

A one-dimensional barium(II) coordination polymer with a coordinated nitro group of 2-nitrobenzoate*

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Abstract. The aqueous reaction of barium carbonate with 2-nitrobenzoic acid (2-nbaH) results in the formation of a one-dimensional coordination polymer, *catena*-poly[[hexa(aqua)dibarium(II)]bis[(μ_2 -2-nitrobenzoate-O,O,O-NO₂)(μ_2 -2-nitrobenzoate-O,O,O')]] **1**. On heating at 100°C compound **1** is dehydrated to anhydrous barium *bis*(2-nitrobenzoate) **2**. The anhydrous compound can be re-hydrated to **1** on exposure to water vapour. Compounds **1** and **2** were characterized by elemental analysis, IR and UV-Vis spectra, DSC thermograms, weight loss studies and the structure of **1** was determined. **1** and **2** can be thermally decomposed to BaCO₃ by heating at 800°C. The polymer [[Ba(H₂O)₃]₂(μ_2 -2-nba-O,O,O-NO₂)₂(μ_2 -2-nba-O,O,O')₂]_n **1** crystallizes in the centrosymmetric triclinic space group P $\bar{1}$ and all atoms are located in general positions. The polymeric structure is based on a dimeric unit and consists of three water molecules coordinated to a central Ba(II) and two unique 2-nitrobenzoate (2-nba) anions, one of which (μ_2 -2-nba-O,O,O-NO₂) functions as a tridentate ligand and is linked to a Ba(II) through the oxygen atom of the –NO₂ group and forms a monoatomic μ_2 -carboxylate bridge between two symmetry related Ba(II) ions with a Ba...Ba distance of 4.5726(14) Å. The second unique 2-nba anion (μ_2 -2-nba-O,O,O') also functions as a tridentate ligand with the carboxylate oxygen atoms linked to a Ba(II) ion in a bidentate fashion and one of the carboxylate oxygen atoms forming a monoatomic bridge between two symmetry related Ba(II) ions resulting in a Ba...Ba separation of 4.5406(15) Å. These differing tridentate 2-nba ligands link {Ba(H₂O)₃} units into a one-dimensional polymeric chain extending along *b* axis. In the infinite chain each nine coordinated Ba(II) is bonded to three water molecules and further linked to six oxygen atoms of four different 2-nitrobenzoate anions with alternating pairs of Ba(II) ions in the chain bridged by a pair of (μ_2 -2-nba-O,O,O-NO₂) and (μ_2 -2-nba-O,O,O') ligands resulting in alternating Ba...Ba distances of 4.5406(15) and 4.5726(14) Å across the chain.

Keywords. Coordination polymer; *catena*-poly[[hexa(aqua)dibarium(II)]bis[(μ_2 -2-nitrobenzoate-O,O,O-NO₂)(μ_2 -2-nitrobenzoate-O,O,O')]]; nitro ligation; tridentate; monoatomic bridge; nine coordination.

1. Introduction

Although an extensive chemistry of metal carboxylates has been developed^{1,2} this field continues to attract the attention of several researchers in view of the importance of metal carboxylates in bioinorganic chemistry, catalysis, porous materials, etc. The use of carboxylic acids as ambidentate and templating ligands for the synthesis of novel coordination polymers, with metals providing interesting connectivity, is an area of topical research.^{3,4} A few years ago we initiated a research programme on metal carboxy-

lates⁵ and as part of this program we are investigating the synthesis, structural aspects and thermal properties of metal 4-nitrobenzoate (4-nba) complexes.^{6–7} The structurally characterized compounds [Mg(H₂O)₆](4-nba)₂·2H₂O, [Ca(H₂O)₄](4-nba-O)(4-nba-O,O'), [Sr(H₂O)₇](4-nba-O,O')(4-nba)·2H₂O, [[Ba(H₂O)₅](4-nba-O,O')](μ_2 -4-nba-O,O')_n, [Mg(H₂O)₂](Im)₂(4-nba-O)₂ (Im = imidazole), [Mg(H₂O)(N-MeIm)₂](4-nba-O)(μ_2 -4-nba-O,O')₂ (N-MeIm = N-methylimidazole), and [Ca(H₂O)₃](Im)(4-nba-O)₂·Im, serve to demonstrate the rich structural chemistry of the alkali-earth 4-nitrobenzoates and the versatile ligational behaviour of 4-nba.^{8–12} An important structural feature of all these compounds is the H-bonding characteristics of the –NO₂ functionality of

*Dedicated to Prof. S. K. Paknikar on the occasion of his 73rd birthday. #For correspondence

the 4-nba anion with the nitro oxygen atom functioning as a H-bond acceptor and the coordinated or lattice water molecules providing the H-donors. In one-dimensional polymer¹² $[[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba-O},\text{O}')] (\mu_2\text{-}4\text{-nba-O},\text{O}')]]_n$ the $-\text{NO}_2$ group is involved in several $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ interactions with the $-\text{NO}_2$ groups in one polymeric chain hydrogen bonded with the coordinated waters and aromatic hydrogen atoms on an adjacent chain. In order to gain more insight on the structure directing influence of the $-\text{NO}_2$ group, we have now initiated a systematic study of the structural chemistry of compounds derived from the isomeric 2- and 3-nitrobenzoic acids. The vibrational spectral characteristics of 2- and 3-nitrobenzoates of alkali metals like Li, Na, K, Rb and Cs have been recently reported.^{13,14} It is interesting to note that the positioning of the $-\text{NO}_2$ functionality ortho to the $-\text{COOH}$ group in 2-nitrobenzoic acid (2-nbaH) results in the formation of a polymeric Ba(II) compound **1**, the structure of which contains a nitro group coordinated to Ba(II). The results of these investigations are described in this paper.

2. Experimental

2.1 Materials and methods

All the chemicals used in this study were of reagent grade and were used as received. 2-nitrobenzoic acid (2-nbaH) was prepared by the oxidation of 2-nitrobenzaldehyde with 30% H_2O_2 in aqueous methanol. The starting materials and reaction products are air stable and hence were prepared under normal laboratory conditions. The details of the instrumentation used for IR and UV-Vis spectra, DSC and weight loss studies are the same as described in our earlier report.¹² Single crystal X-ray diffraction study was performed at the National single crystal X-ray facility at School of Chemistry, University of Hyderabad.

2.2 Preparation of $[[\text{Ba}(\text{H}_2\text{O})_3]_2(\mu_2\text{-}2\text{-nba-O},\text{O},\text{O}-\text{NO}_2)_2(\mu_2\text{-}2\text{-nba-O},\text{O},\text{O})_2]]_n$ **1**

A mixture of barium carbonate (1.98 g, 10 mmol) and 2-nitrobenzoic acid (2-nbaH) (3.34 g, 20 mmol) was taken in water (50 ml) and heated on a steam bath. The insoluble BaCO_3 slowly started dissolving accompanied with brisk effervescence. The heating

of the reaction mixture was stopped when there was no more evolution of CO_2 . At this stage, the reaction mixture was almost clear. The hot solution was filtered and left undisturbed for 7–8 days. The colourless crystalline blocks that separated were filtered, washed thoroughly with ether and dried. Yield: 4.430 g (85%). The crystals obtained in this method were suitable for X-ray studies. **1** can also be prepared starting from BaCl_2 as the Ba source. The sodium salt of 2-nba was first generated *in situ* by reacting 2-nbaH (1.67 g, 10 mmol) with NaHCO_3 (0.84 g, 10 mmol) in water. Into this, an aqueous solution of $\text{BaCl}_2\cdot 4\text{H}_2\text{O}$ (1.221 g, 5 mmol) was added and the reaction mixture was filtered and left aside for crystallization. The crystals that separated after a few days were isolated in 81% yield. The IR spectrum and the DSC thermogram of the product obtained in this method were identical to that of the product obtained using BaCO_3 as the Ba source.

Anal. found (calcd.) for $\text{C}_{14}\text{H}_{14}\text{BaN}_2\text{O}_{11}$ (523.61): Ba, 25.50 (26.33); 2-nbaH, 62.99 (63.83); C, 31.53 (32.46); H, 2.49 (2.7); N 4.91 (5.41).

IR (in cm^{-1}): 3730–2922 (*br*), 2833 (*w*), 2525 (*w*), 1815 (*w*), 1594 (*s*), 1566 (*s*), 1552 (*s*), 1537 (*m*), 1523 (*s*), 1512 (*s*), 1504 (*m*), 1478 (*s*), 1440 (*s*), 1404 (*s*), 1393 (*s*), 1347 (*s*), 1308 (*s*), 1265 (*w*), 1248 (*w*), 1144 (*w*), 1076 (*w*), 1037 (*w*), 1013 (*w*), 863 (*m*), 841 (*s*), 786 (*s*), 735 (*s*), 702 (*s*), 679 (*w*), 630 (*m*), 513 (*s*), 428 (*s*).

UV-vis: 274 nm ($\epsilon = 14,000 \text{ l mol}^{-1} \text{ cm}^{-1}$).

DSC (in $^\circ\text{C}$): 88 (*Endo*), 230 (*Endo*), 277 (*Endo*), 338 (*Exo*), 444 (*Exo*).

2.3 Preparation of barium bis(2-nitrobenzoate) **2**

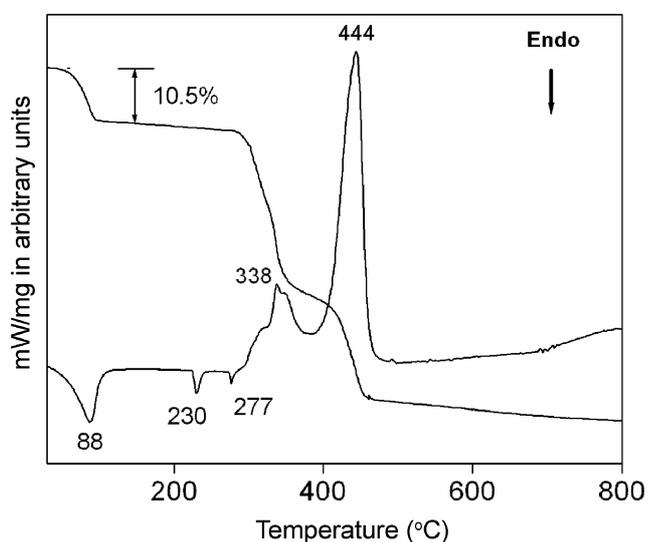
A powdered sample of **1** (0.350 g) was heated on a steam bath for 15 min. This resulted in the formation of the anhydrous compound **2**. The observed mass loss of 10.5% is in good agreement with the expected value (10.32%) for the loss of three moles of water.

IR (in cm^{-1}): 3086 (*w*), 3068 (*w*), 3032 (*w*), 2852 (*w*), 1593 (*s*), 1568 (*s*), 1554 (*s*), 1530 (*s*), 1520 (*s*), 1477 (*m*), 1437 (*s*), 1415 (*s*), 1404 (*s*), 1341 (*s*), 1310 (*s*), 1261 (*s*), 1142 (*s*), 1074 (*s*), 1039 (*w*), 964 (*w*), 862 (*s*), 837 (*s*), 775 (*s*), 780 (*s*), 754 (*s*), 702 (*s*), 648 (*s*), 534 (*w*), 630 (*m*), 432 (*s*).

DSC (in $^\circ\text{C}$): 231 (*Endo*), 272 (*Endo*), 336 (*Exo*), 450 (*Exo*).

Table 1. Technical details of data acquisition and selected refinement results for $[[\text{Ba}(\text{H}_2\text{O})_3]_2(\mu_2\text{-}2\text{-nba-O,O,O-NO}_2)_2(\mu_2\text{-}2\text{-nba-O,O,O'})_2]_n$ **1**.

Empirical formula	$\text{C}_{14}\text{H}_{14}\text{BaN}_2\text{O}_{11}$
Formula weight	$523.61 \text{ g mol}^{-1}$
Temperature	293(2) K
Wavelength	0.71073 \AA
Crystal system	Triclinic
Space group	$\text{P}\bar{1}$
Unit cell dimensions	$a = 8.360(3) \text{ \AA}$, $\alpha = 79.78(6)^\circ$ $b = 8.475(3) \text{ \AA}$, $\beta = 85.52(5)^\circ$ $c = 14.077(6) \text{ \AA}$, $\gamma = 70.49(5)^\circ$
Volume	$925.0(6) \text{ \AA}^3$
Z	2
Density (calculated)	1.880 mg/m^3
Absorption coefficient	2.209 mm^{-1}
$F(000)$	512
Crystal size	$0.42 \times 0.34 \times 0.20 \text{ mm}^3$
Theta range for data collection	2.58 to 25.85°
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-17 \leq l \leq 17$
Reflections collected	8554
Independent reflections	3526 [$R(\text{int}) = 0.0187$]
Completeness to theta = 26.06°	98.6%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3526/9/271
Goodness-of-fit on F^2	1.113
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0227$, $wR2 = 0.0589$
R indices (all data)	$R1 = 0.0230$, $wR2 = 0.0592$
Extinction coefficient	$0.0040(2)$
Largest diff. peak and hole	0.707 and -0.885 e\AA^{-3}

**Figure 1.** TG-DSC thermogram of $[[\text{Ba}(\text{H}_2\text{O})_3]_2(\mu_2\text{-}2\text{-nba-O,O,O-NO}_2)_2(\mu_2\text{-}2\text{-nba-O,O,O'})_2]_n$ **1**. (Heating rate 10 K/min; Air atmosphere).

2.4 Rehydration studies

The anhydrous compound **2** was prepared from **1** as mentioned above. Equilibration of a powdered sam-

ple of **2** over water vapour resulted in the formation of the starting material **1** in near quantitative yield in about a day. The IR spectra and DSC thermogram of the rehydrated compound is identical to that of **1**.

2.5 X-ray crystallography

Intensity data for **1** were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The data integration and reduction were processed with SAINT¹⁵ software. An empirical absorption correction was applied to the collected reflections with SADABS.¹⁶ The structure was solved with direct methods using SHELXS-97¹⁷ and refinement was done against F^2 using SHELXL-97.¹⁷ All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms. The hydrogen atoms of the coordinated water molecules were located in the difference map but were not stable on subsequent refinements and hence were fixed at calculated

Table 2. Selected bond distances (Å) for $[[\text{Ba}(\text{H}_2\text{O})_3]_2(\mu_2\text{-}2\text{-nba-O,O,O-O-NO}_2)_2(\mu_2\text{-}2\text{-nba-O,O,O'})_2]_n$ **1**.

Ba(1)–O(5)	2.703(2)	Ba(1)–O(1)	2.816(2)
Ba(1)–O(11)	2.744(2)	Ba(1)–O(1) ⁱⁱ	2.833(2)
Ba(1)–O(10)	2.767(3)	Ba(1)–O(3)	2.900(2)
Ba(1)–O(6) ⁱ	2.777(2)	Ba(1)–O(5) ⁱ	2.906(2)
Ba(1)–O(9)	2.807(4)	Ba(1)–Ba(1) ⁱ	4.5406(15)
Ba(1)–Ba(1) ⁱⁱ	4.5726(14)		

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

positions by using DFIX command and later refined isotropically using a riding model. The technical details of data acquisition and some selected crystal refinement results for **1** are summarized in table 1.

3. Results and discussion

In an earlier study, the neutralization of a 0.1 M $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ solution by a 0.2 M 2-nbaH solution has been shown to result in the formation of the water soluble barium(II) o-nitrobenzoate trihydrate.¹⁸ In the present work, we have used either BaCO_3 or BaCl_2 as the Ba(II) source. The aqueous reaction of BaCO_3 with 2-nbaH resulted in the formation of the nine coordinated compound $[[\text{Ba}(\text{H}_2\text{O})_3]_2(\mu_2\text{-}2\text{-nba-O,O,O-O-NO}_2)_2(\mu_2\text{-}2\text{-nba-O,O,O'})_2]_n$ **1**. Alternatively, **1** can be prepared by reacting an aqueous BaCl_2 with *in situ* generated sodium 2-nba. The observed analytical and spectral characteristics of compound **1** are in good agreement with the previously reported trihydrate.¹⁸ Crystals of **1** were characterized by elemental analysis, infrared and optical spectra, DSC thermogram, and single crystal X-ray structure determination. As the solid state structure of compound **1** (*vide infra*) turned out to be a one-dimensional polymer, the reaction of the water soluble compound **1** was investigated with aqueous sulfate. The reaction of an aqueous solution of **1** with aqueous Na_2SO_4 resulted in the immediate precipitation of BaSO_4 in quantitative yield. It cannot be unambiguously stated that the polymeric structure of **1** does not persist in solution, based only on its behaviour towards sulfate. Nevertheless this reaction constitutes a convenient method for the incorporation of 2-nba anions in the place of $(\text{SO}_4)^{2-}$ in other metal sulfates. The use of the title compound as a convenient source for delivering 2-nba assumes importance in view of the reported behaviour of 2-nba compounds to exhibit polymorphism.¹⁹

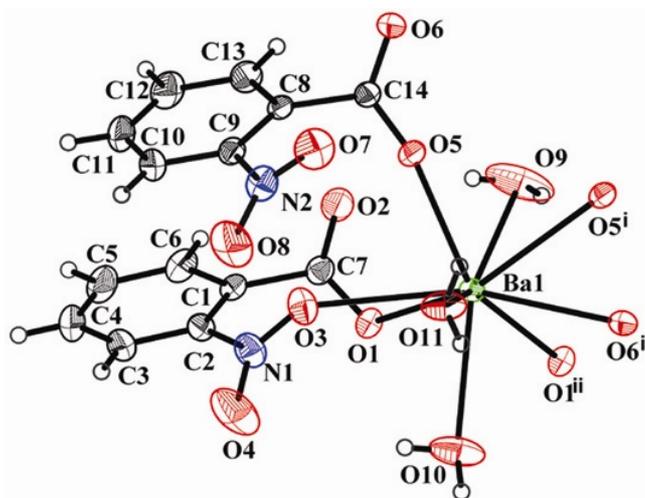


Figure 2. The coordination sphere of Ba(II) in $[[\text{Ba}(\text{H}_2\text{O})_3]_2(\mu_2\text{-}2\text{-nba-O,O,O-O-NO}_2)_2(\mu_2\text{-}2\text{-nba-O,O,O'})_2]_n$ **1** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Symmetry code: (i) $[-x + 1, -y + 1, -z + 1]$; (ii) $[-x + 1, -y + 2, -z + 1]$.

Heating of **1** on a steam bath results in the formation of the anhydrous barium(II) *bis*(2-nitrobenzoate) **2** while the pyrolysis of **1** or **2** in a Bunsen flame results in the formation of BaCO_3 . **1** absorbs strongly in the UV region at 274 nm, which can be assigned to the intramolecular charge transfer transition of the aromatic carboxylate. The IR spectra of **1** and **2** (see web version) exhibit several sharp bands in the mid-infrared region, clearly indicating the presence of the organic moiety. The broad and strong signal in the region $3730\text{--}2922\text{ cm}^{-1}$ in **1** indicates the presence of water and can be assigned to the O–H stretching vibration. The IR spectrum of **2** is devoid of bands above 3100 cm^{-1} , which is indicative of the anhydrous nature of **2**. The spectrum below 3100 cm^{-1} , is similar to that of **1**. Although the IR spectra **1** and **2** exhibit the absorptions due to the vibrations of the

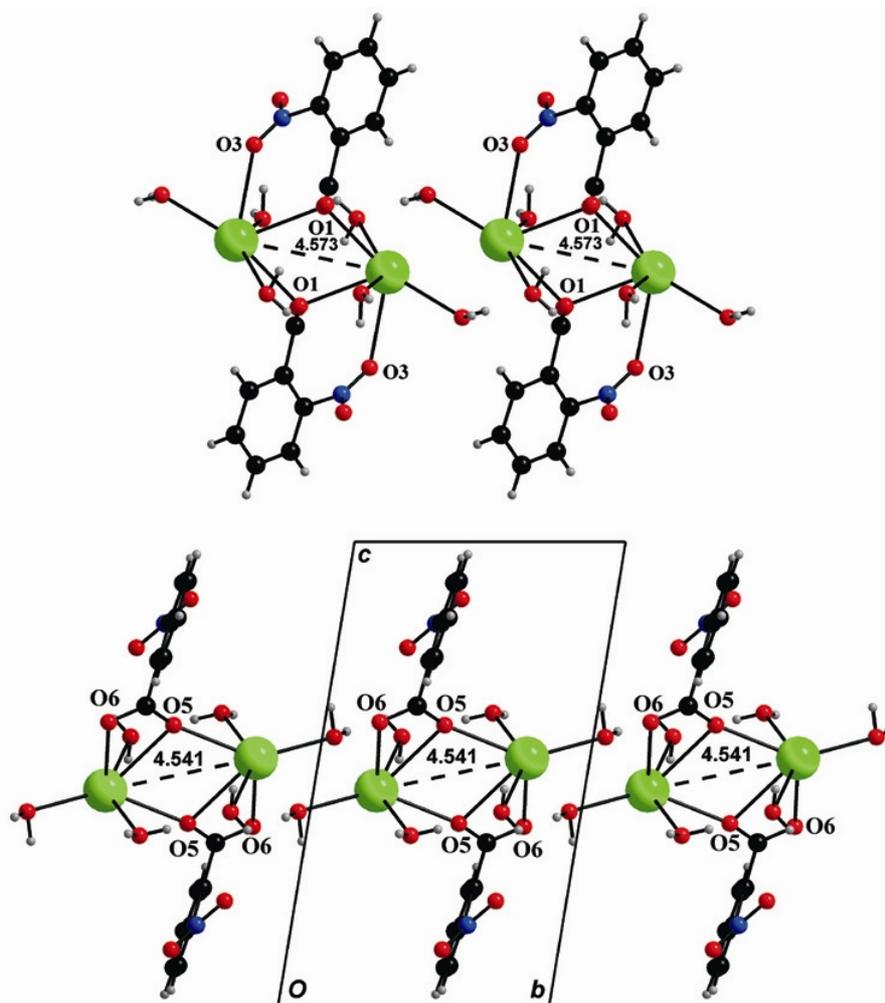


Figure 3. A view along *a* showing the dimeric units of $[\text{Ba}(\text{H}_2\text{O})_3(\mu_2\text{-2-nba-O,O,O-NO}_2)_2]$ formed by the tridentate ligand ($\mu_2\text{-2-nba-O,O,O-NO}_2$). Each Ba(II) is linked to a nitro oxygen O3 and both the Ba(II) are bridged by the carboxylate oxygen O1 (top). A view along *a* of the dimeric units $[\text{Ba}(\text{H}_2\text{O})_3(\mu_2\text{-2-nba-O,O,O}')_2]$ formed by the tridentate ligand ($\mu_2\text{-2-nba-O,O,O}'$). Each Ba(II) is linked to O5 and O6 and both the Ba(II) in the dimer are bridged by the carboxylate oxygen O5 (bottom).

carboxylate and nitro groups, no definite conclusions can be drawn on the nature of the binding of the 2-nba ligand based on infrared data alone.

The TG-DSC thermogram of **1** (figure 1) exhibits an endothermic event at around 88°C accompanied by a mass loss of 10.5% assignable for the removal of three molecules of water. The dehydration process is followed by an endothermic signal at around 230°C , which can be assigned to a phase change. Above this temperature, **1** undergoes a complex decomposition process as evidenced by the strong exothermic events at 338 and 444°C . In the absence of mass spectral data of the emitted fragments no defi-

nite conclusions can be drawn on the exact nature of the decomposition processes. The observed residue is in good agreement for the formation of BaCO_3 . The results of the isothermal weight loss studies at 100°C (steam bath) and at 800°C add credence to the TG-DSC data. As expected, the TG-DSC thermogram of the anhydrous compound **2** (see web version) is devoid of the first endothermic signal observed for the dehydration of **1** and the thermal decomposition pattern of **2** is similar to that of **1** above this temperature, resulting in the formation of BaCO_3 residue. Equilibration of the anhydrous compound **2** in an atmosphere of water vapour results

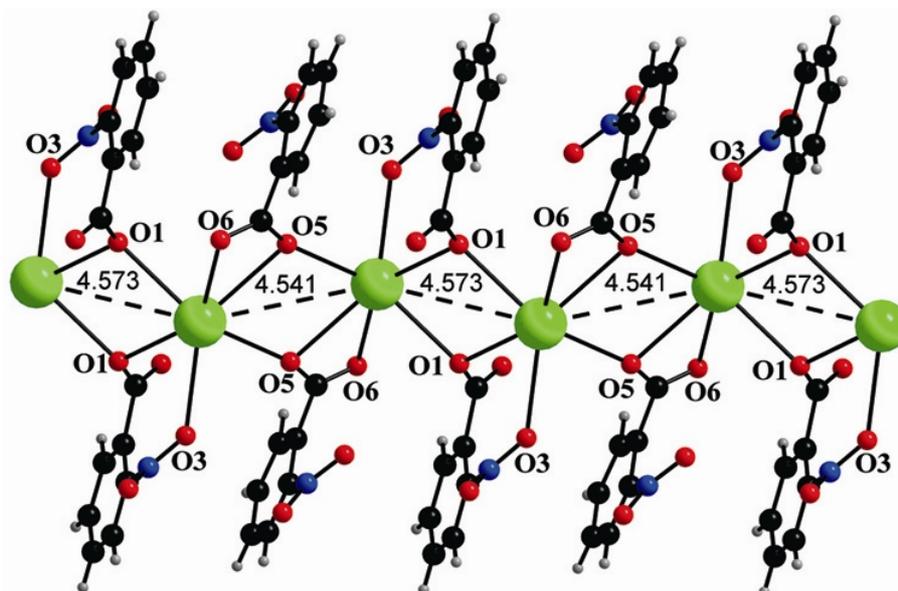


Figure 4. A view along a showing the 1-D polymeric chain of **1**. Alternating pairs of Ba(II) ions are linked by a pair of tridentate (μ_2 -2-nba-O,O,O-NO₂) and (μ_2 -2-nba-O,O,O') ligands resulting in alternating Ba...Ba distances of 4.5406(15) and 4.5726(14) Å. For clarity, the coordinated water molecules on Ba(II) are not shown.

in the regeneration of compound **1** as confirmed by a comparison of the IR spectrum of the rehydrated product with that of **1**.

The coordination polymer $[\text{Ba}(\text{H}_2\text{O})_3]_2(\mu_2\text{-2-nba-O,O,O-NO}_2)_2(\mu_2\text{-2-nba-O,O,O}')_2]_n$ **1** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ and all atoms are located in general positions. The observed Ba–O bond distances vary between 2.703(2) and 2.906(2) Å (table 2). These values are comparable with those reported for other Ba(II)-carboxylates.^{12,20} In the crystal structure, the Ba(II) is nine coordinated and is bonded to three O atoms from the three aqua ligands and six oxygen atoms from four symmetry related 2-nba anions (figure 2). The central metal is linked to the O atoms (O9–O11) of three water molecules and the Ba–O(H₂O) distances range from 2.744(2) to 2.807(4) Å.

The polymeric structure is based on a dimer and each formula unit of **1** contains three coordinated water ligands and two unique 2-nitrobenzoate ligands both of which function as tridentate ligands in different fashion. The first unique 2-nba ligand (O1, O2, O3) functions as a monoatomic bridging ligand, linking two symmetry related Ba(II) ions via O1 with Ba1–O1 bond distances of 2.816(2) and 2.833(2) Å respectively. It is interesting to note that the O3 oxygen of the nitro functionality makes a Ba1–O3 bond at 2.900(2) Å. This unique tridentate

2-nba ligand is designated as (μ_2 -2-nba-O,O,O-NO₂). It is to be noted that the proximity of the nitro group to the carboxylate has resulted in this bond. A similar behaviour was earlier reported for the 2D-coordination polymer of Ba(II) derived from 2-aminobenzoic acid with a Ba–N bond at 3.047(4) Å.²⁰ To the best of our knowledge compound **1** constitutes the first example of a structurally characterized 2-nitrobenzoate showing a coordinated nitro group. The second independent 2-nba ligand (O5, O6) also functions as a tridentate ligand with each Ba(II) linked to O5 and O6 in a bidentate manner (Ba1–O5 2.703(2); Ba1–O6 2.777(2) Å) and the O5 further linked to a symmetry related Ba(II) ion at 2.906(2) Å resulting in a monoatomic bridging mode. However, the nitro oxygen atoms are not at bonding distance to Ba(II) for this ligand. This second tridentate 2-nba ligand is designated as (μ_2 -2-nba-O,O,O'). The structure of **1** can be explained as being composed of a pair of $\{\text{Ba}(\text{H}_2\text{O})_3\}$ units linked via two μ_2 -carboxylate bridges by a pair of (μ_2 -2-nba-O,O,O-NO₂) ligands leading to a (Ba₂O₂) four-membered ring (figure 3) with a Ba...Ba distance of 4.5726(14) Å resulting in the formation of dimeric units of composition $[\text{Ba}(\text{H}_2\text{O})_3(\mu_2\text{-2-nba-O,O,O-NO}_2)_2]_2$ along b axis. The linking of a pair of $\{\text{Ba}(\text{H}_2\text{O})_3\}$ units by a pair of tridentate (μ_2 -2-nba-O,O,O') ligands results in the formation of dimeric units of

Table 3. Hydrogen-bonding geometry (Å, °) for $[[\text{Ba}(\text{H}_2\text{O})_3]_2(\mu_2\text{-2-nba-O,O,O-O-NO}_2)_2(\mu_2\text{-2-nba-O,O,O'})_2]_n$ **1**.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	D(D...A)	<DHA
O11–H11A...O9 ⁱ	0.836	1.949	2.780	173
O9–H9A...O10 ⁱⁱ	0.797	2.275	2.775	121
O10–H10A...O6 ⁱⁱⁱ	0.857	1.899	2.752	174
O11–H11B...O2 ^{iv}	0.847	1.870	2.714	175
O9–H9B...O2	0.817	2.429	3.224	165
C12–H12...O8 ^v	0.930	2.689(3)	3.612	172

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

composition $[\text{Ba}(\text{H}_2\text{O})_3(\mu_2\text{-2-nba-O,O,O'})_2]_2$ along *b* axis (figure 3). It is interesting to note that this binding mode of 2-nba results in a Ba...Ba separation of 4.5406(15) Å, which is slightly shorter than the Ba...Ba separation observed earlier for the tridentate 2-nba ligand binding through the nitro oxygen. The extended structure is arrived at by the linking of two $[\text{Ba}(\text{H}_2\text{O})_3(\mu_2\text{-2-nba-O,O,O-NO}_2)_2]$ units by a pair of $(\mu_2\text{-2-nba-O,O,O'})$ ligands. Thus the two different tridentate 2-nba ligands link the $\{\text{Ba}(\text{H}_2\text{O})_3\}$ units into a one-dimensional polymeric chain extending along *b*. In the infinite chain, each nine coordinated Ba(II) is bonded to three water molecules and further linked to six oxygen atoms of four different 2-nba anions with alternating pairs of Ba(II) ions in the chain bridged by a pair of $(\mu_2\text{-2-nba-O,O,O',O-NO}_2)$ and $(\mu_2\text{-2-nba-O,O,O'})$ ligands resulting in alternating Ba...Ba distances of 4.5406(15) and 4.5726(14) Å across the chain (figure 4).

An analysis of the crystal structure of **1** reveals that each nine coordinated Ba(II) complex in the polymeric chain is H-bonded to neighbouring complexes in the polymeric chain with the aid of two varieties of H-bonding interactions. All the hydrogen atoms attached to the coordinated waters excepting H10B and one hydrogen atom on a benzene ring function as H-donors. Two oxygen atoms from the coordinated water molecules O9 and O10, the free carboxylate oxygen O2 and a coordinated oxygen O6 and the nitro oxygen O8 function as H-acceptors. Thus each Ba(II) complex in **1** is linked to five other complexes with the aid of five O–H...O bonds and a C–H...O interaction (table 3). The C–H...O interaction between the nitro oxygen O8 and an aromatic H serves to link parallel chains resulting in a two-dimensional H-bonded network (see web version).

The short ring interactions and distances between the ring centroids (Cg–Cg) in **1** were analysed by us-

ing the program PLATON.²¹ The Cg–Cg distance between the two 2-nba ligands is 4.089 Å and the perpendicular distance from the centre of the first ring to the second (interplanar distance) is 3.644 Å accompanied by a dihedral angle of 5.58°. These values indicate that the rings do not overlap and the magnitude of the values is suggestive of no stacking interactions.

The availability of structural information of many Ba(II) coordination polymers of varying dimensionalities derived from several carboxylic acids permits a comparative study of Ba(II) coordination polymers.^{22–33} In these compounds the Ba...Ba distance across the polymeric chain varies from 4.069(2) in the three dimensional (3-D) coordination polymer derived from 2,2'-dithiobis(benzoic acid) to 7.467 Å in the 1-D Ba(II) polymer derived from the N-substituted amino acid containing the N-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl) group (table 4). In all these compounds, the carboxylate anions function as bridging ligands. The coordination number of Ba(II) varies from 8 to 10 with nine coordination observed in several compounds. In four of the polymers the Ba...Ba separations are shorter than the sum of the van der Waals radii (4.28 Å) indicating weak metal–metal interactions, while in other compounds the observed metal–metal contacts are longer. Interestingly, the observed Ba...Ba distances of 4.5406(15) and 4.5726(14) Å in **1** are much shorter than the Ba...Ba separation of 6.750(1) Å in the related 1-D polymer $[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba})_2]_n$ derived from 4-nitrobenzoic acid where the nitro group is disposed *trans* to the carboxylate. It is to be noted that the polymeric complex $[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba})_2]_n$ contains two unique 4-nba ligands one of which functions as a bidentate ligand with the other functioning as a bridging bidentate ligand.¹² In the Ba(II) polymer of 4-nba the oxygen atoms of the nitro

Table 4. Ba···Ba distances across the chain in some Ba(II) coordination polymers containing bridging carboxylates.

Compound	C.N.	Ba···Ba distance (Å)*	Dimensionality (<i>D</i>) of polymer	Reference
[{Ba ₂ (DTBB) ₂ (H ₂ O) ₂ }·0.5H ₂ O] _n [#]	9, 8, 8	4.069(2)	3-D	22
[Ba(C ₆ H ₄ (COO) ₂) ₂] _n	8	4.123	3-D	23
[Ba(HbpdC) ₂ (H ₂ O) ₂] _n	9	4.1386(17)	1-D	24
[Ba ₉ (CH ₃ COO) _{1,4} (ClO ₄) ₄] _n [#]	8, 9, 9	4.27	3D	25
[Ba(2-aba) ₂ (H ₂ O) ₂] _n	9	4.32	2-D	20
[Ba(C ₇ H ₅ O ₂ S) ₂ (H ₂ O) ₄] _n	9	4.335	1-D	26
[Ba(C ₈ H ₅ O ₃) ₂ (H ₂ O) ₂] _n	8	4.4336(3)	1-D	27
[[Ba(PY-met) ₂ (H ₂ O) ₄]·3H ₂ O] _n	10	4.4451(2)	3-D	28
[[Ba(H ₂ O) ₃ (2-nba) ₂] ₂] _n 1	9	4.5406(15) 4.5726(14)	1-D	This work
[Ba(C ₅ H ₄ O ₄) ₂ (H ₂ O) ₄] _n	9	4.595(4)	2-D	29
[Ba(1,3-BDOA)(H ₂ O) ₂] _n	10	4.755(3)	3-D	30
[Ba(C ₁₀ H ₁₂ N ₅ O ₆) ₂ (H ₂ O) ₆] _n	9	6.575(0)	1-D	31
[Ba(H ₂ PMA)(H ₂ O) ₅] _n	9	6.65	2-D	32
[Ba(H ₂ O) ₅ (4-nba) ₂] _n	9	6.750(1)	1-D	12
[[Ba(H ₂ IDC) ₂ (H ₂ O) ₄]·2H ₂ O] _n	10	6.765(3)	2-D	33
[[Ba(PY-glycinato) ₂ (H ₂ O) ₅]·H ₂ O] _n	9	6.916(1)	1-D	28
[[Ba(PY-serinato) ₂ (H ₂ O) ₄]·3H ₂ O] _n	10	7.139(0)	1-D	28
[[Ba(PY-glycylglycinato) ₂ (H ₂ O) ₂] _n	8	7.467	2-D	28

Abbreviations used: CN = coordination number; [#]three unique Ba(II) ions; DTBB = 2,2'-dithiobis(benzoate); (C₆H₄(COO)₂) = terephthalate; HbpdC = 2'-carboxybiphenyl-2-carboxylate; 2-aba = 2-aminobenzoate; (C₇H₅O₂S) = thiosalicylate; (C₈H₅O₃) = 2-formylbenzoate; PY = N-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxypyrimidin-2-yl); met = monoanion of methionine; C₅H₄O₄ = mesaconate anion; (1,3-BDOA) = *m*-phenylenedioxyacetate; (C₁₀H₁₂N₅O₆) = N-4-amino-1,6-dihydro-1-methyl-5-nitroso-6-oxypyrimidin-2-yl)-(S)-glutamato; (H₂PMA) = pyromellitic acid; 4-nba = 4-nitrobenzoate; H₂IDC = 1H-imidazole-4,5-dicarboxylate monoanion; *For 2-D and 3-D polymers only the shortest Ba···Ba contact is given.

group are not involved in coordination unlike in compound **1**. It is interesting to note that both the oxygen atoms of the nitro functionalities in both the unique 4-nba ligands in [Ba(H₂O)₅(4-nba)₂]_n are involved in C–H···O interactions unlike in compound **1** where one oxygen atom (O8) of the tridentate (μ_2 -2-nba-O,O,O') ligand is involved in C–H···O bonding. In the Ba(II) coordination polymer derived from 2-aminobenzoic acid the Ba(II) exhibits a Ba–N bond but the coordination polymer is three-dimensional. Hence it appears that the Ba···Ba distances in Ba-carboxylate coordination polymers are probably determined by a combination of several factors, which include the electronic and steric requirements of the central metal, the denticity, flexibility, bridging behaviour and H-bonding characteristics of the carboxylate ligand.

4. Conclusions

In summary, we have described the synthesis, structural characterization and properties of a one-dimen-

sional Ba(II) coordination polymer **1**, containing 2-nba as a bridging ligand. Compound **1** constitutes an example of a structurally characterized 2-nitrobenzoate showing nitro ligation. The observed Ba···Ba distances of 4.5406(15) and 4.5726(14) Å across the chain in the 1-D polymer **1** are much shorter than the Ba···Ba separation of 6.750(1) Å between adjacent metal atoms in the 1-D polymeric Ba(II) compound of 4-nitrobenzoate. The reaction of the title compound with aqueous sulphate constitutes a useful method for the incorporation of 2-nba in lieu of sulphate. Current efforts in our laboratory are directed to exploit this reaction for the synthesis of new 2-nba compounds.

Supplementary material

Illustrations describing the infrared spectra of compounds **1** and **2**, the TG-DSC thermogram of **2** and the crystallographic packing diagram of compound **1** are available on the web version of this paper. Crys-

tallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 666968. 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).

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