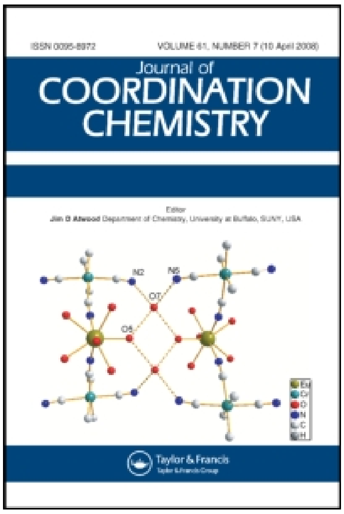

Journal of
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Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Srinivasan, Bikshandarkoil R. and Shetgaonkar, Santosh Y.(2010) 'A calcium(II) coordination polymer showing two different bridging 2-carbamoyl-4-nitrobenzoate coordination modes', Journal of Coordination Chemistry, 63: 19, 3403 — 3412, First published on: 27 August 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.512955

URL: http://dx.doi.org/10.1080/00958972.2010.512955

Journal of Coordination Chemistry
Vol. 63, No. 19, 10 October 2010, 3403–3412

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A calcium(II) coordination polymer showing two different bridging 2-carbamoyl-4-nitrobenzoate coordination modes†

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(*Received 10 March 2010; in final form 16 June 2010*)

Aqueous reaction of $CaCO_3$ with 2-carbamoyl-4-nitrobenzoic acid (2-ca-4nbaH) results in the formation of a 1-D coordination polymer $[Ca(H_2O)_2(2\text{-ca-4nba})_2]$ (**1**), which crystallizes in the centrosymmetric triclinic space group $P\bar{1}$. The structure consists of a central Ca(II), two coordinated waters, a symmetrical bridging $(\mu_2\text{-}\eta^1:\eta^1)$ 2-ca-4nba, and a tridentate bridging $(\mu_2\text{-}\eta^2:\eta^1)$ 2-ca-4nba. The calcium in **1** is coordinated by two water molecules and five oxygens of four symmetry-related 2-ca-4nba, resulting in a distorted pentagonal bipyramidal $\{CaO_7\}$ polyhedron. Pairs of $\{Ca(H_2O)_2\}$ units are linked into a 1-D coordination polymer extending along the *a*-axis with the aid of pairs of bridging 2-ca-4nba ligands. In the infinite chain, alternating pairs of Ca(II) ions exhibit $Ca\cdots Ca$ separations of 4.124 and 4.855 Å.

Keywords: 2-Carbamoyl-4-nitrobenzoic acid; Coordination polymer; Crystal structure; Symmetrical bridging; Tridentate bridging; Pentagonal bipyramid

1. Introduction

Coordination polymers or metal–organic frameworks (MOFs) have attracted much attention because of their topologies and potential applications in catalysis, adsorption (gas storage), separation, luminescence, etc. [1–3]. Compared to the extensive chemistry of coordination polymers based on transition metals, the coordination chemistry of group 1 and 2 metals with organic linkers is less explored, although there is growing interest in coordination polymers of s-block elements as alkali and/or alkaline earth metal cations are preferred to transition or lanthanide metal ions because they are nontoxic, cheap, and soluble in aqueous media. In a recent article, Fromm [4] reviewed the different ligand and polymer types of the s-block compounds.

Depending on the electronic and steric requirements of the central metal, the flexibility, binding modes, and hydrogen bonding characteristics of the organic linker (ligand), coordination polymers of differing dimensionalities can be constructed. For oxophilic s-block metals, carboxylic acid based ligands are useful for the construction of coordination polymers as the metals can be linked into an extended chain with bridging carboxylate. For the preparation of coordination polymers

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†Dedicated to Prof. Dr Shashikumar K. Paknikar on the occasion of his 75th birthday.

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.512955

different synthetic methodologies, namely, aqueous reaction of metal carbonate or hydroxide with the carboxylic acid under ambient conditions [5–12], reaction of aqueous metal chloride or nitrate with the carboxylic acid in the presence of a mild base [13–21], and hydrothermal reaction of metal sources with carboxylic acids [22–30] are employed. Several coordination polymers based on alkaline earth metals have been synthesized and structurally characterized [5–30].

As a part of an ongoing research program, we are investigating coordination chemistry of nitrobenzoates of s-block elements. In an earlier study, we reported synthetic aspects, spectral characteristics, structural features, and thermal properties and have unraveled a rich structural chemistry of the alkaline earth nitrobenzoates [31–38]. In a recent report, we used 2-carbamoyl-4-nitrobenzoic acid (2-ca-4nbaH) in which an amide (H-donor) and a nitro group (H-acceptor) disposed *ortho* and *trans*, respectively, with respect to the carboxylate to form a monomeric Mg(II) carboxylate $[Mg(H_2O)_6](2\text{-ca-4nba})_2$, which exhibits a supramolecular bilayer of 2-carbamoyl-4-nitrobenzoate (2-ca-4nba) anions sandwiched between layers of $[Mg(H_2O)_6]^{2+}$ cations [39]. In continuation of this study, we have synthesized and structurally characterized a 1-D coordination polymer of Ca(II) using 2-ca-4nba as a bridging ligand.

2. Experimental

2.1. *Materials and methods*

All chemicals used in this study were of reagent grade and used as received. The free acid 2-ca-4nbaH was prepared as described earlier [39]. Infrared (IR) spectra were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from 4000 to 400 cm^{-1}. Samples for IR spectra were diluted with KBr in the solid state and the signals referenced to polystyrene bands. UV-Vis diffuse reflectance spectra were obtained using a Shimadzu UV-2450 double beam spectrophotometer using $BaSO_4$ powder as reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka–Munk function ($a/S=(1-R)^2/2R$, where a is the absorption coefficient, R the reflectance, and S the scattering coefficient). Luminescence spectra of the solid samples were recorded at room temperature (RT) using a Perkin Elmer LS 55 Luminescence spectrophotometer. Isothermal weight loss studies were performed in an electric furnace fitted with a temperature controller. Thermogravimetry–differential thermal analyzer (TG–DTA) measurements were performed in flowing air using a heating rate of 10 K min^{-1} in Al_2O_3 crucibles on a STA-409PC simultaneous thermal analyzer from Netzsch.

2.2. *Preparation of $[Ca(H_2O)_2(2\text{-ca-4nba})_2]$ (1)*

A mixture of 2-ca-4nbaH (0.420 g, 2 mmol) and $CaCO_3$ (0.100 g, 1 mmol) in water (25 mL) was heated on a steam bath for ~2 h until the effervescence ceased completely to obtain a clear pale yellow solution. The hot reaction mixture was filtered and kept undisturbed at RT. Pale yellow crystalline blocks of $[Ca(H_2O)_2(2\text{-ca-4nba})_2]$ (**1**) separated after several days were filtered, washed with a little ice cold water and then by ether, and dried in air. Yield 0.32 g (64%). Crystals obtained in this method were suitable for X-ray structure determination. Compound **1** was also prepared by reacting 2-ca-4nbaH (0.420 g, 2 mmol) with Na_2CO_3 (0.106 g, 1 mmol) at RT in water (25 mL) to obtain the Na salt. To the clear solution thus obtained, $CaCl_2 \cdot 2H_2O$ (0.147 g, 1 mmol) was added. The reaction mixture was filtered and left aside to isolate the product as before in ~75% yield.

Analytical data: Calcd for $CaC_{16}H_{14}N_4O_{12}$, $M = 494.39$ (**1**) (%): C, 38.87; H, 2.85; N, 11.33; and CaO, 11.32. Found (%): C, 38.47; H, 2.79; N, 11.03; and CaO, 11.1. IR data (in cm^{-1}): 3613, 3464, 3358, 3115, 3082, 2843, 2787, 2467, 2251, 2102, 1942, 1827, 1680, 1574, 1512, 1487, 1416, 1358, 1273, 1163, 1149, 1113, 1070, 974, 914, 858, 849, 833, 795, 787, 746, 692, 642, 584, 569, 488, and 447. UV-Vis (diffused reflectance): 294 nm. DTA data (°C): 152 (endo), 297 (endo), 440 (exo), and 557 (exo).

2.3. *X-ray crystal structure determination*

Intensity data for **1** were collected on a Bruker Smart Apex CCD diffractometer (CCD, charged coupled device) using graphite-monochromated Mo-Kα radiation. Data integration and reduction were carried out with SAINT software [40] and an empirical absorption correction was applied to the collected reflections with Siemens Area Detector Absorption (SADABS) [40]. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were introduced in calculated positions and included in the refinement riding on their respective carbons. Hydrogens attached to O of water and N of amide were located in the difference map and refined isotropically with restraints for hydrogens attached to O using a riding model. Crystal data of (**1**): $C_{16}H_{14}CaN_4O_{12}$, $M = 494.39\,g\,mol^{-1}$, triclinic, space group $= P\bar{1}$, $\lambda = 0.71073\,Å$, $a = 7.8884(16)\,Å$, $b = 8.2028(16)\,Å$, $c = 15.5763(16)\,Å$, $\alpha = 75.15(3)°$, $\beta = 80.71(3)°$, $\gamma = 87.58(3)°$, $V = 961.5(3)\,Å^3$, $Z = 2$, $D_{Calcd} = 1.708\,mg\,m^{-3}$, $\mu = 0.406\,mm^{-1}$, $F(0\,0\,0) = 508$, index range $= -9 \le h \le 10$, $-10 \le k \le 8$, and $-18 \le l \le 20$, and completeness to $\theta = 28.35°$ (95.0%). A total of 6349 reflections ($2.57 < \theta < 28.35°$) were collected of which 4556 were unique ($R_{int} = 0.0208$) and used for structure solution. Structure was solved using SHELXS-97 [41] and refined using SHELXL-97 [41] to R_1 (wR_2) = 0.0615 (0.1617) for 3231 reflections with ($I > 2\sigma(I)$) using 330 parameters. The highest peak and the deepest hole were observed at −0.694 and +0.863 $eÅ^{-3}$, respectively.

3. Results and discussion

3.1. *Description of crystal structure of 1*

Compound **1** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with all atoms situated in general positions. Its structure consists of a central Ca(II), two coordinated water molecules, and two crystallographically independent 2-ca-4nba ligands (figure 1). The Ca(II) is seven coordinate, ligated by two terminal waters and five oxygens of four symmetry-related 2-ca-4-nba ligands, resulting in a distorted pentagonal bipyramidal $\{CaO_7\}$ (figure 1). The geometric parameters of the carboxylates are in the normal range. The O–Ca–O angles scatter in a wide range between 50.46(9)° and 172.13(18)° (table 1). The two terminal waters (O20 and O21) are bonded to calcium with Ca1–O20

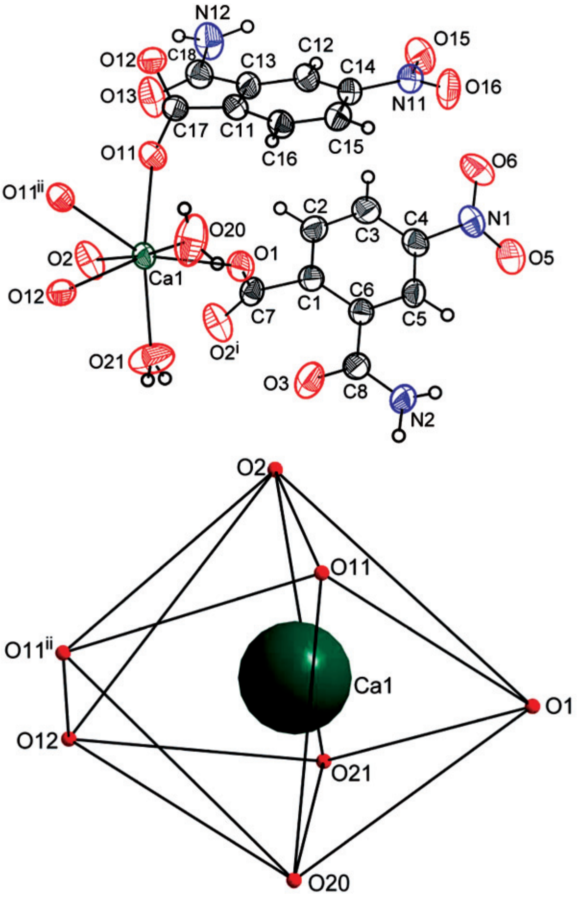


Figure 1. The coordination sphere of Ca(II) in **1** showing the atom-labeling scheme. Displacement ellipsoids are drawn at 50% probability excepting for hydrogens, which are shown as circles of arbitrary radius (top). The distorted pentagonal bipyramidal coordination polyhedron around Ca(II) in **1** (bottom). Symmetry code: ^{i} $-x, -y+1, -z+1$; ^{ii} $-x+1, y+1, -z+1$. Color code: C, black; H, gray; N, blue; O, red; and Ca, green.

and Ca1–O21 distances of 2.351(4) and 2.380(4) Å, respectively. The bidentate 2-ca-4nba is ligated to Ca *via* O1 with a Ca1–O1 distance of 2.400(3) Å and O2 is further bonded to a neighboring Ca(II) at 2.299(3) Å. The tridentate ligand (O11 and O12) bridges two neighboring Ca(II) ions with Ca1–O11 and Ca1–O12 bond lengths of 2.337(3) and 2.467(3) Å, respectively. The O11 is further linked to a symmetry-related Ca(II) at a very long distance of 2.656(3) Å. Recently, Dietzel *et al.* [25] reported a long Ca–O bond of 2.8384(16) Å in $[Ca(H_2dhtp)(H_2O)_2]_n$ (H_4dhtp = 2,5-dihydroxyterephthalic acid).

Compound **1** is a coordination polymer and its structure is based on dinuclear $\{Ca_2(H_2O)_4(2\text{-ca-4nba})_2\}^{2+}$. The crystallographically independent 2-ca-4nba in each formula unit coordinate to Ca(II) differently, namely, a symmetrical bridging mode (μ_2-$\eta^1:\eta^1$) and a tridentate bridging mode (μ_2-$\eta^2:\eta^1$). A pair of 2-ca-4nba ligands related by an inversion center bridges a pair of $\{Ca(H_2O)_2\}^{2+}$ units. The symmetrical

Table 1. Selected bond lengths and angles (Å, °) for **1**.

Ca(1)–O(2)	2.299(3)	Ca(1)–O(12)	2.467(3)
Ca(1)–O(11)	2.337(3)	Ca(1)–O(11)^{ii}	2.656(3)
Ca(1)–O(20)	2.351(4)	Ca(1)–Ca(1)^{i}	4.855
Ca(1)–O(21)	2.380(4)	Ca(1)–Ca(1)^{ii}	4.124
Ca(1)–O(1)	2.400(3)		
O(2)–Ca(1)–O(11)	87.76(13)	O(11)–Ca(1)–O(12)	119.19(10)
O(2)–Ca(1)–O(20)	172.13(18)	O(20)–Ca(1)–O(12)	86.18(15)
O(11)–Ca(1)–O(20)	87.0(2)	O(21)–Ca(1)–O(12)	74.96(13)
O(2)–Ca(1)–O(21)	87.30(19)	O(1)–Ca(1)–O(12)	151.06(11)
O(11)–Ca(1)–O(21)	165.12(14)	O(2)–Ca(1)–O(11)^{ii}	91.83(12)
O(20)–Ca(1)–O(21)	99.2(2)	O(11)–Ca(1)–O(11)^{ii}	68.80(11)
O(2)–Ca(1)–O(1)	100.68(12)	O(20)–Ca(1)–O(11)^{ii}	80.81(15)
O(11)–Ca(1)–O(1)	87.79(11)	O(21)–Ca(1)–O(11)^{ii}	125.39(13)
O(20)–Ca(1)–O(1)	84.97(15)	O(1)–Ca(1)–O(11)^{ii}	153.05(10)
O(21)–Ca(1)–O(1)	79.36(14)	O(12)–Ca(1)–O(11)^{ii}	50.46(9)
O(2)–Ca(1)–O(12)	91.28(11)		

Symmetry transformations used to generate equivalent atoms: ^{i} $-x, -y+1, -z+1$; ^{ii} $-x+1, -y+1, -z+1$.

bridging binding mode (μ_2-$\eta^1:\eta^1$) binding through carboxylate oxygens (O1 and O2) results in the formation of dimeric units with a Ca···Ca separation of 4.855 Å. In the dimer, a pair of $\{Ca(H_2O)_2\}^{2+}$ units is bridged by a pair of (μ_2-$\eta^1:\eta^1$) bridging 2-ca-4nba ligands resulting in the formation of an eight-membered ring (figure S1). The second 2-ca-4nba (O11 and O12) functions as a bridging tridentate ligand (μ_2-$\eta^2:\eta^1$) and a pair of such ligands links two symmetry-related $\{Ca(H_2O)_2\}^{2+}$ units *via* O11 and O12 resulting in the formation of dimers as a tricyclic dicalcium–*bis*(2-ca-4nba) unit with a shorter Ca···Ca separation of 4.124 Å (figure S1). A tricyclic dicalcium–*bis*(2-nba) (2-nba = 2-nitrobenzoate) unit has been reported recently in the polymeric carboxylate $[Ca(H_2O)_2(2\text{-nba})_2]_n$ [5]. The net result of the differing bridging 2-ca-4nba ligands in **1** is the linking of pairs of $\{Ca(H_2O)_2\}^{2+}$ units into a 1-D polymer extending along the *a*-axis (figure 2). In the infinite chain, pairs of $\{Ca(H_2O)_2\}^{2+}$ units are bridged *via* pairs of bridging 2-ca-4nba ligands and alternating pairs of Ca(II) ions exhibit Ca···Ca separations of 4.124 and 4.855 Å. The observed values of Ca···Ca distances are comparable with Ca···Ca distances in coordination polymers based on 4-nitrobenzoate [37, 38].

The structure reveals several H-bonding interactions. All oxygens of the amide, carboxylate, and nitro of 2-ca-4nba except O4 and O15 function as H-bond acceptors. Hydrogens of coordinated water, the amide, and two attached to carbon function as H-donors. Eleven O···H distances ranging from 1.901 to 2.583 Å (table 2) are comprised of four N–H···O, five O–H···O, and two C–H···O interactions. In several structurally characterized nitrobenzoates, oxygen of nitro functions as a H-acceptor and is involved in C–H···O interactions, in addition to O–H···O bonds [35–39, 42, 43]. In **1**, a similar feature is observed. The N2–H2A···O16, C5–H5···O16, and C13–H13···O6 interactions which link adjacent chains (figure 2) are interchain interactions and they extend the H-bonding network.

3.2. *Synthesis, spectroscopy, and thermal studies*

The reaction of $CaCO_3$ with 2-ca-4nbaH in boiling water followed by crystallization resulted in the formation of $[Ca(H_2O)_2(2\text{-ca-4-nba})_2]$ (**1**), containing

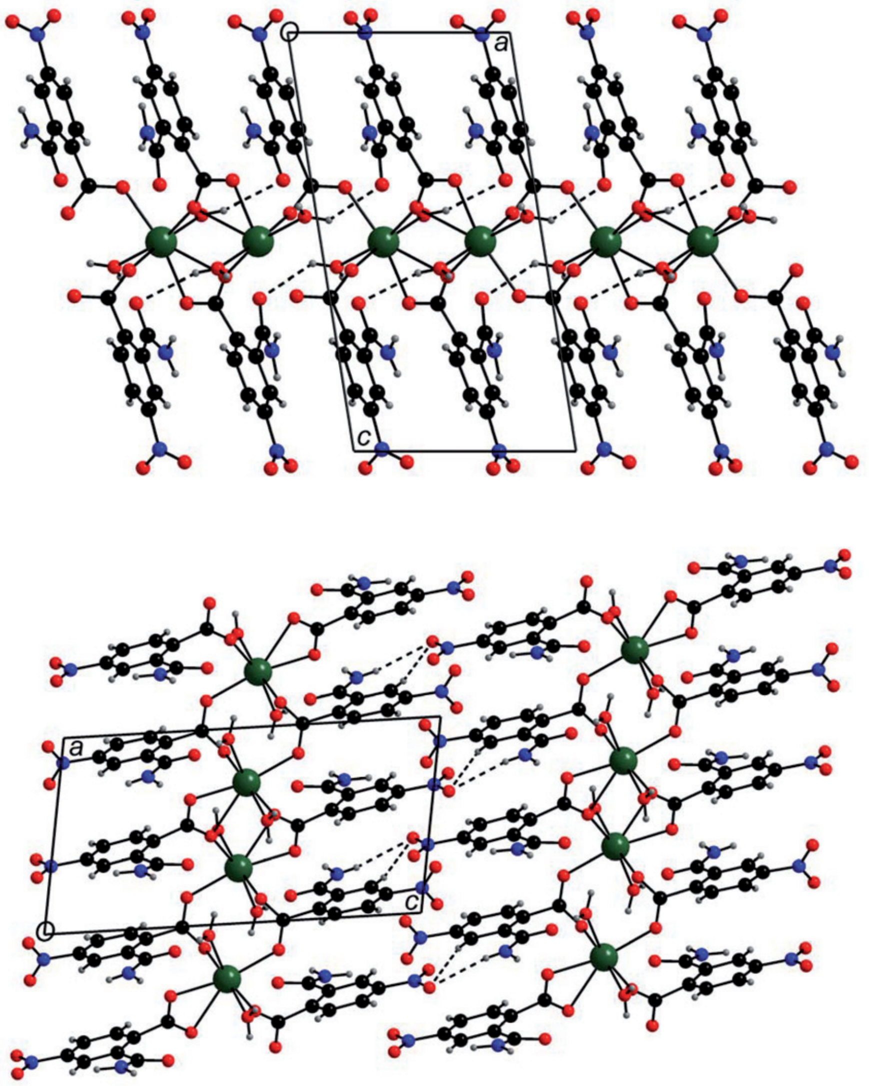
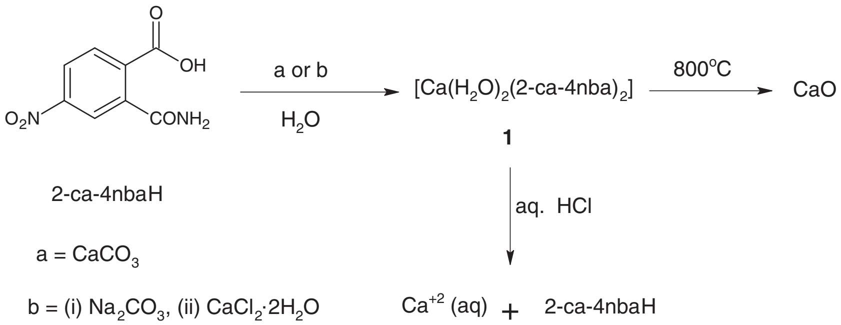


Figure 2. A view along the *b*-axis showing a part of the 1-D chain extending along the *a*-axis due to the bridging 2-ca-4nba in **1**. Intrachain H-bonding is shown by broken lines (top). Two adjacent polymeric chains of **1** in the *ac* crystallographic plane are linked by weak N–H · · · O and C–H · · · O bonds shown in broken lines (bottom). Color code: C, black; H, gray; N, blue; O, red; and Ca, green.

Ca : water : 2-ca-4nba in 1 : 2 : 2 ratio. Reaction of $CaCO_3$ with 4-nitrobenzoic acid (4-nbaH) under identical conditions resulted in the formation of $[Ca(H_2O)_4(4\text{-nba})_2]$ containing Ca : water : 4-nba in a 1 : 4 : 2 ratio [32]. Hence, it appears that the presence of the carbamoyl (amide) group at the 2-position in 2-ca-4nbaH is responsible for the different reactivities. Compound **1** was also prepared by the reaction of the water-soluble Na salt of 2-ca-4nbaH with $CaCl_2$ (scheme 1). Reaction of **1** with dilute HCl results in quantitative formation of the free acid, 2-ca-4nbaH.

Table 2. Hydrogen bonding geometry (Å, °) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA	Symmetry code
N2–H2A···O16	0.821	2.583	3.395	171	$-x, -y+1, -z$
N12–H12A···O5	0.970	2.465	3.412	165	$-x, y+2, -z$
O20–H20A···O3	0.836	2.495	3.192	142	$x+1, y, z$
O21–H21A···O13	0.865	2.530	3.142	128	$-x, -y+1, -z+1$
O21–H21A···O2	0.865	2.538	3.043	118	$-x, -y+1, -z+1$
N2–H2B···O12	0.926	1.965	2.884	171	$-x, -y, -z+1$
N12–H12B···O1	0.928	2.125	3.038	167	$x, y+1, z$
O20–H20B···O13	0.847	1.988	2.813	164	$x, y-1, z$
O21–H21B···O3	0.859	1.901	2.755	173	$-x, -y, -z+1$
C5–H5···O16	0.931	2.400	3.302	163	$-x, 1-y, -z$
C13–H13···O6	0.930	2.537	3.368	149	$-x, 2-y, -z$



Scheme 1. Synthesis of compound **1**.

Compound **1** was formulated based on the elemental analysis and the mass loss leading to the formation of CaO on pyrolysis. The diffuse reflectance spectrum of **1** is nearly identical to that of the free acid (figure S2) exhibiting a maximum centered at 294 nm which can be assigned as intraligand charge transfer of 2-ca-4nba anion. The luminescence spectrum of **1** exhibits two emission maxima at 450 and 490 nm, both of which are also observed in the free acid (figure S3). A comparison of the emission spectra reveals that the first emission band of the Ca(II) compound is enhanced in intensity.

The IR spectrum of **1** exhibits several signals in the mid IR region, many of which are also observed in the free acid (figure S4), thus indicating the presence of the organic moiety in **1**. The presence of water can be readily inferred from the strong signal at 3613 cm^{-1}. The peak at 3464 cm^{-1} can be assigned for the N–H stretching vibration of the amide functionality, while the band due to the C=O of the amide is observed as a strong signal at 1680 cm^{-1}. Intense bands at 1512 and 1358 cm^{-1} can be assigned to the asymmetric and symmetric stretching vibrations of $–NO_2$. The asymmetric and symmetric stretching vibrations of the carboxylate are strong bands at 1574 and 1416 cm^{-1}, respectively.

The TG–DTA thermogram of **1** (figure 3) exhibits four thermal events. The first endothermic process at 152°C accompanied by a weight loss of 6.0% (expected to be 7.2%) can be assigned to the loss of two coordinated waters. Heating of **1** at 150°C

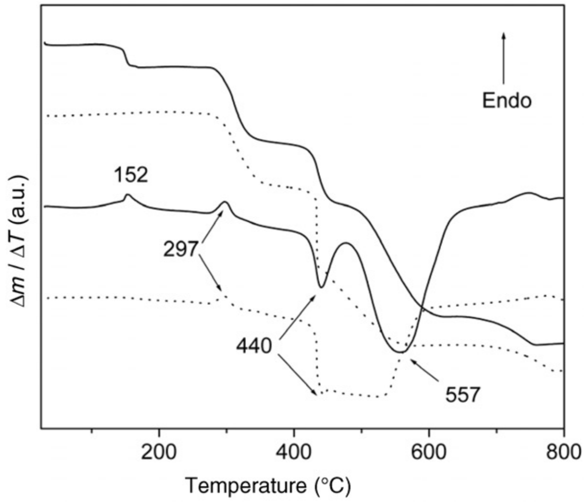


Figure 3. TG–DSC thermogram of **1** (solid line) and the anhydrous compound (dotted lines) obtained by heating **1** at 150°C.

in an oven results in the formation of an anhydrous compound, whose IR spectrum is devoid of the strong O–H signal at 3600 cm^{-1}. The second endothermic signal at 297°C as well as the exothermic events at 440°C and 557°C can be assigned as decomposition of the organic ligand leading to the formation of the oxide residue. Although the exact nature of these ligand decomposition processes cannot be commented upon, in the absence of associated mass spectral data of the emitted fragments, the formation of CaO as the final residue can be inferred as the residue based on mass loss. The complete loss of organics was also evidenced from the featureless IR spectrum of the residue. As expected, the thermogram of the anhydrous product (figure 3) is nearly identical to that of **1** except for the absence of an endothermic signal at around 152°C. Similar results were obtained from the isothermal weight loss studies which add credence to the above observations.

4. Conclusions

Several Ca(II) coordination polymers based on aromatic carboxylic acids have been hydrothermally synthesized and structurally characterized [22–27]. Linkers containing two or more –COOH groups like terephthalic acid, isophthalic acid, 2,5-dihydroxyterephthalic acid, pyrazole-3,5-dicarboxylic acid, pyridine-2,4,6-tricarboxylic acid, etc., were used for synthesis in hydrothermal reactions (table S1). In this study, we have reported on the structural characterization of a 1-D Ca(II) coordination polymer using monocarboxylic 2-ca-4nbaH as the organic linker. The synthesis of the title compound was performed under ambient conditions. The role of the 2-carbamoyl (amide) substituent in 2-ca-4nbaH forming a differently hydrated Ca(II) product can be shown by comparison of the reaction of $CaCO_3$ with 2-ca-4nbaH and (4-nbaH) under identical conditions. Based on the analysis of the structural features of several Ca-carboxylates, we recently showed that when the number of coordinated waters in a Ca-carboxylate is three or less, the carboxylate bridges [5]. The observation of bridging carboxylate for 2-ca-4nba in **1** is in accordance with the earlier result. The coordination polymer **1** reported herein constitutes a new example to the growing list of structurally characterized polymeric alkaline earth coordination compounds.

Supplementary material

CCDC 760722 contains the supplementary crystallographic data for the structure reported in this article. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk). Additional figures related to the crystal structure and diffused reflectance UV-Vis, IR, and luminescence spectra of **1** are available as "Supplementary data" for this article and can be found in the online version.

Acknowledgments

BRS thanks Prof P.K. Bharadwaj, Department of Chemistry, Indian Institute of Technology (IIT), Kanpur for providing the X-ray intensity data of **1**, Dr P. Raghavaiah, School of Chemistry, University of Hyderabad, for facilitating helpful discussions, and Department of Science and Technology (DST), New Delhi, for financing a visit to IIT Kanpur under the DST-SERC Visiting Fellowship.

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