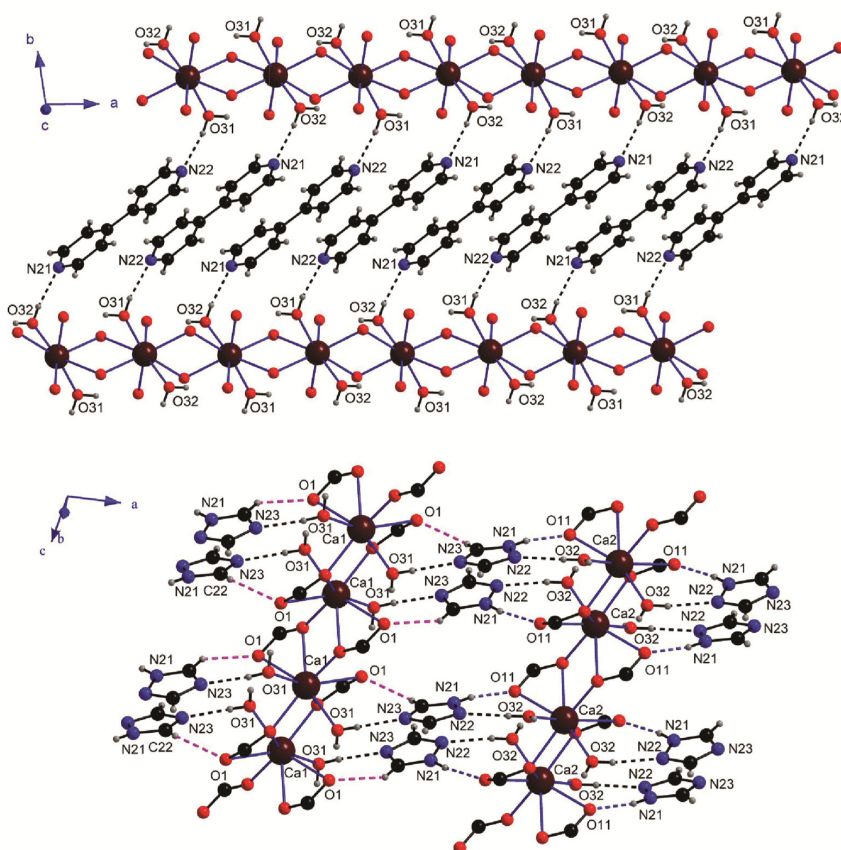


Fig. 3 — The 4,4'-bipyridine solvate links adjacent chains with the aid of O-H...N interactions involving the coordinated waters (O31 and O32) and the N21 and N22 atoms of 4,4'-bipyridine in compound **1** (top). A view showing that 1,2,4-triazole serving as link between chains of Ca1 and Ca2 in **2** with the aid of H-bonding interactions (bottom). For clarity only the oxygen atoms of the carboxylate coordinated to Ca(II) is shown

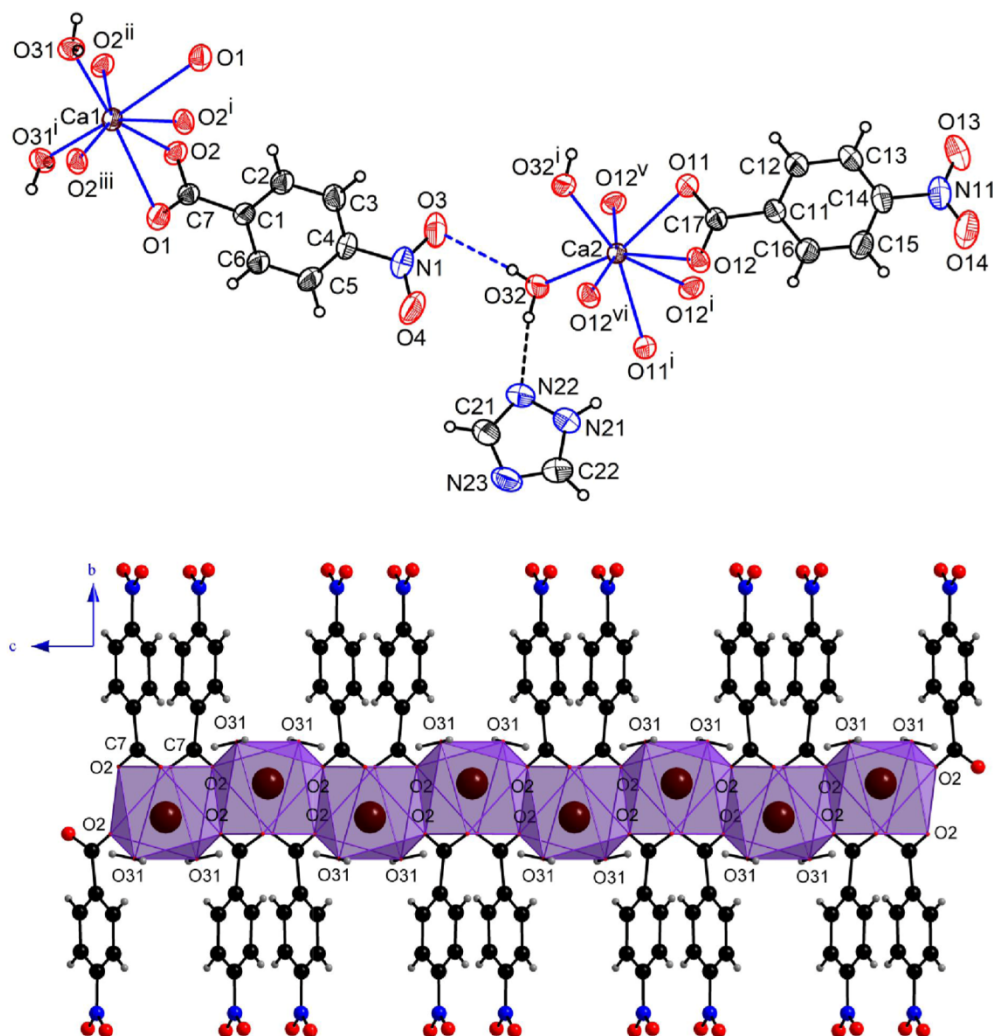


Fig. 4 — The crystal structure of **2** showing the atom labelling scheme and the eight coordination around the unique Ca(II). Displacement ellipsoids are drawn at the 50% probability level for the non-hydrogen atoms. Intramolecular H-bonding is shown in broken lines. Symmetry code: i) $-x+1, y, -z+1/2$, ii) $-x+1, -y+3, -z$, iii) $x, -y+3, z+1/2$, iv) $-x+1, -y+3, -z+1$, v) $x, -y+2, z-1/2$, vi) $-x+1, -y+2, -z+1$ (**top**). A view along '*a*' showing a portion of an infinite chain extending along *c*-axis due to the $\mu_2\text{-}\eta^2\text{:}\eta^1$ tridentate binding mode of the first unique ligand (O1, O2) with $\text{Ca1}\cdots\text{Ca1}$ separations of 3.8569(4) Å. (See Fig S8) Each Ca1 in the chain is bonded to two monodentate water ligands O31 and O31ⁱ. The edge-sharing $\{\text{CaO}_8\}$ polyhedral chain is flanked by the 4-nitrobenzoate wings (**bottom**).

of Ca2). As in **1** the $\{\text{CaO}_8\}$ polyhedral chain exhibits an edge-sharing architecture (Fig. 4, Supplementary Data, Fig S8) and is flanked by 4-nitrobenzoate wings.

Compound **2** exhibits four varieties of hydrogen bonding interactions (Table 3) viz. O-H \cdots N, O-H \cdots O, N-H \cdots O and C-H \cdots O, respectively. All of the hydrogen atoms attached to the terminal waters O31 and O32, the H21N and H22 attached to N21 and C22 of 1,2,4-triazole and the hydrogen atoms H2, H5 and H16 of the unique 4-nba function as hydrogen donors while the oxygen atoms, O1, O3, O11, O13 and O31 and the nitrogen atoms N22 and N23 of 1,2,4-triazole function as hydrogen acceptors resulting in a total of

nine hydrogen bonds. The 1,2,4-triazole molecule functions as a solvate and is not bonded to Ca(II). Instead the N-heterocycle links the one-dimensional chain of Ca1 with the chain of Ca2 via O31-H31A \cdots N23, O32-H32B \cdots N22, C22-H22-O1 and N21-H21N \cdots O11 hydrogen bonding interactions (Fig. 3). As a result the structure is organized in the following sequence viz. chain 1(Ca1) \cdots 1,2,4-triazole \cdots chain 2 (Ca2) \cdots 1,2,4-triazole and so on.

In addition to compounds **1** and **2** described in this work, ten more structures of Ca(II) compounds based on 4-nitrobenzoic acid are archived in the Cambridge Structural Database (CSD)³⁷. The rich and variable structural chemistry of calcium can be evidenced from

Table 4 — Comparative structural features of 4-nitrobenzoates (4-nba) of Ca(II)

Compound	S.G.	C.N. ^a	C.S	binding mode of 4-nba	D	{CaOx} linking	Ref.
[Ca(NMF) ₂ (4-nba) ₂] ^b	<i>P</i> $\bar{1}$	6 (4)	{CaO ₆ }	$\mu_2\text{-}\eta^1\text{:}\eta^1$	1	Type 1 ^e	39
[Ca(BA) ₂ (4-nba) ₂] ^b	<i>C2/c</i>	6 (4)	{CaO ₆ }	$\mu_2\text{-}\eta^1\text{:}\eta^1$	1	Type 1 ^e	39
[Ca(pyr) ₂ (4-nba) ₂] ^b	<i>P</i> $\bar{1}$	6 (4)	{CaO ₄ N ₂ }	$\mu_2\text{-}\eta^1\text{:}\eta^1$	1	Type 1a ^f	40
[Ca(L ¹)(4-nba) ₂]	<i>P</i> $\bar{1}$	6 (5)	{CaO ₅ N}	$\mu_2\text{-}\eta^1\text{:}\eta^1, \mu_3\text{-}\eta^2\text{:}\eta^1$	1	Type 2 ^g	34
[Ca(H ₂ O)(L ²)(4-nba) ₂]	<i>P2₁/n</i>	7 (4)	{CaO ₆ N}	$\mu_2\text{-}\eta^1\text{:}\eta^1, \mu_2\text{-}\eta^2$	1	Type 3 ^h	35
[Ca(H ₂ O) ₂ (4-nba) ₂] \cdot 2dmp	<i>P</i> $\bar{1}$	8 (4)	{CaO ₈ }	$\mu_2\text{-}\eta^2\text{:}\eta^1, \mu_2\text{-}\eta^2\text{:}\eta^1$	1	Edge-sharing	38
[Ca(H ₂ O) ₂ (4-nba) ₂] \cdot L 1	<i>P</i> $\bar{1}$	8 (4)	{CaO ₈ }	$\mu_2\text{-}\eta^2\text{:}\eta^1, \mu_2\text{-}\eta^2\text{:}\eta^1$	1	Edge-sharing	This work
[Ca(H ₂ O) ₂ (4-nba) ₂] \cdot L 2 ^c	<i>C2/c</i>	8 (4)	{CaO ₈ }, {CaO ₈ }	$\mu_2\text{-}\eta^2\text{:}\eta^1, \mu_2\text{-}\eta^2\text{:}\eta^1$	1	Edge-sharing	This work
[Ca(H ₂ O) ₄ (4-nba) ₂] 3	<i>P2₁/c</i>	7 (2)	{CaO ₇ }	η^1, η^2	0 ^d	Discrete	25
[(H ₂ O) ₄ (4-nba)Ca) ₂ (μ_2 -H ₂ O) ₂](4-nba) ₂ \cdot 8H ₂ O ^c	<i>P2₁</i>	8 (1)	{CaO ₈ }, {CaO ₈ }	η^2 , anion η^2 , anion	0 ^d	Discrete	30
[Ca(H ₂ O) ₆ (4-nba)](4-nba) \cdot (2-ap)H ₂ O	<i>P</i> $\bar{1}$	7 (1)	{CaO ₇ }	η^1 , anion	0 ^d	Discrete	41
[Ca(H ₂ O) ₅ (Im)(4-nba) ₂] \cdot Im	<i>P2₁/c</i>	6 (2)	{CaO ₅ N}	η^1, η^1	0 ^d	Discrete	42

Abbreviations used: S.G.= space group; C.N. =Coordination number ^aNumber in parentheses is the number of 4-nba linked to each unique Ca; C.S = Coordination sphere; D=Dimensionality; ^bunique 4-nba ligand; ^ctwo unique Ca(II); ^dmolecular solid;

^echain of {CaO₆} octahedra bridged by two carboxylate C; ^fchain of {CaO₄N₂} octahedra bridged by two carboxylate C; ^gchain of edge sharing {CaO₅N} bioctahedra bridged by four carboxylate carbons; ^hedge-sharing {CaO₆N} polyhedra with a carboxylate C bridge; NMF = N-methyl-formamide; BA = benzamide; pyr = pyrazole; L¹ = N-methylimidazole; L² = 2-methylimidazole; dmp = 3,5-dimethylpyrazole; 2-ap = 2-aminopyridine; Im = imidazole

the structurally characterized 4-nitrobenzoate compounds of Ca(II) listed in Table 4^{25,30,34,35,38-42}. In all these compounds (except entry No. 10) which crystallize in centrosymmetric space groups, the coordination number of the central metal varies from six (entry nos. 1-4 and 12) to eight showing the structural flexibility of Ca(II). Although this list has four examples of Ca(II) bonded to N-donor ligands, the oxophilic nature of Ca can still be evidenced by the fact that a maximum of two N-donor ligands (entry no. 3) can be incorporated into the calcium coordination sphere. Excepting the last four entries in Table 4 which are molecular solids, the rest are one-dimensional (1D) coordination polymers and contain one or two or no coordinated water molecules. In seven of the eight coordination polymers each Ca(II) is bonded to four carboxylate groups as originally predicted by Einspaar and Bugg⁴³ for calcium carboxylates. In the molecular solids each Ca(II) is bonded to either one^{30,41} or two^{25,42} 4-nitrobenzoates. In addition to being a charge balancing anion in all the compounds, the 4-nitrobenzoate moiety functions as a monodentate (η^1) or bidentate (η^2) or a bridging ligand. In all the 1-D coordination polymers, the 4-nba ligand exhibits a bridging binding mode which is responsible for the extended structure. Although both μ_2 - and μ_3 -bridging binding modes are observed

the symmetric $\mu_2\text{-}\eta^1\text{:}\eta^1$ binding mode is observed in five compounds and the $\mu_2\text{-}\eta^2\text{:}\eta^1$ tridentate binding mode is observed in four different compounds including **1** and **2**. In addition, $\mu_2\text{-}\eta^2$ bridging where only one carboxylate oxygen binds to two different Ca(II) (entry no. 5) and a $\mu_3\text{-}\eta^2\text{:}\eta^1$ bridging tridentate binding mode are also observed. Only three coordination polymers in Table 4 have a maximum of two moles of water, while four are anhydrous. The degree of hydration of a Ca(II)-carboxylate is an important property which determines its structure. In the case of 4-nitrobenzoic acid linker, the degree of hydration can explain the dimensionality of the Ca(II) compound as [Ca(H₂O)₄(4-nba)₂]**3** containing four coordinated water molecules is a molecular solid (zero dimensional) while the partial removal of the water molecules as in **1** (or **2**) leads to a chain structure. The coordination polymers listed in Table 4 exhibit different kinds of polyhedral linking. For example, the chain of {CaO₆} octahedra (entry nos 1 and 2) are bridged by a pair of carboxylate carbon atoms (Supplementary Data, Fig. S9). A similar bridging by carboxylate C is observed for the anhydrous coordination polymer [Ca(pyr)₂(4-nba)₂] (pyr=pyrazole) but the octahedra in this case are made up of {CaN₂O₄} (Supplementary Data, Fig. S9). In the ladder coordination polymer [Ca(L¹)(4-nba)₂]

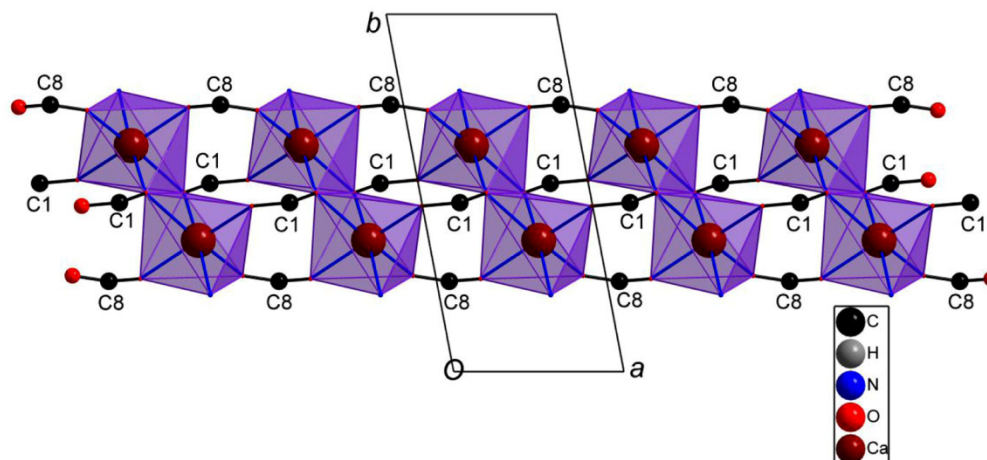


Fig. 5 — A chain of edge-sharing bioctahedra bridged by four carboxylate carbon atoms in $[\text{Ca}(\text{L}^1)(4\text{-nba})_2]$ ($\text{L}^1 = \text{N-methyl-imidazole}$). For clarity only the N atom of L^1 , oxygen atoms of the carboxylate and the bridging carbons are shown. (Fig S12 shows all the ligand atoms)

($\text{L}^1 = \text{N-methylimidazole}$) $\{\text{CaNO}_3\}$ edge-sharing bioctahedra bridged by four carboxylate carbons are linked into an infinite chain (Fig. 5, Supplementary Data, Fig. S10). In the case of the seven coordinated mixed ligand Ca(II) compound $[\text{Ca}(\text{H}_2\text{O})(\text{L}^2)(4\text{-nba})_2]$ $\text{L}^2 = 2\text{-methylimidazole}$, the $\{\text{CaO}_6\text{N}\}$ polyhedra exhibit an edge sharing architecture like the title compounds. Interestingly the adjacent polyhedra in the chain are bridged by a carboxylate carbon resulting in an infinite chain (Fig. S10). A study of this series of compounds reveals that the presence of each of a symmetric bridging ($\mu_2\text{-}\eta^1:\eta^1$) ligand results in the polyhedra being bridged by a carboxylate carbon. The eight coordinated title compounds **1** and **2** and $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}$ exhibit an edge sharing architecture of the $\{\text{CaO}_8\}$ polyhedra.

Conclusions

The synthesis, spectra and structures of two new calcium coordination polymers based on a chain of edge sharing $\{\text{CaO}_8\}$ polyhedra are reported. A comparative study of eight Ca(II) coordination polymers based on the 4-nitrobenzoate linker reveals a rich and variable structural chemistry. The two calcium coordination polymers described herein are two new additions to a growing list of structurally characterized alkaline-earth metal coordination polymers based on 4-nitrobenzoic acid linker.

Supplementary Data

Deposition Numbers CCDC 892774 and CCDC 892773 contain the supplementary crystallographic data for the structures of (**1**) and (**2**) described in this

paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures. Supplementary Data associated with this article are available in the electronic form at [http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A\(06\)785-796_SupplData.pdf](http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(06)785-796_SupplData.pdf).

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