

Notes

On the syntheses and structures of two calcium coordination polymers containing terminal amide ligands

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The syntheses and crystal structure of the calcium coordination polymers $[\text{Ca}(\text{NMF})_2(4\text{-nba})_2]$ **1** (4-nba = 4-nitrobenzoate; NMF=N-methylformamide) and $[\text{Ca}(\text{BA})_2(4\text{-nba})_2]$ **2** (BA= benzamide) is reported. An unique $\mu_2\text{-}\eta^1\text{:}\eta^1$ bridging bidentate 4-nba ligand links the hexacoordinated Ca(II) ions situated on a special position in both compounds into a one-dimensional (1-D) chain with Ca...Ca separations of 5.561 and 5.482 respectively. Each Ca(II) in the chain is bonded to a pair of symmetry related terminal amide ligands (NMF in **1**; BA in **2**) which are disposed *trans* to each other. A comparative study of several 4-nitrobenzoates of calcium is described.

Keywords: Coordination chemistry, Coordination polymers, Calcium, 4-Nitrobenzoate, Methylformamide, Benzamide

In a very early study of the structural chemistry of Ca(II), Einspaar and Bugg¹ reported that in all calcium carboxylates the Ca ion lies near the plane of the carboxylate group and usually binds to several carboxylate groups. The most commonly observed number of carboxylates bound to each Ca was three and the carboxylate group coordinates to more than one Ca ion. However such a behavior, i. e., binding to more than one metal, is not observed for the Ca(II) salt of 4-nitrobenzoic acid (4-nbaH) $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ **1a**². The crystal structure revealed that the neutral compound **1a** exhibits seven coordination of Ca(II) due to the four terminal water molecules, a monodentate (η^1) and a bidentate (η^2) 4-nitrobenzoate (4-nba) ligand.

We have earlier demonstrated that a partial or total removal of the aqua ligands in **1a** leads to a reorganisation of the coordination sphere to obtain one-dimensional (1-D) coordination polymers due to attainment of a bridging binding mode of 4-nba ligand³⁻⁶. Using this strategy, we have incorporated N-donors, viz., N-methylimidazole³, 2-methylimidazole⁴, pyrazole⁵ into the coordination

sphere of Ca(II) to obtain 1-D polymers of Ca(II). However, the use of 2-aminopyridine (2-ap) afforded a zero-dimensional water rich compound, viz, $[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap})\cdot\text{H}_2\text{O}$ ⁷. With imidazole (Im) two different products namely a zero-dimensional $[\text{Ca}(\text{H}_2\text{O})_3(\text{Im})(4\text{-nba})_2]\cdot\text{Im}$ ⁸ and an anhydrous $[\text{Ca}(\text{Im})(4\text{-nba})_2]$ ³, were obtained depending on the reaction conditions. Interestingly in the case of 3,5-dimethylpyrazole (dmp), a 1-D compound $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2]\cdot 2\text{dmp}$ containing two terminal aqua ligands and 2 moles of dmp in the lattice could be obtained⁶.

In view of the oxophilic nature of Ca(II) it was of interest to investigate the chemistry of incorporation of neutral O-donor ligands. Hence, we have undertaken a study of the reactivity characteristics of $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ towards some O-donors. The results of these studies reporting on the synthesis and structures of two calcium coordination polymers containing terminal amide ligands are described.

Experimental

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 precursor compound $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ **1a** used for the synthesis of **1** and **2** was prepared by literature method². 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} . Raman spectra were recorded using 785 nm radiation for excitation on an Agiltron Peak Seeker Pro Raman instrument from 4000–200 cm^{-1} . UV-visible spectra were recorded on a Shimadzu UV-2450 double beam spectrophotometer. TG-DSC 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. Elemental analyses (C, H and N) were performed on a Variomicro cube CHNS analyser.

A finely powdered sample of **1a** (2.221 g, 5 mmol) was mixed well with ~10 drops of N-methylformamide (NMF) and the reaction mixture was heated on a

water bath for ~ 30 minutes. After this the hot reaction mixture was allowed to cool and washed well with ether to remove any unreacted NMF to obtain **1** as a fine powder in near quantitative yield.

To obtain crystals of **1** suitable for crystallography, compound **1a** was first generated *in situ* by the reaction of a mixture of CaCO₃ (0.500 g, 5 mmol) and 4-nbaH (1.671 g, 10 mmol) in water (80–100 mL) in a microwave oven to obtain a clear solution. At this point, the colour of solution was light yellow, and pH was close to neutral. This solution was then filtered and concentrated to 25 mL by heating it over steam bath followed by addition of an equal volume of NMF (25 mL). Heating on water bath was continued with addition of small aliquots of NMF (1-2 mL) after every 10 minutes till most of the water was evaporated. The clear reaction mixture was allowed to cool and left undisturbed for crystallization. Crystals suitable for single crystal analysis appeared within a day. Transparent crystals obtained after two days were separated washed with ether and air dried (Yield: 76%). The use of calculated amount of benzamide (BA) to maintain 1:2 Ca:BA ratio, in place of NMF afforded crystals of **2** in good yield.

(1): Anal. (%): Calc. for C₁₈H₁₈CaN₄O₁₀ (490.44 g/mol) **1**: C, 44.08; H, 3.70; N, 11.42. Found: C, 43.61; H, 3.539; N, 11.19. IR data (KBr, cm⁻¹): 3374 (m), 3244 (m), 3100-2700, 1678 (s), 1614 (s), 1585 (s), 1514 (s), 1398 (s), 1344 (s), 1317 (s), 1284 (m), 1149 (m), 1105 (m), 1049 (m), 1012 (m), 879 (s), 831 (s), 800 (s), 729 (s), 708 (m), 627 (s), 557 (m), 505 (s), 440 (m), 417 (m); Raman data (cm⁻¹): 3921 (w), 3083 (w), 1596 (s), 1407 (m), 1334 (s), 1098 (m), 861 (m), 624 (w). UV-vis data: 291 nm. DSC data (°C): 182 (endo), 431 (exo).

(2): Anal. (%): Calc. for C₂₈H₂₂CaN₄O₁₀ (614.58 g/mol) **2**: C, 54.72; H, 3.61; N, 9.12. Found: C, 55.17; H, 3.560; N, 9.09. IR data (KBr, cm⁻¹): 3474 (s), 3300-3000, 1651 (s), 1603 (s), 1572 (s), 1514 (s), 1492 (m), 1447 (m), 1412 (s), 1344 (s), 1323 (s), 1304 (m), 1287 (m), 1105 (m), 1016 (m), 880 (m), 831(s), 768 (m), 727 (s), 710 (m), 681 (m), 613 (m), 542 (s), 509 (m), 432 (m); Raman data (cm⁻¹): 3926 (w), 3067 (w), 1596 (s), 1407 (m), 1339 (s), 1103 (m), 999 (m), 861 (m), 624 (w). UV-vis data: 289 nm. DSC data (°C): 200 (endo), 411 (exo), 589 (exo).

The single crystal X-ray structure analysis of **1** and **2** was performed at the Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology (IIT) Madras. Intensity data were collected using Bruker AXS Kappa Apex II CCD

diffractometer. The structures were solved with direct methods using SHELXS-97 and refinement was done against F² using SHELXL-97⁹. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to the aromatic ring were introduced in calculated positions and included in the refinement by riding on their respective parent C atoms. The technical details of data acquisition and selected refinement results are summarised in Table 1.

Table 1—Selected refinement data for [Ca(NMF)₂(4-nba)₂] (**1**) and [Ca(BA)₂(4-nba)₂] (**2**)

Empirical formula	C ₁₈ H ₁₈ CaN ₄ O ₁₀ (1)	C ₂₈ H ₂₂ CaN ₄ O ₁₀ (2)
Formula weight (g mol ⁻¹)	490.44	614.58
Temperature (K)	293(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	5.5615(4)	29.9079(9)
<i>b</i> (Å)	8.0661(6)	5.4818(2)
<i>c</i> (Å)	12.4074(9)	16.2473(5)
α (°)	96.625(2)	90
β (°)	96.2810(10)	90.683(2)
γ (°)	106.443(2)	90
Volume (Å ³)	524.33(7)	2663.54 (7)
<i>Z</i>	1	4
Density (calc.) (mg/m ³)	1.553	1.533
Abs. coeff. (mm ⁻¹)	0.365	0.305
F(000)	254	1272
Crystal size (mm ³)	0.35 × 0.30 × 0.25	0.35 × 0.35 × 0.30
Theta range for data collection (°)	2.66 to 26.99	2.51 to 26.00
Completeness to theta	100.0%	100.0 %
Index ranges	-7 ≤ <i>h</i> ≤ 7, -10 ≤ <i>k</i> ≤ 10, -15 ≤ <i>l</i> ≤ 15	-36 ≤ <i>h</i> ≤ 36, -6 ≤ <i>k</i> ≤ 6, -20 ≤ <i>l</i> ≤ 20
Reflections collected	15259	21000
Independent reflections	2277 [R(int) = 0.0660]	2614 [R(int) = 0.0201]
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Data / restraints / parameters	2277 / 1 / 156	2614 / 3 / 203
Goodness-of-fit on F ²	1.088	1.130
Final <i>R</i> indices [I > 2σ(I)]	R1 = 0.0313, wR2 = 0.0804	R1 = 0.0317, wR2 = 0.0747
<i>R</i> indices (all data)	R1 = 0.0366, wR2 = 0.0865	R1 = 0.0404, wR2 = 0.0851
Largest diff. peak and hole (e.Å ⁻³)	0.209 and -0.248	0.212 and -0.179
CIF deposition No.	CCDC 1523408	CCDC 1523409

Results and discussion

The synthetic methodology for the preparation of **1** is very similar to the method employed by us for the incorporation of N-donor ligands³⁻⁵ in the coordination sphere of Ca in $[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]$. Thus, a direct thermal reaction (at 100 °C) of a powdered sample of **1a** with excess NMF followed by ether washing afforded the mixed ligand compound **1** in good yields. Alternatively, compound **1** could also be prepared by a mechanochemical synthesis, viz., grinding of **1a** with NMF for ~20 min followed by washing with ether. However, with BA both the thermal and mechanochemical reactions did not afford a clean product of **2**, but instead yielded a mixture. The reason for this is very not clear. Hence, a solution based synthesis was employed for obtaining **2** as well as X-ray quality crystals of **1**. Crystals suitable for single crystal work could be grown by using an excess of the O-donor ligand in water and concentrating the reaction mixture before leaving for crystallization. An excess of the neutral ligand and less water was necessary in order to avoid reversible hydration of the product to the starting tetraqua compound **1a**.

The composition of **1** or **2** as consisting of Ca: 4-nba:amide in 1:2:2 ratio was inferred from elemental analytical data and the amount of CaCO_3 residue obtained at 600 °C by pyrolysis of **1** or **2**. It is interesting to note that the incorporation of the neutral amide (NMF or BA) resulted in the reorganisation of the coordination sphere of Ca(II) to afford anhydrous products. Unlike the precursor compound **1a** which exhibits a mass loss of ~12% on heating at 100 °C, compounds **1** and **2** are thermally stable and do not show any loss in mass even when heated up to 150 °C.

The TG-DSC curves add credence to the thermal stability of **1** and **2**. Compound **1**, exhibits an endothermic event (182 °C) assignable to the loss of neutral NMF ligands from **1** (Fig. 1), which is followed by an exothermic process at 431 °C resulting in the decomposition of **1** leading to the formation of CaCO_3 at 600 °C. It is to be noted that exothermic events are observed in several Ca-nitrobenzoates above 400 °C. The delayed occurrence of endothermic events in **1** and also **2** at 200 °C can be taken as indication of the absence of water and high thermal stability. Similarly, the thermal processes occurring in **2** (Supplementary data, Fig. S1) with exothermic decompositions at 411 and 589 °C can be explained as above. A comparison of the infrared

spectra (Supplementary data, Fig. S2) of **1** and **2** with that of $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ reveals the formation of new product as can be evidenced by the changes in the profile especially in the region 3000–3600 cm^{-1} . It is interesting to note that **2** exhibits a sharp signal at 3474 cm^{-1} which can be attributed to the $\nu_{\text{N-H}}$ vibration of the amino group of benzamide. Although such a prominent signal is not observed for the NMF compound, both the spectra are very nearly the same in the carboxylate and the nitro regions, especially the occurrence of the symmetric stretching vibration of the $-\text{NO}_2$ functionality occurring at 1344 cm^{-1} . Interestingly this same vibration is observed as the most intense signal in the Raman spectra of both compounds (Supplementary data, Fig. S3) (1334 cm^{-1} for **1**; 1339 cm^{-1} for **2**) which is also in good agreement with the band at 1334 cm^{-1} for **1a**. The optical spectra (Supplementary data, Fig. S4) exhibit absorption maxima at 291 nm for **1** and 289 nm for **2** which can be attributed to the intraligand charge transfer transitions of the 4-nba ligand.

Both compounds which crystallize in centrosymmetric space groups (triclinic $P\bar{1}$ for **1**; monoclinic $C2/c$ for **2**) are structurally related and exhibit several similarities, the only difference being the differing amide coligand in **1** and **2**. Both crystal structures consist of a crystallographically unique Ca(II) ion located in a special position (centre of inversion in **1**; two-fold axis in **2**), an independent 4-nba anion and a unique amide ligand which is NMF in **1** (Fig. 2) and BA in **2** (Fig. 3). In view of the special position of the central metal, the asymmetric unit in both compounds consists of a half of the formula unit. The geometric parameters of the 4-nba

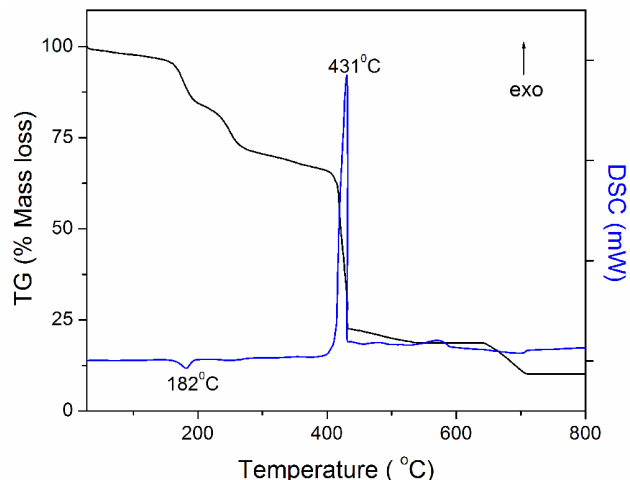


Fig. 1—TG-DSC curves of $[\text{Ca}(\text{NMF})_2(4\text{-nba})_2]$ (**1**).

ligand and NMF and BA ligands are in the normal range (Supplementary data, Tables S1 & S2). In both compounds, the central metal exhibits an octahedral geometry and is bonded only to O-donor sites of 4-nba and NMF or BA ligands. Two of the six vertices of the $\{CaO_6\}$ octahedron consist of the monodentate amide ligands (NMF in **1**; BA in **2**) disposed *trans* to each other. The remaining four vertices of the octahedron are occupied by the O atoms of the unique μ_2 -bridging bidentate 4-nba ligand (O1, O2), which links the Ca(II) ions into an infinite one-dimensional (1-D) chain (Fig 4).

The *trans* O-Ca-O bond angles in **1** exhibit ideal values of 180° while the *cis* O-Ca-O angles range from $84.13(4)^\circ$ to $95.87(4)^\circ$ indicating a slight distortion of the $\{CaO_6\}$ octahedron (Table 2). In the

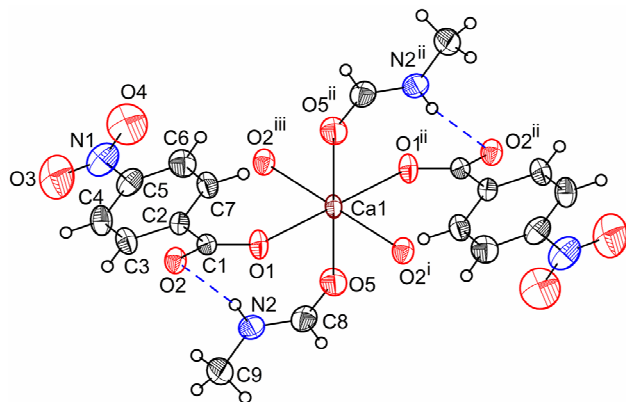


Fig. 2—Crystal structure of $[Ca(NMF)_2(4-nba)_2]$ (**1**) showing the atom labeling scheme. [Displacement ellipsoids are drawn at the 50% probability level for all atoms excepting the H-atoms which are shown as spheres of arbitrary radii. Intramolecular H-bonding is shown in broken lines. Symmetry code: i) $-x+2, -y, -z+2$ ii) $-x+1, -y, -z+2$ iii) $x+1, y, z$].

case of **2**, the $\{CaO_6\}$ octahedron is much more distorted as evidenced by *trans* O-Ca-O bond angles ranging from $167.11(4)^\circ$ to $170.66(7)^\circ$. The *cis* O-Ca-O angles scatter in a larger range between $82.59(5)^\circ$ and $101.34.87(5)^\circ$ unlike in **1**. The Ca-O bond distances range from $2.3054(10) \text{ \AA}$ to $2.3632(11) \text{ \AA}$ in **1** (Table 2) while the Ca-O bond lengths lie between $2.3132(13) \text{ \AA}$ and $2.3544(12) \text{ \AA}$ in **2**. In both compounds, the central Ca(II) is bonded to two terminal amide ligands disposed *trans* to each other, which function as monodentate O-donor coligands. It is interesting to note that the Ca-O5(amide) distance in the NMF compound **1** is considerably shorter at $2.3087(11) \text{ \AA}$, unlike the Ca-O5(amide) distance of $2.3544(12) \text{ \AA}$ in **2**. Although the reason for this is not clear, it is to be noted that benzamide is an aromatic amide unlike NMF. All the Ca-O bond lengths are in the expected range of Ca-O distances reported in several Ca(II) compounds.

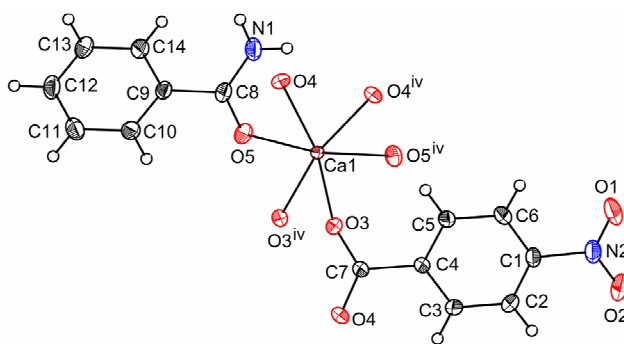


Fig. 3—Crystal structure of $[Ca(BA)_2(4-nba)_2]$ (**2**) showing the atom labeling scheme. [Displacement ellipsoids are drawn at the 30% probability level for all atoms excepting the H-atoms which are shown as spheres of arbitrary radii. Symmetry code: iv) $-x+1, y, -z+1/2$].

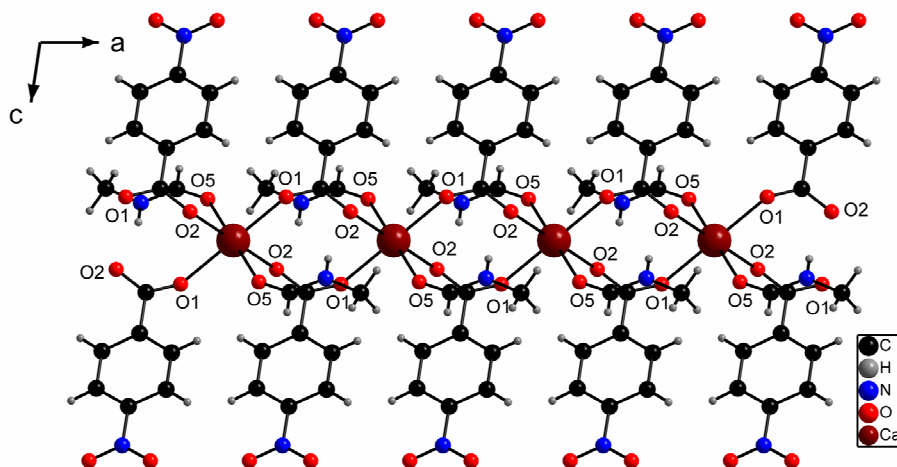


Fig. 4—The $\mu_2\text{-}\eta^1: \eta^1$ bridging binding mode of the 4-nba ligand (O1, O2) linking the Ca(II) ions into a 1-D chain extending along *a* axis. O5 is the binding site for the terminal NMF ligand. [For the 1-D chain in **2**, see Supplementary data, Fig. S7].

Table 2—Selected geometric parameters for (1) and (2)

[Ca(NMF) ₂ (4-nba) ₂] (1)			
Bond lengths (Å)		Bond angles (deg.)	
Ca1-O1	2.3054(10)	O1-Ca1-O1 ⁱ	180.0
Ca1-O1 ⁱ	2.3054(10)	O5-Ca1-O5 ⁱ	180.0
Ca1-O5	2.3087(11)	O2 ⁱⁱ -Ca1-O2 ⁱⁱⁱ	180.00(4)
Ca1-O5 ⁱ	2.3087(11)	O1-Ca1-O5 ⁱ	90.75(4)
Ca1-O2 ⁱⁱ	2.3632(10)	O1-Ca1-O5	89.25(4)
Ca1-O2 ⁱⁱⁱ	2.3632(10)	O1-Ca1-O2 ⁱⁱ	84.13(4)
Ca1...Ca1 ⁱⁱⁱ	5.561(0)	O5-Ca1-O2 ⁱⁱ	90.99(4)
		O1-Ca1-O2 ⁱⁱⁱ	95.87(4)
		O5-Ca1-O2 ⁱⁱⁱ	89.01(4)
[Ca(BA) ₂ (4-nba) ₂] (2)			
Ca1-O4	2.3132(13)	O4-Ca1-O3	167.11(4)
Ca1-O4 ^{iv}	2.3132(13)	O4 ^{iv} -Ca1-O3 ^{iv}	167.11(4)
Ca1-O3	2.3200(12)	O5-Ca1-O5 ^{iv}	170.66(7)
Ca1-O3 ^{iv}	2.3200(12)	O4-Ca1-O4 ^{iv}	92.17(7)
Ca1-O5	2.3544(12)	O4-Ca1-O3 ^{iv}	93.32(4)
Ca1-O5 ^{iv}	2.3544(12)	O4-Ca1-O5	82.59(5)
Ca1...Ca1 ^{**}	5.482(1)	O4-Ca1-O5 ^{iv}	90.92(5)
		O3-Ca1-O5	85.67(4)
		O3-Ca1-O5 ^{iv}	101.34(5)

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

Table 3—Structure features of 4-nitrobenzoates of Ca(II)

No.	Compound ^a	Space group	Ca:H ₂ O ^b	Coord. no. ^c	Coord. sphere	Binding mode of unique 4-nba ligand	D ^d	Ref.
1	[Ca(H ₂ O) ₄ (4-nba) ₂] 1a	<i>P2₁/c</i>	1:4	7 (2)	{CaO ₇ }	η ¹ , η ²	0	2
2	[Ca(H ₂ O) ₆ (4-nba)(4-nba)-(2-ap)H ₂ O]	<i>P</i> $\bar{1}$	1:6	7 (1)	{CaO ₇ }	η ¹ , anion	0	7
3	[Ca(H ₂ O) ₃ (Im)(4-nba) ₂]Im	<i>P2₁/c</i>	1:3	6 (2)	{CaO ₅ N}	η ¹ , η ¹	0	8
4	[Ca(NMF) ₂ (4-nba) ₂] 1	<i>P</i> $\bar{1}$	1:0	6 (4)	{CaO ₆ }	μ ₂ -η ¹ :η ^{1 e}	1	This work
5	[Ca(BA) ₂ (4-nba) ₂] 2	<i>C2/c</i>	1:0	6 (4)	{CaO ₆ }	μ ₂ -η ¹ :η ^{1 e}	1	This work
6	[Ca(pyr) ₂ (4-nba) ₂]	<i>P</i> $\bar{1}$	1:0	6 (4)	{CaO ₄ N ₂ }	μ ₂ -η ¹ :η ^{1 e}	1	5
7	[Ca(L ¹)(4-nba) ₂]	<i>P</i> $\bar{1}$	1:0	6 (5)	{CaO ₅ N}	μ ₂ -η ¹ :η ¹ , μ ₃ -η ² :η ¹	1 ^f	3
8	[Ca(H ₂ O)(L ²)(4-nba) ₂]	<i>P2₁/n</i>	1:1	7 (4)	{CaO ₆ N}	μ ₂ -η ¹ :η ¹ , μ ₂ -η ²	1	4
9	[Ca(H ₂ O) ₂ (4-nba) ₂].2dmp	<i>P</i> $\bar{1}$	1:2	8 (4)	{CaO ₈ }	μ ₂ -η ² :η ¹ , μ ₂ -η ² :η ¹	1	6
10	[Ca(4-nba) ₂]	--	1:0	--	--	--	--	2
11	[Ca(Im)(4-nba) ₂]	--	1:0	--	--	--	--	2
12	[Ca(H ₂ O)(4-nba) ₂]	--	1:1	--	--	--	--	2

^a4-nba = 4-nitrobenzoate; 2-ap = 2-aminopyridine; Im = imidazole; NMF = N-methylformamide; BA = benzamide; L¹ = N-methylimidazole; L² = 2-methylimidazole; pyr = pyrazole; dmp = 3,5-dimethylpyrazole; ^bNo. of coordinated water; ^cNumber in parentheses is the number of carboxylates linked to each Ca; ^dDimensionality; ^eunique 4-nba ligand; ^f1-D ladder.

A scrutiny of the crystal structures reveals that the unique 4-nba ligand in **1** (or **2**) functions as a μ₂-η¹:η¹ bridging bidentate ligand with each of the O atoms of the carboxylate moiety of 4-nba linking two symmetry related Ca(II) ions resulting in a Ca...Ca separation of 5.561 Å (or 5.482 Å in **2**) (Supplementary data, Figs S5 & S6). The linking of a pair of Ca(II) ions by a pair of μ₂-η¹:η¹ bridging 4-nba ligands results in the formation of an eight-membered cyclic ring which can explain the longer

separation between the adjacent Ca(II) ions which are also coordinated to terminal amide ligands. This binding mode has been reported by us for 4-nba in three other Ca(II) compounds (Table 3). Compounds **1** and **2** are topologically similar to [Ca(pyr)₂(4-nba)₂] (pyr = pyrazole) which exhibits a 1-D polymeric chain due to the μ₂-η¹:η¹ bridging binding mode of the 4-nba ligand. The net result of the binding of the terminal amide ligands and the bridging bidentate 4-nba ligands is the linking of Ca(II) ions into an

infinite chain (Fig. 4), leading to a polymeric structure. Each Ca(II) in the 1-D chain is bonded to four symmetry related 4-nba ligands via the carboxylate oxygen atoms which constitute the square plane of the $\{CaO_6\}$ octahedron. The terminal amide coligands disposed *trans* to each other complete the octahedron.

Analysis of the crystal structure reveals that the H-atoms attached to the N of the NMF or BA act as H-donors and are involved in N-H \cdots O interactions with the O atoms (O2 in **1**; O3 and O4 in **2**) of the carboxylate moiety of the 4-nba ligand. In **1** this results in a single short intramolecular H-bond accompanied by a DHA angle of 165.7°, while **2** exhibits two intermolecular N-H \cdots O bonds (Supplementary data, Table S3).

The rich and variable structural chemistry of calcium can be evidenced from the many structurally characterized 4-nitrobenzoate compounds of Ca(II) (Table 3). In all these compounds which crystallize in centrosymmetric space groups, the coordination number of the central metal varies from 6 to 8. Although the structures of the last three entries in Table 3 could not be refined due to the inability to prepare X-ray quality single crystals, their composition has been very accurately determined. The ratio of Ca:coordinated water exhibits quite a variation with six compounds being anhydrous while one compound (entry No. 2) is water-rich and contains seven water molecules of which six are coordinated and one water is in the lattice. The oxophilic nature of Ca can be evidenced from the compounds listed in Table 3 by the fact that a maximum of two N-donor ligands (entry no. 6) can be incorporated into the calcium coordination sphere. The first three entries in Table 3 are zero-dimensional, while entries 4 to 9, which contain one or two or no coordinated water molecules, are 1-D coordination polymers. In addition to functioning as a charge balancing anion in all the compounds in Table 3, the 4-nitrobenzoate moiety functions as a monodentate (η^1) or bidentate (η^2) or a bridging ligand. It is interesting to note that in all the 1-D coordination polymers, the 4-nba ligand exhibits a bridging binding mode, which extends the structure. Although both μ_2 - and μ_3 -bridging binding modes are observed the symmetric μ_2 - η^1 : η^1 bridging bidentate binding mode in **1** and **2** is observed in a total of five compounds. In addition, a μ_2 - η^2 : η^1 bridging tridentate binding mode (entry no. 9), a μ_2 - η^2 bridging where only one of the

carboxylate O atoms binds to two different Ca(II) (entry no. 8) and a μ_3 - η^2 : η^1 bridging tridentate binding mode are also observed. Interestingly all the coordination polymers in Table 3 have either one or two moles of water or no water. The degree of hydration of a Ca(II)-carboxylate is an important property which determines the structure and several examples of structurally characterized coordination polymers of Ca, other than the ones in Table 3 containing one or two water molecules are reported in the literature¹⁰⁻²⁴. Based on the level of hydration it is expected that the last three compounds (entry no. 10 to 12) also exhibit a polymeric structure. In the case of 4-nitrobenzoic acid linker, the degree of hydration can explain the dimensionality of the Ca(II) compound as the parent compound $[Ca(H_2O)_4(4-nba)_2]$ **1a** containing four coordinated water molecules exhibits a discrete structure (zero dimensional) while the partial or total removal of the water molecules as in the case of **1** and **2** leads to a chain structure.

In summary, 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

Crystallographic data in CIF format containing embedded reflection data for the crystal structures of $[Ca(NMF)_2(4-nba)_2]$ **1** and $[Ca(BA)_2(4-nba)_2]$ **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1523408 (**1**) and CCDC 1523409 (**2**) respectively. 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). Other supplementary data associated with this article are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_56A\(04\)387-393_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_56A(04)387-393_SupplData.pdf).

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