

A new calcium(II) coordination polymer based on a μ_2 -bridging tridentate 4-nitrobenzoate

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Reaction of a heptacoordinated Ca(II) compound $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (4-nba = 4-nitrobenzoate) with 3,5-dimethylpyrazole (dmp) leads to the formation of an eight coordinated Ca(II) compound, $[[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}]_n$, containing two coordinated water molecules, two unique 4-nba ligands and two free dmp molecules in the lattice. The μ_2 -bridging tridentate binding mode of the unique 4-nba ligands results in the formation of a one-dimensional (1-D) coordination polymer. The title compound exhibits enhanced fluorescence emission. An analysis of the six different bridging binding modes of the 4-nba ligand in twenty two different structurally characterized 4-nitrobenzoate compounds is described.

Keywords: Coordination chemistry, Calcium, 4-Nitrobenzoates, 3,5-Dimethylpyrazole, Coordination polymers, Metal organic frameworks

Coordination polymers (CPs) also known as metal organic frameworks (MOFs) have attracted much attention because of their topology and applications in catalysis, adsorption (gas storage), separation and luminescence¹⁻³. Compared to the extensive chemistry of CPs based on transition metals, the coordination chemistry of *s*-block metals with organic linkers has remained a relatively less explored area. The reluctance in using alkali metal or alkaline earth cations as building blocks for open framework materials can be attributed to their unpredictable coordination numbers and geometries as no ligand field stabilization effects govern their bonding. Although the closed shell *s*-block metal cations lack useful properties like magnetism or variable oxidation states, alkali and alkaline-earth metals are preferred to transition or lanthanide metal ions because many of the *s*-block cations have the advantage of being non-toxic, cheap and soluble in aqueous media. Several recent reports reveal the growing interest in the coordination chemistry of *s*-block elements⁴⁻¹⁷ and the chemistry of *s*-block metal compounds has been recently reviewed^{18,19}.

Depending on the electronic and steric requirements of the central metal, the flexibility, binding modes and hydrogen bonding characteristics of the organic ligand, coordination polymers of

differing dimensionalities can be constructed. For the oxophilic *s*-block metals, carboxylic acids are useful linkers for the construction of coordination polymers as the metals can be linked into an extended chain with the aid of bridging binding modes of the carboxylate ligand. In view of their known affinity for oxygen donors, especially water, *s*-block metal carboxylates are normally synthesized in aqueous medium by reactions between alkaline earth metal sources and aromatic carboxylic acids under ambient conditions^{13-17,20-30}. Reaction of metal source with carboxylic acids under hydrothermal conditions is another method employed by many groups for compound synthesis⁵⁻¹².

As part of an ongoing research program we are investigating the chemistry of alkaline earth nitrocarboxylates³⁰. The seven coordinated Ca(II) compound $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ ³¹ (**1**) reported by us in a very early work differs from several other Ca-carboxylates in that the 4-nba ligand does not exhibit bridging coordination. We have shown in earlier work^{32,35} that on reaction with N-donor ligands the zero-dimensional compound, $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$, can be transformed into mixed ligand Ca(II) compounds containing less or no water as evidenced by the characterization of $[\text{Ca}(\text{Im})(\text{H}_2\text{O})_3(4\text{-nba})_2]\cdot \text{Im}$ ³², $[\text{Ca}(\text{N-MeIm})(4\text{-nba})_2]_n$, $[\text{Ca}(\text{H}_2\text{O})(2\text{-MeIm})(4\text{-nba})_2]_n$

and $[\text{Ca}(\text{pyr})_2(4\text{-nba})_2]_n$ (Im = imidazole³³; N-MeIm = N-methylimidazole³³; 2-MeIm = 2-methylimidazole³⁴; pyr = pyrazole³⁰). Recently we reported that compound (1) on reaction with 2-aminopyridine in an aqueous medium is transformed into a water-rich Ca(II) compound³⁵. In this work, we have investigated the reaction of $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ with 3,5-dimethylpyrazole (dmp) and the results of this research are described herein.

Materials and Methods

All the chemicals used in this study were of reagent grade and were used as received. The starting materials and reaction products are air stable and hence were prepared under normal laboratory conditions. The compound $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (1) was prepared by a published procedure^{31,35}. 3,5-Dimethylpyrazole (dmp) was prepared by condensation of acetylacetone with hydrazine³⁶. 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 spectra were recorded on a Shimadzu UV-2450 double beam spectrophotometer. X-ray powder pattern were recorded on a Rigaku Miniflex II diffractometer using Cu-K_α radiation. Photoluminescence of solid samples was studied using a Perkin Elmer LS55 fluorescence spectrometer. TG-DTA 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 weight loss studies were performed in a temperature controlled electric furnace.

Preparation of $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2] \cdot 2\text{dmp}]_n$ (2)

A mixture of $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (1) (0.445 g, 1 mmol) and 3,5-dimethylpyrazole (0.392 g, 4 mmol) was taken in water (~5 mL) and the reaction mixture was heated on a steam bath to obtain a clear solution. The clear reaction mixture was left aside for crystallization. The pale yellow crystalline blocks suitable for structure determination which separated after ~3 h were isolated by filtration, washed with a little ice cold water followed by ether and air dried. $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2] \cdot 2\text{dmp}]_n$ (2) (Yield 0.46 g, 77%). Anal. (%): Found (calcd) for $\text{CaC}_{24}\text{H}_{28}\text{N}_6\text{O}_{10}$ (600.60): C 46.92 (48.00), H 4.54 (4.70), N 13.75 (13.99), CaO 9.2 (9.34). 4-nbaH 54.84 (55.65). IR (KBr cm^{-1}): 3600 (br, ν_{OH}), 3387, 3269 (ν_{NH}), 3148, 3105, 1614, 1568 $\nu_{\text{as}}(-\text{COO})$, 1514 $\nu_{\text{as}}(-\text{NO}_2)$,

1416 $\nu_{\text{s}}(-\text{COO})$, 1342 $\nu_{\text{s}}(-\text{NO}_2)$, 1317, 1288, 1151, 1105, 1015, 974, 878, 843, 797, 726, 694, 660, 592, 511. DTA data (in $^\circ\text{C}$): 110 (endo), 236 (endo), 411 (exo), 545 (exo).

X-ray crystal structure determination

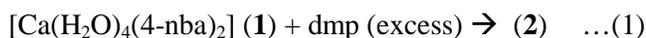
Intensity data for (2) were collected on an Image Plate Diffraction System (IPDS-II) from STOE. All non-hydrogen atoms were refined using anisotropic displacement parameters. The C-H hydrogen atoms were positioned with idealized geometry and refined using a riding model. The hydrogen atoms attached to the O21 and O22 of water and N21 and N31 of lattice dmp were located in the difference map and were refined isotropically using a riding model. Crystal data of (2) $\text{C}_{24}\text{H}_{28}\text{CaN}_6\text{O}_{10}$, $M = 600.60 \text{ g mol}^{-1}$, triclinic, space group = $P\bar{1}$, $\lambda = 0.71073 \text{ \AA}$, $a = 7.4030(4) \text{ \AA}$, $b = 14.4078(7) \text{ \AA}$, $c = 14.8293(6) \text{ \AA}$, $\alpha = 110.419(3)^\circ$, $\beta = 91.214(4)^\circ$, $\gamma = 99.765(4)^\circ$, $V = 1455.31(12) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.371 \text{ mg m}^{-3}$, $\mu = 0.278 \text{ mm}^{-1}$, $F(000) = 628$, index range = $-9 \leq h \leq 9$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$; completeness to $\theta = 26.00^\circ$ (99.8 %). A total of 17792 reflections ($1.54 < \theta < 26.0^\circ$) were collected, of which 5713 were unique ($R_{\text{int}} = 0.0624$) and used for the structure solution. Structure was solved using SHELXS-97³⁷ and refined using SHELXL-97³⁷ to $R1$ ($wR2$) = 0.0577 (0.1103) for 4473 reflections with ($I > 2\sigma(I)$) using 374 parameters. The final Fourier difference synthesis showed minimum and maximum peaks of -0.187 and $+0.254 \text{ e \AA}^{-3}$.

Results and Discussion

Synthetic aspects, spectral and thermal studies

The nature of products of the reaction of CaCO_3 with the isomeric 2- or 4-nitrobenzoic acids depends on the positioning of the nitro group with respect to the carboxylate functionality in the aromatic ring as can be evidenced by the formation of a one-dimensional polymer $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$ for the *ortho* isomer¹⁷, while a zero-dimensional compound $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (1) is the only isolable product for the *para* isomer^{31,35}. In earlier works we have demonstrated that N-donor ligands like N-methylimidazole³³ (N-MeIm), 2-methylimidazole³⁴ (2-MeIm), pyrazole³⁰ (pyr) and imidazole³² (Im) can be incorporated into the coordination sphere of Ca(II) by an aqueous reaction of the zero-dimensional compound $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (1) with an excess of N-donor ligand. Use of excess ligand is essential

to suppress the hydrolysis of mixed ligand compounds into the starting tetraqua compound (1) (Supplementary Data Fig. S1). In the present study we have investigated the reaction of (1) with an excess of 3,5-dimethylpyrazole, which results in the formation of a new Ca(II) coordination polymer (2) as shown in Eq. 1. In contrast, reaction of $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$ with dmp under similar conditions does not result in the formation of any new product.



The formation of a new crystalline product was evidenced based on a comparison of the powder diffractograms of the starting material and (2) (Supplementary Data Fig. S2). Thermal and analytical data provide additional evidence for the proposed formula. Pyrolysis of (2) leads to the formation of binary oxide, while reaction with dilute HCl results in decomposition leading to the quantitative formation of insoluble 4-nbaH, which can be filtered and weighed as described earlier³⁸. The composition of (2) was arrived at based on elemental analysis, 4-nbaH content obtained by acidification and CaO formed on pyrolysis and weight loss studies. Analytical data of (2) indicates the presence of Ca:4-nba:dmp:water in a 1:2:2:2 ratio. The two moles each of water and dmp in (2) can be accounted for by two coordinated water molecules and two lattice dmp molecules based on the single crystal data (*vide infra*).

The diffuse reflectance spectrum of compound (2) (Supplementary Data Fig. S3) with a strong signal at ~280 nm is very similar to that of the free acid and can be assigned to the intramolecular charge transfer transition of 4-nitrobenzoate. The UV-vis spectrum of a dilute aqueous solution of (2) is identical to that of the spectrum of compound (1) (Supplementary Data Fig. S4) indicating the transformation of (2) to (1) on hydrolysis. Unlike the polymeric $[\text{Ca}(\text{N-MeIm})(4\text{-nba})_2]_n$ compound which exhibits a diminished fluorescence emission intensity, the fluorescence emission spectrum of compound (2) shows an enhanced emission as compared to that of free 4-nbaH (Fig. 1). These emissions are neither ligand-to-metal charge transfer (LMCT) nor metal-to-ligand charge transfer (MLCT) and can be assigned to the intraligand fluorescent emission. The luminescent property of (2) can be attributed to ligand centered π or n to π^* orbital transitions since similar emissions are also observed for the free

ligand. The IR spectrum of (2) exhibits several sharp bands in the mid-infrared region, indicating the presence of the organic moieties. A comparison of the IR spectra of (2) and that of $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (1) (Supplementary Data Fig. S5) reveals changes in profile of the spectra in the 3000-3500 cm^{-1} region and the 1600-1300 cm^{-1} region due to the differently hydrated nature of (1) and (2). Although the IR spectrum of (2) exhibits absorptions due to the vibrations of the carboxylate and nitro groups, no definite conclusions can be drawn on the exact nature of the binding of the 4-nba ligand based only on IR data. The symmetric (ν_s) and asymmetric (ν_{as}) stretching vibrations of the carboxylate group are observed at 1568 and 1416 cm^{-1} , while those of the nitro group are observed at around 1514 and 1342 cm^{-1} .

The TG-DTA thermogram of (2) (Supplementary Data Fig. S6) exhibits two endothermic processes at 110 and 236 $^\circ\text{C}$ which can be assigned to the loss of the neutral water ligands and lattice dmp molecules respectively. The strong exothermic signal observed at 411 $^\circ\text{C}$ and a further exothermic event at 545 $^\circ\text{C}$ can be attributed to the decomposition of the 4-nitrobenzoate leading to the formation of a binary oxide material. Exothermic events assignable for the decomposition of 4-nba have been reported by us for the coordination polymers $[\text{Ca}(\text{N-MeIm})(4\text{-nba})_2]_n$, $[\text{Ca}(\text{H}_2\text{O})(2\text{-MeIm})(4\text{-nba})_2]_n$ and $[\text{Ca}(\text{pyr})_2(4\text{-nba})_2]_n$ at 412, 410 and 421 $^\circ\text{C}$ respectively. The removal of organics was evidenced by the featureless infrared spectrum of the residue, while the formation of CaO as the final residue was further confirmed based on isothermal weight loss studies by heating

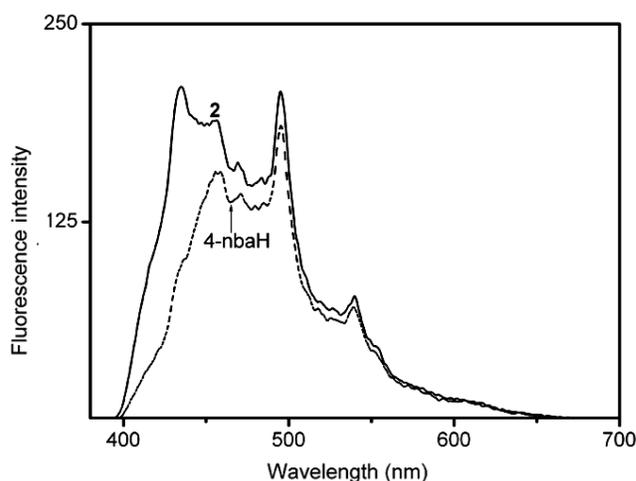


Fig. 1 — Fluorescence spectra of 4-nbaH and the complex, $[[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2] \cdot 2\text{dmp}]_n$ (2).

compound (**2**) at 800 °C in a temperature controlled furnace. The results of the isothermal weight loss studies add more credence to the thermal data.

Crystal structure of $[[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}]_n$ (**2**)

Compound (**2**) crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with all atoms situated in general positions. The crystal structure consists of a central Ca(II), two terminal water ligands, two crystallographically independent 4-nba ligands and two free 3,5-dimethylpyrazole molecules in the lattice (Fig. 2). The central metal is eight coordinated and is bonded to two oxygen atoms of two terminal aqua ligands and six oxygen atoms from four symmetry related 4-nba anions. The coordination polyhedron around Ca can perhaps be best described as a distorted trigonal prism that has two of its rectangular faces capped. In compound (**2**), the atoms O2ⁱ and O11 on the rectangular faces function as capping atoms (Fig. 2). The geometric parameters of the 4-nba ligand and the lattice dmp molecules are in the normal range. The observed Ca-O bond distances vary between 2.334(2) to 2.6995(19) Å (Table 1) while the O-Ca-O angles range from 49.47(5) to 155.36(6)°. The Ca(II) is linked to the O21 and O22 atoms of the water molecules at 2.334(2) and 2.3476(19) Å respectively. Based on a study of the structural chemistry of several Ca(II)-carboxylates, we have shown that in Ca(II) carboxylates containing three or fewer coordinated water molecules the carboxylate ligand adopts a bridging ligation leading to the formation of a chain polymer¹⁷. In accordance with this, compound (**2**) which contains two coordinated water molecules exhibits a polymeric chain

structure. Several polymeric complexes containing Ca:coordinated water in a 1:2 ratio have been reported in the literature^{17,39-42}.

Each formula unit of (**2**) contains a Ca(II) coordinated to two aqua ligands and two unique 4-nitrobenzoate ligands both of which function as μ_2 -bridging tridentate (μ_2 -²:¹) ligands. The first unique μ_2 -²:¹ 4-nba ligand (O1, O2) binds to Ca(II) in a bidentate fashion with Ca1-O1 and Ca1-O2 distances of 2.6995(19) and 2.5277(19) Å respectively. The O2 oxygen is further linked to a symmetry related Ca(II) at a distance of 2.3857(16) Å, resulting in a Ca...Ca separation of 3.8893(10) Å. A pair of such μ_2 -²:¹ 4-nba ligands are linked to two Ca(II) ions resulting in the formation of a tricyclic dicalcium-dicarboxylate unit (Fig. 3) which constitutes the basic building block of the coordination polymer. This tricyclic unit differs from the well-known eight membered cyclic dimetal-dicarboxylate unit in several dinuclear carboxylates where the (-COO)⁻ functions as a symmetrical μ_2 -¹:¹ bidentate bridging ligand. The second independent 4-nba ligand (O11, O12) binds to two symmetry related Ca(II) ions in an identical fashion resulting in a tricyclic dicalcium-dicarboxylate unit with a Ca...Ca separation of 3.9083(10) Å (Supplementary Data Fig. S7). The Ca-O bond lengths formed by this ligand are different. With this ligand a Ca(II) ion is linked to the O11 and O12 oxygen atoms in a bidentate manner (Ca1-O11ⁱⁱ 2.5326(18); Ca1-O12ⁱⁱ 2.5508(18) Å) and the O11 is further linked to a second Ca(II) ion at 2.3603(16) Å. In the crystal structure of (**2**) alternating pairs of the two crystallographically

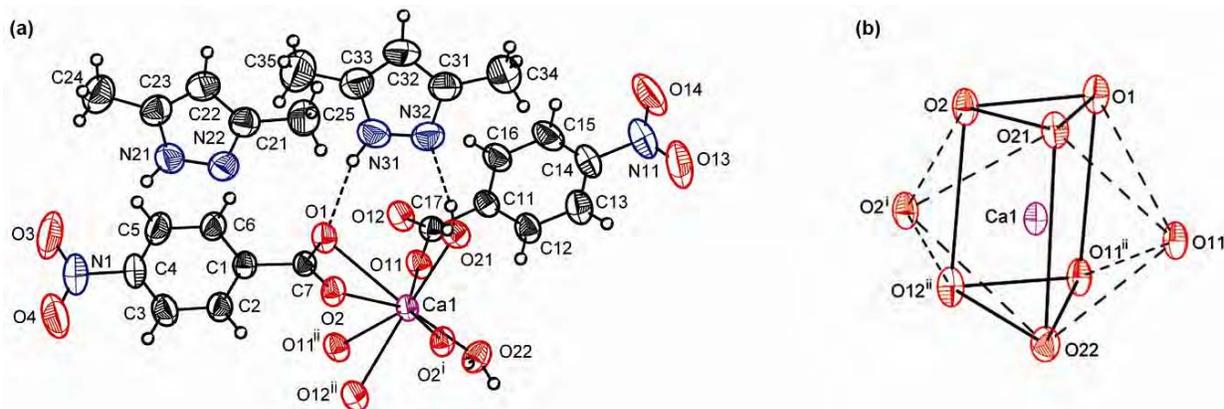


Fig. 2 — (a) Crystal structure of $[[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}]_n$ (**2**) showing atom-labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown as broken lines. (b) The distorted bicapped trigonal prismatic coordination environment of Ca1. The atoms O2ⁱ and O11 on the rectangular faces of the trigonal prism function as capping atoms. [Symmetry codes: (i) $-x+2,-y,-z+1$; (ii) $-x+1,-y,-z+1$].

Table 1 — Selected bond lengths (Å) and angles (°) for $[[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}]_n$ (**2**)

Bond lengths (Å)			
Ca1-O(22)	2.334(2)	Ca1-O(2)	2.5277(19)
Ca1-O(21)	2.3476(19)	Ca1-O(11) ⁱⁱ	2.5326(18)
Ca1-O(11)	2.3603(16)	Ca1-O(12) ⁱⁱ	2.5508(18)
Ca1-O(2) ⁱ	2.3857(16)	Ca1-O(1)	2.6995(19)
Ca1...Ca1 ⁱ	3.8893(10)	Ca1...Ca1 ⁱⁱ	3.9083(10)
Bond angles (°)			
O(22)-Ca1-O(21)	100.57(7)	O(2)-Ca1-O(11) ⁱⁱ	87.99(6)
O(22)-Ca1-O(11)	76.32(6)	O(22)-Ca1-O(12) ⁱⁱ	88.53(7)
O(21)-Ca1-O(11)	84.32(6)	O(21)-Ca1-O(12) ⁱⁱ	153.46(6)
O(22)-Ca1-O(2) ⁱ	85.47(6)	O(11)-Ca1-O(12) ⁱⁱ	122.17(6)
O(21)-Ca1-O(2) ⁱ	76.82(6)	O(2) ⁱ -Ca1-O(2) ⁱⁱ	79.15(6)
O(11)-Ca1-O(2) ⁱ	150.87(6)	O(2)-Ca1-O(12) ⁱⁱ	72.94(6)
O(22)-Ca1-O(2)	155.36(6)	O(11) ⁱⁱ -Ca1-O(12) ⁱⁱ	51.05(5)
O(21)-Ca1-O(2)	90.13(7)	O(22)-Ca1-O(1)	153.10(6)
O(11)-Ca1-O(2)	127.21(6)	O(21)-Ca1-O(1)	83.81(6)
O(2) ⁱ -Ca1-O(2)	75.37(6)	O(11)-Ca1-O(1)	77.75(6)
O(22)-Ca1-O(11) ⁱⁱ	92.87(7)	O(2) ⁱ -Ca1-O(1)	121.20(6)
O(21)-Ca1-O(11) ⁱⁱ	151.04(6)	O(2)-Ca1-O(1)	49.47(5)
O(11)-Ca1-O(11) ⁱⁱ	74.03(6)	O(11) ⁱⁱ -Ca1-O(1)	73.11(6)
O(2) ⁱ -Ca1-O(11) ⁱⁱ	130.19(6)	O(12) ⁱⁱ -Ca1-O(1)	99.32(6)

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

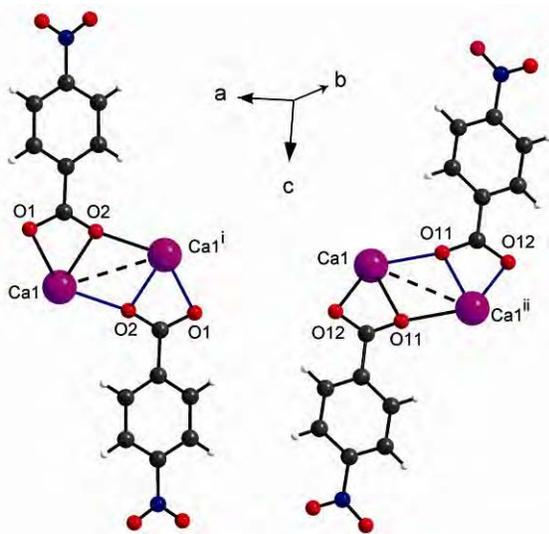


Fig. 3 — A view showing the μ_2 -^{2:1} bridging binding modes of the unique 4-nba ligands containing the donor sites (O1, O2) or (O11, O12). A pair of the unique ligands (O1, O2) or (O11, O12) bridge a pair of Ca(II) ions resulting in the formation of the tricyclic dicalcium-bis(4-nitrobenzoate) building block with a Ca1...Ca1 separation of 3.8893(10) or 3.9083(10) Å respectively.

independent μ_2 -^{2:1} 4-nba ligands link pairs of $\{\text{Ca}(\text{H}_2\text{O})_2\}^{2+}$ units into a 1-D polymeric chain extending along *a* axis (Fig. 4). As a result, alternating Ca...Ca separations of 3.8893(10) and

3.9083(10) Å respectively are observed in the infinite chain. These values are comparable to the Ca...Ca separations of 3.8585(7) and 3.8432(3) Å reported for other 4-nba based coordination polymers like $[\text{Ca}(\text{N-MeIm})(4\text{-nba})_2]_n$ ³³ and $[\text{Ca}(\text{H}_2\text{O})(2\text{-MeIm})(4\text{-nba})_2]_n$ ³⁴ respectively and shorter than the Ca...Ca separation of 5.335 Å in $[\text{Ca}(\text{pyr})_2(4\text{-nba})_2]_n$ ³⁰.

Comparison of structure of (2) with $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$

Comparison of the structure of compound (2) with that of the earlier reported $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$ ¹⁷ reveals both similarities and differences. Both compounds which crystallize in the triclinic space group *P* $\bar{1}$ contain Ca:nitrobenzoate:water in a 1:2:2 ratio and are 1-D polymers based on tricyclic dicalcium-dicarboxylate units. The central metal in both compounds are linked to four different carboxylate ligands and the binding mode of the crystallographically unique carboxylate ligand as well as the coordination sphere of the Ca(II) are identical in both compounds. Topologically both the coordination polymers are identical. Compound (2) differs from $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$ in terms of the positioning of the nitro substituent in the aromatic ring and the presence of two unique 3,5-dimethylpyrazole molecules, which are located between the one dimensional polymeric chains in

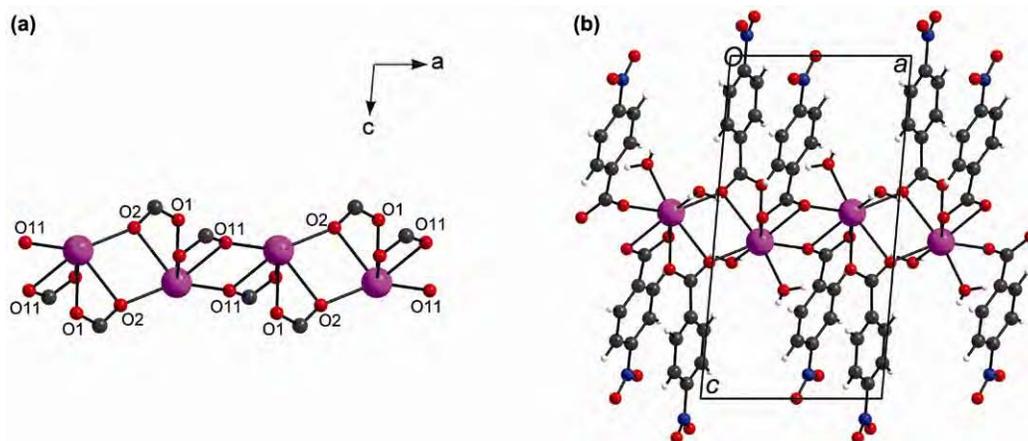


Fig. 4 – (a) A portion of the 1-D polymer of (2) viewed along *b* axis, showing the linking of tricyclic dicalcium-bis(4-nitrobenzoate) units into an infinite chain. For clarity, coordinated H_2O molecules and aromatic ring are not shown. (b) Aromatic rings and coordinated water molecules are included in the polymeric chain.

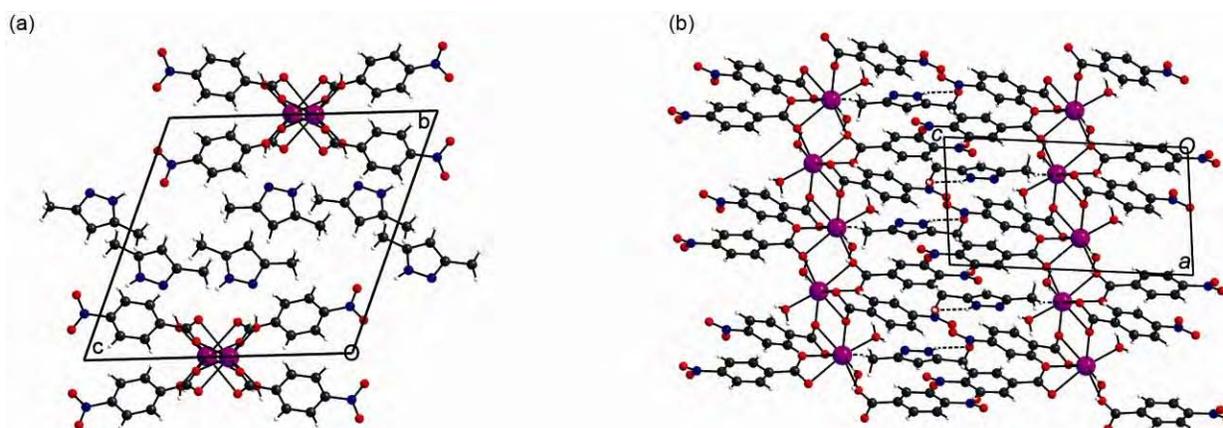


Fig. 5 — (a) A view along *a* showing the neutral dmp molecules situated between the one dimensional parallel chains. (b) A view along *b* showing the lattice dmp molecules which function as linkers between adjacent polymeric chains via H-bonding interactions shown in broken lines.

the lattice (Fig. 5). The presence of these neutral N-ligands in the lattice results in more varieties of secondary interactions, namely N-H \cdots O and O-H \cdots N, in addition to O-H \cdots O and C-H \cdots O observed in $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$. Our efforts to incorporate dmp into the lattice of $[\text{Ca}(\text{H}_2\text{O})_2(2\text{-nba})_2]_n$ in view of its structural similarity with that of (2) have not been fruitful so far.

Secondary interactions in (2)

An analysis of the crystal structure of (2) reveals that each eight coordinated Ca(II) complex in the polymeric chain is H-bonded to six neighboring complexes with the aid of four varieties of H-bonding interactions comprising of two O-H \cdots O interactions, two N-H \cdots O interactions, two O-H \cdots N interactions and three weak C-H \cdots O interactions (Supplementary

Data Fig. S8). All these O \cdots H contacts (Table 2) are shorter than the sum of their van der Waals radii. The neutral dmp molecules in the lattice function as linkers between adjacent one-dimensional chains with the aid of N21-H21 \cdots O14, O22-H30 \cdots N22 and C25-H25A \cdots O12 interactions (Fig. 5) and further extend the network. Of these, the H-bonding between the nitro oxygen (O14) and the H atom (H21) attached to the N of dmp seems to be important for the formation of (2).

Six different bridging binding modes of 4-nba ligand

The synthesis and structural characterization of several metal 4-nitrobenzoate compounds showing different binding modes^{31-35, 43-58} of the 4-nba ligand serves to demonstrate the versatile ligational behaviour of the 4-nitrobenzoate ligand. A survey of

Table 2 — Hydrogen-bonding geometry for $[[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}]_n$ (2)

D-H...A	<i>D</i> (D-H) (Å)	<i>D</i> (H...A) (Å)	<i>D</i> (D...A) (Å)	<DHA (°)	Symmetry code
N21-H21...O14	0.860	2.244	3.055	157	<i>x, y, z</i> +1
N31-H31...O1	0.860	2.058	2.889	162	<i>x, y, z</i>
O21-H10...N32	0.820	1.960	2.770	169	<i>x, y, z</i>
O21-H20...O12	0.820	1.994	2.798	166	<i>x</i> +1, <i>y, z</i>
O22-H30...N22	0.820	1.944	2.762	176	- <i>x</i> +1, - <i>y, -z</i> +1
O22-H40...O1	0.820	2.035	2.843	168	- <i>x</i> +1, - <i>y, -z</i> +1
C2-H2...O21	0.930	2.664	3.565	163	2- <i>x, -y, 1-z</i>
C3-H3...O4	0.930	2.630	3.460	149	2- <i>x, -y, 2-z</i>
C25-H25A...O12	0.959	2.576	3.452	152	<i>x, y, z</i>

the structurally characterized metal 4-nba compounds reveals that in addition to serving as a monodentate (η^1) ligand^{31,35,44,45} or a bidentate (η^2) ligand^{31,43,44}, the anionic 4-nba exhibits six different bridging binding modes (Fig. 6). An analysis of twenty two compounds (Supplementary Data Table S1) was undertaken and in these compounds only the bridging binding modes of the 4-nba ligand are considered. It is observed in all these compounds which crystallize in the centrosymmetric triclinic or monoclinic space groups, the 4-nba ligand is involved in six different bridging binding modes, four of which (mode A to D in Fig. 6) are μ_2 -bridging in nature and one each of μ_3 -bridging (mode E) and μ_4 -bridging type (mode F) respectively. Of the four μ_2 -bridging modes, there are two different symmetric $\mu_2^{-1:1}$ bridging modes, namely mode A (involving both the carboxylate oxygen atoms) and mode B (involving both the nitro oxygen atoms), observed so far in a single compound, namely, $[\text{Na}(\text{H}_2\text{O})_3(4\text{-nba})]_n$ ⁵⁷. The symmetric bridging bidentate mode A appears to be the most common as this mode is observed in seventeen compounds (77 %) and results in the formation of dimeric compounds in four cases⁴⁵⁻⁴⁸ in addition to two tetramers^{49,50} and a pentamer⁵¹ and hexamer⁵². In the remaining cases, mode A results in the formation of a chain polymer. Fourteen of the compounds are coordination polymers^{30,33-35,44,53-58} and the formation of the infinite O-M-O chain in these polymeric compounds is due to the presence of at least one of the six bridging binding modes of 4-nba. In addition to the symmetric bridging modes A and B, two more μ_2 -bridging modes, namely $\mu_2^{-2:0}$ (mode C) and $\mu_2^{-1:2}$ (mode D), are also observed in some of the compounds. In both these binding modes one of the carboxylate oxygen atoms binds to two metal ions; it is interesting to note that compounds like $[\text{KH}(4\text{-nba})_2]_n$

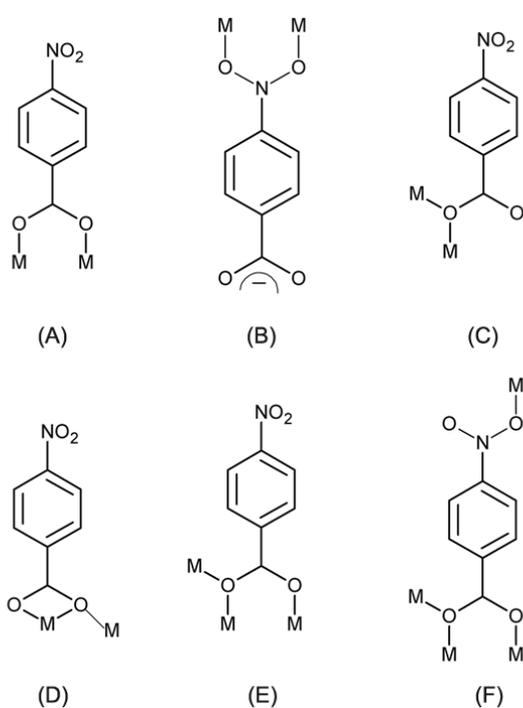


Fig. 6 — Six different bridging coordination modes of 4-nba ligand. [Mode A, $\mu_2^{-1:1}$; Mode B, $\mu_2^{-1:1}(-\text{NO}_2)$; Mode C, $\mu_2^{-2:0}$; Mode D, $\mu_2^{-1:2}$; Mode E, $\mu_3^{-1:1}$; Mode F, $\mu_4^{-1:1}(\text{O})$; $\eta^1(\text{O})$: $\eta^1(\text{O})$: $\eta^1(\text{O})$: $\eta^1(\text{O})$ of nitro].

or $[\text{Ca}(\text{H}_2\text{O})(2\text{-meIm})(4\text{-nba})_2]_n$ showing the $\mu_2^{-2:0}$ bridging mode are always accompanied by another binding mode like the $\mu_2^{-1:1}$ in the Ca coordination polymer or the μ_4 -bridging mode involving both the carboxylate and nitro oxygen atoms in the K compound⁵⁸. The $\mu_2^{-1:2}$ mode observed in the title compound $[[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}]_n$ has earlier been reported in the isostructural *f*-block compounds⁵⁶ $[\text{M}_2(4\text{-nba})_6(\text{H}_2\text{O})_5]_n$ (M = Eu or Tb) and in the lead coordination polymers⁵⁴, $[\text{Pb}(4\text{-nba})(\text{PyO})_2(\text{NO}_2)]_n$ and $[\text{Pb}(4\text{-nba})_2(\text{PyO})]_n$.

Conclusions

In this work, we have described the synthesis and characterization of a new calcium(II) coordination polymer $[[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}]_n$ based on a μ_2 -bridging tridentate 4-nba ligand. An analysis of the six bridging binding modes of 4-nba ligand reveals that the symmetrical μ_2 - $1:1$ bridging binding mode is very common and observed in a majority of 4-nba compounds. The two binding modes involving the oxygen atom of the nitro group is observed only in the alkali metal 4-nitrobenzoates, where the alkali metal Na^{57} or K^{58} is linked to the oxygen of the nitro functionality. The compounds $[\text{Ca}(\text{pyr})_2(4\text{-nba})_2]_n$ ³⁰, $[\text{Ca}(\text{N-MeIm})(4\text{-nba})_2]_n$ ³³ and $[\text{Ca}(\text{H}_2\text{O})(2\text{-MeIm})(4\text{-nba})_2]_n$ ³⁴ which contain terminal N-donor ligands and a solvent dmp in the lattice in the title compound (2) constitute examples of coordination polymers which show the four different bridging modes of the 4-nba ligand involving only the carboxylate oxygen atoms.

Supplementary Data

Crystallographic data (excluding structure factors) for the structure of $[[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}]_n$ reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 799281. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or Email: deposit@ccdc.cam.ac.uk). The other supplementary data associated with this article, viz., Table S1 and Figs S1–S8, are available in electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA51A\(03\)435-443_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA51A(03)435-443_SupplData.pdf).

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