

catena*-Poly[[*(pentaqua)*(4-nitrobenzoato-O,O')barium(II)](*μ*-4-nitrobenzoato-O,O')]: A barium(II) coordination polymer showing O–H...O and C–H...O interactions

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Abstract. The reaction of barium carbonate with 4-nitrobenzoic acid (4-nbaH) results in the formation of a Ba(II) coordination polymer, *catena*-poly[[*(pentaqua)*(4-nitrobenzoato-O,O')barium(II)](*μ*-4-nitrobenzoato-O,O')] **1**. The polymeric compound [[Ba(H₂O)₅(4-nba-O,O')](*μ*-4-nba-O,O')] **1** was characterized by elemental analysis, IR and UV–Vis spectra, weight loss studies, X-ray powder diffraction and its structure determined. In **1** five water molecules are coordinated to the central metal and one of the 4-nba ligands is bonded to Ba(II) in a bidentate manner (4-nba-O,O') through the carboxylate O atoms. The [*(pentaqua)*(4-nitrobenzoato-O,O')barium(II)] units are linked into an infinite one-dimensional chain along *b*-axis with the aid of the second 4-nba anion, which functions as a bridging bidentate (*μ*-4-nba-O,O') ligand. This results in nine coordination around each Ba(II) ion in the coordination polymer. A long Ba...Ba distance of 6.750(1) Å is observed between adjacent Ba(II) ions in the chain and the oxygen atoms of the carboxylate group and the nitro functionalities of the 4-nba ligand are involved in several O–H...O and C–H...O interactions.

Keywords. Coordination polymer; *catena*-poly[[*(pentaqua)*(4-nitrobenzoato-O,O')barium(II)](*μ*-4-nitrobenzoato-O,O')]; bridging bidentate; nine coordination; O–H...O and C–H...O interactions.

1. Introduction

The design of supramolecular architectures employing carboxylic acids as ambidentate and templating ligands with metals providing interesting connectivity, is an area of current research.^{1,2} The ready availability of benzene based carboxylic acids in pure form, combined with the fact that the carboxylate group is a versatile donor that can bind in a variety of ways,^{3,4} has led to the structural characterization of several metal carboxylates with novel structural features.^{5–12} Potential donor groups like –NH₂, –OH, –SH, or another –COOH can be introduced into the rigid six-membered ring and the positioning of these groups can be altered with respect to the carboxylate functionality, are additional advantages of using benzene based systems. The introduction of additional groups affects the acidity of the carboxylic acid, which is an

important aspect from a synthetic point of view of metal carboxylates. Substituents in the benzene ring like –NO₂, F[–], Cl[–], Br[–] etc. lack the donor characteristics to form a strong metal-ligand bond. However, the resulting acids are stronger acids as compared to benzoic acid and hence can exhibit different reactivity characteristics when treated with metal sources. The nitro group can participate in secondary interactions by forming H-acceptor bonds.^{13,14} In this context we are investigating the synthetic, spectral, thermal and structural aspects of metal-nitrobenzoates with a view to prepare new compounds by exploiting the H-bonding characteristics of the –NO₂ group. In recent reports we have described the synthesis and structural characterization of 4-nitrobenzoate (4-nba) complexes of Mg(II), Ca(II) and Sr(II).^{15–18} In continuation of this work, we have structurally characterized a one dimensional Ba(II) coordination polymer using 4-nba as ligand, which exhibits O–H...O and C–H...O interactions. The results of these investigations are described in this paper.

*Dedicated to the memory of Late Prof. Bhaskar G. Maiya

**For correspondence

2. Experimental

2.1 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 routinely prepared under normal laboratory conditions. Infrared (IR) spectra were recorded on a Shimadzu (IR Prestige-21) FTIR spectrometer in the range 4000–400 cm^{-1} . The samples were prepared as KBr diluted pellets in the solid state and the IR signals were referenced to polystyrene bands. Electronic spectra were recorded using matched quartz cells on a Shimadzu (UV-2450) spectrophotometer. DSC studies were performed in a Netzsch Thermal Analyser STA (Luxx) while isothermal weight loss studies were done using a temperature-controlled oven. Single crystal X-ray diffraction study was performed at the National single crystal X-ray facility at School of Chemistry, University of Hyderabad.

2.1 Preparation of $[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba-O}, \text{O}')(\mu\text{-}4\text{-nba-O}, \text{O}')_n]$ **1**

A mixture of barium carbonate (1.98 g, 10 mmol) and 4-nitrobenzoic acid (4-nbaH) (3.34 g, 20 mmol) was taken in water (50 ml) and heated on a steam bath. The insoluble starting materials 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 and the pH was close to neutral. The hot solution was filtered and left undisturbed for 4–5 days. The colourless crystalline blocks that separated were filtered, washed thoroughly with ether and dried. Yield: 4.6534 g (83%). The crystals obtained in this method were suitable for X-ray studies. Alternatively **1** can be prepared by using BaCl_2 as the Ba source. The sodium salt of 4-nba was first generated *in situ* by reacting 4-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 80% yield. The IR spectrum and X-ray powder pattern of the product obtained in this method was identical to that of the spectrum of the product obtained using BaCO_3 as the Ba source.

Anal. Found (calcd.) for $\text{C}_{14}\text{H}_{18}\text{BaN}_2\text{O}_{13}$ (559.64): Ba, 24.50 (24.53); 4-nbaH, 60.99 (59.72); C, 29.86(30.00); H, 3.114 (3.23); N 5.073 (5.00)

IR (KBr cm^{-1}): 3730–2922(*bm*), 2833(*w*), 2525(*w*), 2440(*w*), 2361(*w*), 1950(*w*), 1815(*w*), 1630(*m*), 1612(*m*), 1566(*s*), 1552(*s*), 1537(*m*), 1516(*m*), 1512(*s*), 1504(*m*), 1449(*w*), 1402(*s*), 1352(*s*), 1323(*s*), 1279(*w*), 1248(*w*), 1177(*w*), 1136(*w*), 1109(*m*), 1013(*w*), 881(*m*), 839(*s*), 806(*s*), 797(*s*), 725(*s*), 679(*w*), 630(*m*), 513(*s*). UV-vis: 274 nm ($\epsilon = 14000 \text{ l mol}^{-1} \text{ cm}^{-1}$).

2.2 X-ray crystallography

Intensity data for **1** were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069 \text{ \AA}$). The data integration and reduction were processed with SAINT¹⁹ software. An empirical absorption correction was applied to the collected reflections with SADABS.²⁰ The structure was solved with direct methods using SHELXS-97²¹ and refinement was done against F^2 using SHELXL-97.²¹ 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 all the coordinated water molecules excepting one H atom attached to O24, were located in the difference map. The O–H bond lengths were set to ideal values (0.820 \AA) and afterwards 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

The aqueous reaction of BaCO_3 with 4-nbaH resulted in the formation of the nine coordinated $[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba-O}, \text{O}')(\mu\text{-}4\text{-nba-O}, \text{O}')_n]$ **1**, which can also be crystallized from an aqueous BaCl_2 solution and *in situ* generated sodium 4-nitrobenzoate. It is interesting to note that the reaction of BaCl_2 with 4-abaH (abaH is aminobenzoic acid) in the presence of a weak base results in the formation of the chloride containing compound $[\text{BaCl}(4\text{-aba})]^{22}$ while the reaction of BaCO_3 with 4-abaH leads to the formation of a hydrated *bis*(4-aba) complex of barium.²³ With 4-nbaH the use of both the chloride or the carbonate of Ba(II) results in the formation of an identical product. It has been reported²⁴ that in the structure of the polymeric complex $[\text{Ba}(\text{H}_2\text{O})(2\text{-aba})_2]_n$ the Ba(II)

ion is coordinated to the amino N atom of the 2-abaH. A recent report describes the synthesis of a 1 : 2 adduct of diaquabarium *bis*(3-hydroxybenzoate) with 1,10-phenanthroline.²⁵ In addition, we have incorporated imidazole (Im) ligand into the coordination sphere of Mg and Ca 4-nitrobenzoates.¹⁵ In view of this, the reactivity of the title complex was investigated with N-donor ligands to incorporate other ligands and get new compounds. So far, our attempts to incorporate ligands like Im into the coordination sphere of Ba(II) in **1** have not been successful.

Crystals of **1** were characterized by elemental analysis, infrared and optical spectra, X-ray powder diffraction and single crystal X-ray structure determination. Treatment of **1** with dilute HCl resulted in the formation of the insoluble 4-nbaH. The insoluble 4-nitrobenzoic acid (4-nbaH) obtained on acid treatment of complex **1** was weighed and analysed as descri-

bed earlier.¹³ The filtrate obtained from this procedure was analysed gravimetrically for Ba(II) content. Pyrolysis of **1** in a Bunsen flame results in the formation of BaCO₃. The formula of the complex **1** was arrived at based on these data. The X-ray powder pattern of **1** (figure 1) exhibits several strong lines indicating its crystalline nature. A comparison of the experimental powder pattern of the bulk sample with that of the pattern calculated from single crystal data (see below) reveals the phase purity of **1**.

Complex **1** absorbs strongly in the UV region at 274 nm, which can be assigned to the intramolecular charge transfer transition of the aromatic acid and the observed absorption maximum is comparable to the value observed for other nitrobenzoate complexes.^{15–18}

Table 1. Technical details of data acquisition and selected refinement results for $[[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba-}O,O')](\mu\text{-}4\text{-nba-}O,O')]_n$ **1**.

Empirical formula	C ₁₄ H ₁₈ Ba ₁ N ₂ O ₁₃
Formula weight	559.64 g mol ⁻¹
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 6.6217(4) Å <i>b</i> = 10.7141(6) Å <i>c</i> = 29.1006(16) Å β = 102.77(1)°
Volume	2013.5(2) Å ³
<i>Z</i>	4
Density (calculated)	1.846 mg/m ³
Absorption coefficient	2.043 mm ⁻¹
<i>F</i> (000)	1104
Crystal size	0.42 × 0.34 × 0.28 mm ³
Theta range for data collection	1.43 to 26.06°
Index ranges	-8 ≤ <i>h</i> ≤ 7, -13 ≤ <i>k</i> ≤ 12, -30 ≤ <i>l</i> ≤ 35
Reflections collected	11119
Independent reflections	3637 [<i>R</i> (int) = 0.0163]
Completeness to theta = 26.06°	99.3%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3956/0/272
Goodness-of-fit on <i>F</i> ²	1.082
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0238, <i>wR</i> 2 = 0.0534
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0265, <i>wR</i> 2 = 0.0548
Extinction coefficient	0.0040(2)
Largest diff. peak and hole	0.569 and -0.436 eÅ ⁻³

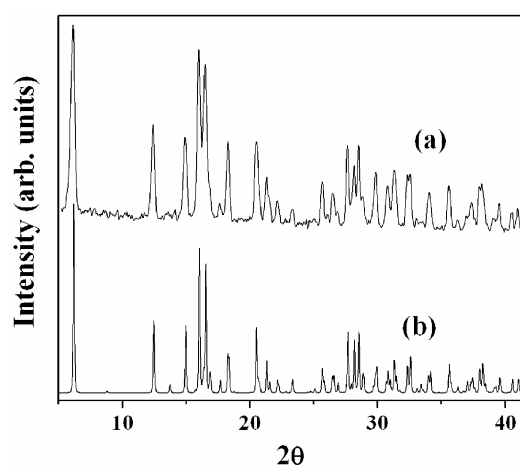


Figure 1. X-ray powder pattern of $[[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba-}O,O')](\mu\text{-}4\text{-nba-}O,O')]_n$ **1**: (a) Experimental (b) Calculated from single crystal data.

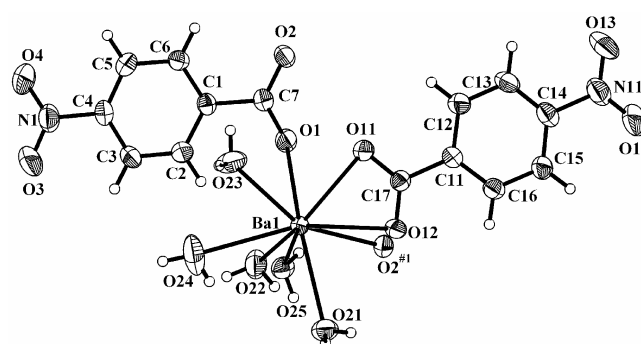


Figure 2. The coordination sphere of Ba(II) in $[[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba-}O,O')](\mu\text{-}4\text{-nba-}O,O')]_n$ **1** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Symmetry code: #1 - *x* + 1, *y* + 1/2, -*z* + 3/2.

The IR spectrum of **1** exhibits several sharp bands in the mid-infrared region, clearly indicating the presence of the organic moiety. A comparison of the IR spectra of the title complex with those of the other alkali-earth 4-nitrobenzoate like $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$, $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ and $[\text{Sr}(\text{H}_2\text{O})_7(4\text{-nba})](4\text{-nba}) \cdot 2\text{H}_2\text{O}$ reveals that all these spectra show strong and broad signals centered around 3000 cm^{-1} with differing profiles which can be attributed to the different degrees of hydration of these compounds. Interestingly the IR spectra of all the complexes are nearly identical in the region between $1600\text{--}1300\text{ cm}^{-1}$, where the absorptions due to the vibrations of the carboxylate and nitro functionalities occur. Hence no definite conclusions can be drawn on the nature of the binding of the 4-nba ligand in **1** based on only infrared data. The broad and strong signal in the region $3730\text{--}2922\text{ cm}^{-1}$ indicates the complex is hydrated and can be assigned to the O–H stretching vibration of water.

The Ba(II) coordination polymer **1** crystallizes in the monoclinic space group $P2_1/c$ and all atoms are located in general positions. The observed Ba–O bond distances vary between $2.7616(18)$ to $2.8981(18)\text{ \AA}$ while the O–Ba–O bond angles range from $45.27(5)$ to $155.92(6)^\circ$ (table 2). These values are comparable with those reported for other polymeric Ba-carboxy-

lates.^{24,26–31} The central metal is nine coordinated and is linked to the O atoms (O21–O25) of the five water molecules (figure 2). The observed Ba–O (water) distances range from $2.7729(19)$ to $2.876(2)\text{ \AA}$. Each formula unit of **1** contains five coordinated water ligands and two 4-nitrobenzoate ligands one of which functions as a bidentate ligand (4-nba-O,O') through O11 and O12 at $2.8161(18)$ and $2.8981(18)\text{ \AA}$ respectively. The O1 atom of the second 4-nba is linked to the central metal at $2.7616(18)\text{ \AA}$ while the O2 is linked to a neighbouring Ba(II) atom at $2.8049(18)\text{ \AA}$ and thus functions as a bridging ligand (μ -4-nba-O,O'). This binding mode of 4-nba results in the formation of an infinite O–Ba–O chain along *b* axis consisting of pentaquo Ba(II) ions with the 4-nba ligands linked to the Ba(II) on either side of the chain (figure 3). A long Ba...Ba distance of $6.750(1)\text{ \AA}$ is observed between adjacent Ba(II) ions in the chain accompanied by a O–Ba–O angle of $83.66(6)^\circ$. Polymeric Ba(II) carboxylates of varying dimensionalities have been structurally characterized earlier using carboxylic acids like 2-aminobenzoic acid (2-abaH), 2,2'-dithiobis(benzoic acid), diphenic acid, the α,β -unsaturated mesaconic acid, thiosalicylic acid, terephthalic acid and pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid).^{26–31} In all these com-

Table 2. Selected bond distances (\AA) and bond angles ($^\circ$) for $[[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba-O,O}')] (\mu\text{-4-nba-O,O}')_n \mathbf{1}$.

Ba(1)–O(1)	2.7616(18)	Ba(1)–O(25)	2.8476(18)
Ba(1)–O(21)	2.7729(19)	Ba(1)–O(24)	2.848(2)
Ba(1)–O(2)#1	2.8049(18)	Ba(1)–O(23)	2.858(2)
Ba(1)–O(11)	2.8161(18)	Ba(1)–O(22)	2.876(2)
Ba(1)–O(12)	2.8981(18)		
O(1)–Ba(1)–O(21)	143.07(6)	O(11)–Ba(1)–O(23)	74.85(6)
O(1)–Ba(1)–O(2)#1	83.66(6)	O(25)–Ba(1)–O(23)	68.53(6)
O(21)–Ba(1)–O(2)#1	68.38(6)	O(24)–Ba(1)–O(23)	60.25(8)
O(1)–Ba(1)–O(11)	77.59(6)	O(1)–Ba(1)–O(22)	73.72(6)
O(21)–Ba(1)–O(11)	122.16(6)	O(21)–Ba(1)–O(22)	75.57(6)
O(2)–Ba(1)–O(11)	86.50(5)	O(2)#1–Ba(1)–O(22)	73.82(6)
O(1)–Ba(1)–O(25)	145.64(6)	O(11)–Ba(1)–O(22)	146.62(6)
O(21)–Ba(1)–O(25)	70.60(6)	O(25)–Ba(1)–O(22)	125.56(6)
O(2)#1–Ba(1)–O(25)	126.77(5)	O(24)–Ba(1)–O(22)	67.45(8)
O(11)–Ba(1)–O(25)	87.82(6)	O(23)–Ba(1)–O(22)	114.39(6)
O(1)–Ba(1)–O(24)	98.48(7)	O(1)–Ba(1)–O(12)	116.19(5)
O(21)–Ba(1)–O(24)	88.14(7)	O(21)–Ba(1)–O(12)	76.93(5)
O(2)#1–Ba(1)–O(24)	138.68(8)	O(2)#1–Ba(1)–O(12)	69.55(5)
O(11)–Ba(1)–O(24)	134.49(8)	O(11)–Ba(1)–O(12)	45.27(5)
O(25)–Ba(1)–O(24)	70.05(7)	O(25)–Ba(1)–O(12)	69.34(5)
O(1)–Ba(1)–O(23)	77.62(6)	O(24)–Ba(1)–O(12)	139.35(7)
O(21)–Ba(1)–O(23)	134.74(6)	O(23)–Ba(1)–O(12)	105.41(6)
O(2)#1–Ba(1)–O(23)	155.92(6)	O(22)–Ba(1)–O(12)	140.19(6)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$

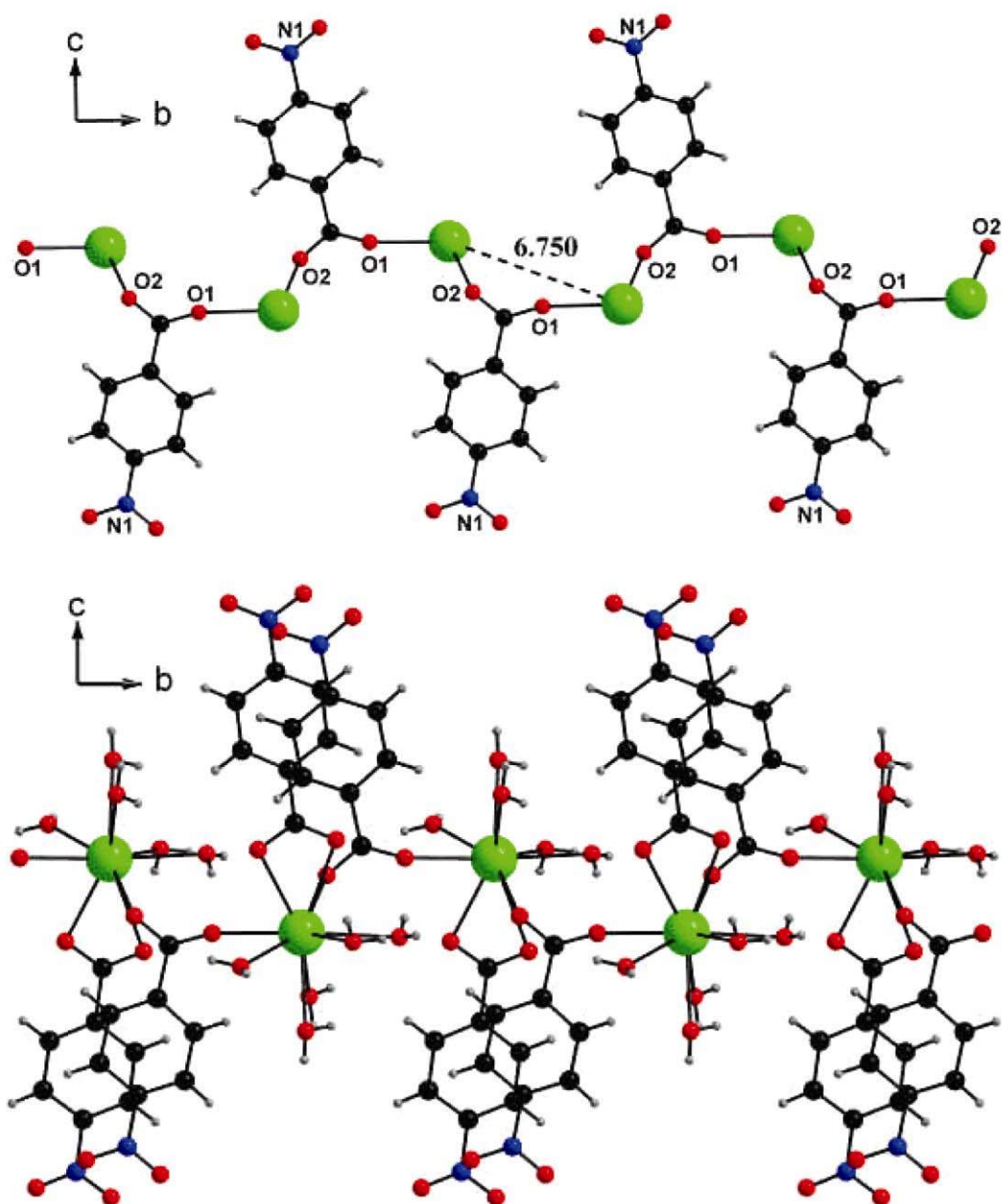


Figure 3. A view of the polymeric chain in **1** showing the linking of Ba(II) (green) by the bridging bidentate 4-nba ligand in the *bc* crystallographic plane. For clarity the coordinated waters and the bidentate 4-nba ligand on the Ba(II) are not shown (top). The coordinated waters and the bidentate 4-nba ligand are included showing the infinite chain along *b*. (bottom).

plexes where the carboxylate functions as a bridging ligand, the shortest Ba...Ba distance between adjacent Ba(II) ions in the polymeric chain varies from 4.069 Å in the coordination polymer derived from 2,2'-dithiobis(benzoic acid) to 6.750(1) Å in the title complex (table 3). In some polymers the Ba...Ba contacts are shorter than the sum of the van der Waals radii (4.28 Å) indicating weak metal-metal interactions, while in some others the observed metal-

metal distances are around 4.5 Å. Interestingly, the observed Ba...Ba distance of 6.750(1) Å in **1** is comparable with the Ba...Ba distance in the 2-D polymer [Ba(H₂PMA)(H₂O)₅]_n derived from pyromellitic acid (H₄PMA). In this polymer, the dianion of 1,2,4,5-benzenetetracarboxylic acid (H₂PMA) is linked to four different Ba(II) ions. It appears that the Ba...Ba distances in Ba-carboxylate coordination polymers are probably determined by a combination

Table 3. Ba...Ba distances across the chain in some Ba(II) coordination polymers containing bridging carboxylates.

Compound	Ba...Ba distance in Å*	Dimensionality (D) of polymer	Reference
[Ba(2-aba) ₂ (H ₂ O) ₂] _n	4.32	2-D	24
[{Ba ₂ (DTBB) ₂ (H ₂ O) ₂ }0.5H ₂ O] _n	4.069(2)	3-D	26
[Ba(HbpdC) ₂ (H ₂ O) ₂] _n	4.1386(17)	1-D	27
[Ba(C ₅ H ₄ O ₄) ₂ (H ₂ O) ₄] _n	4.595(4)	2-D	28
[Ba(C ₇ H ₅ O ₂ S) ₂ (H ₂ O) ₄] _n	4.335	1-D	29
[Ba(C ₆ H ₄ (COO) ₂)] _n	4.123	3-D	30
[Ba(H ₂ PMA)(H ₂ O) ₅] _n	6.65	2-D	31
[Ba(H ₂ O) ₅ (4-nba) ₂] _n	6.750(1)	1-D	This work

Abbreviations used: 2-aba = 2-aminobenzoate; DTBB = 2,2'-dithiobis(benzoate); HbpdC = 2'-carboxybiphenyl-2-carboxylate; C₅H₄O₄ = mesaconate anion; (H₂PMA) = pyromellitic acid; (C₇H₅O₂S) = thiosalicylate; (C₆H₄(COO)₂) = terephthalate; 4-nba = 4-nitrobenzoate. *For 2-D and 3-D polymers only the shortest Ba...Ba contact is given

Table 4. Hydrogen-bonding geometry (Å, °) for [[Ba(H₂O)₅(4-nba-O,O')](μ-4-nba-O,O')]_n **1**.

D-H...A	d(D-H)	d(H...A)	D(D...A)	<DHA	Symmetry code
Intrachain interactions					
O21-H10...O1	0.820	2.070	2.868	164	[-x + 1, y + 1/2, -z + 3/2]
O21-H20...O11	0.820	2.090	2.899	169	[-x, y + 1/2, -z + 3/2]
O22-H30...O25	0.820	2.002	2.731	148	[x + 1, y, z]
O23-H50...O12	0.820	1.920	2.736	174	[-x, y - 1/2, -z + 3/2]
O23-H60...O22	0.820	2.384	3.075	142	[x - 1, y, z]
O25-H90...O2	0.820	1.993	2.806	172	[-x, y + 1/2, -z + 3/2]
O25-H90...O1	0.820	2.684	3.296	133	[-x, y + 1/2, -z + 3/2]
O25-H100...O11	0.820	1.945	2.758	171	[-x, y + 1/2, -z + 3/2]
C2-H2...O22	0.930	2.585	3.462	157	
C6-H6...O21	0.930	2.630	3.522	161	[x, y - 1, z]
Interchain interactions					
O22-H40...O14	0.820	2.233	3.017	160	[x + 1, -y + 3/2, z + 1/2]
O24-H70...O4	0.820	2.317	3.115	165	[-x + 1, -y + 1, -z + 2]
O24-H70...O3	0.820	2.497	3.184	142	[-x + 1, -y + 1, -z + 2]
C13-H13...O4	0.930	2.482	3.398	169	[x - 1, -y + 1/2, z - 1/2]
C15-H15...O3	0.930	2.599	3.385	143	[x - 1, -y + 3/2, z - 1/2]
C3-H3...O14	0.930	2.500	3.238	137	[x + 1, -y + 3/2, z + 1/2]
C5-H5...O13	0.930	2.618	3.529	167	[x + 1, -y + 1/2, z + 1/2]

of several factors, which include the electronic and steric requirements of the central metal, the denticity, flexibility and H-bonding characteristics of the carboxylate ligand.

An analysis of the crystal structure of **1** reveals that each nine coordinated Ba(II) complex in the polymeric chain is H-bonded to several neighbouring complexes through all possible sites involving all the four O atoms of both the 4-nba ligands, and three water O atoms (O21, O22, O25) functioning as H-acceptors. All the H-atoms attached to the coordinated waters excepting H80 and six H atoms on the aromatic rings function as H-donors. Thus each

Ba(II) complex in **1** is linked to eleven other complexes with the aid of several O-H...O and C-H...O bonds (see web version). The eleven O-H...O interactions range from 1.920 to 2.684 Å while the six C-H...O interactions are weaker and vary between 2.482 and 2.630 Å. All these O...H contacts are shorter than the sum of their van der Waals radii³² and the geometric parameters of these interactions are summarized in table 4. Several of these interactions between the H atoms attached to O21, O22, O23, O25, C2, C6 and the acceptors O1, O2, O11, O25, O12, O22, O21 are within the one dimensional polymeric chain and are intrachain interactions. All the O

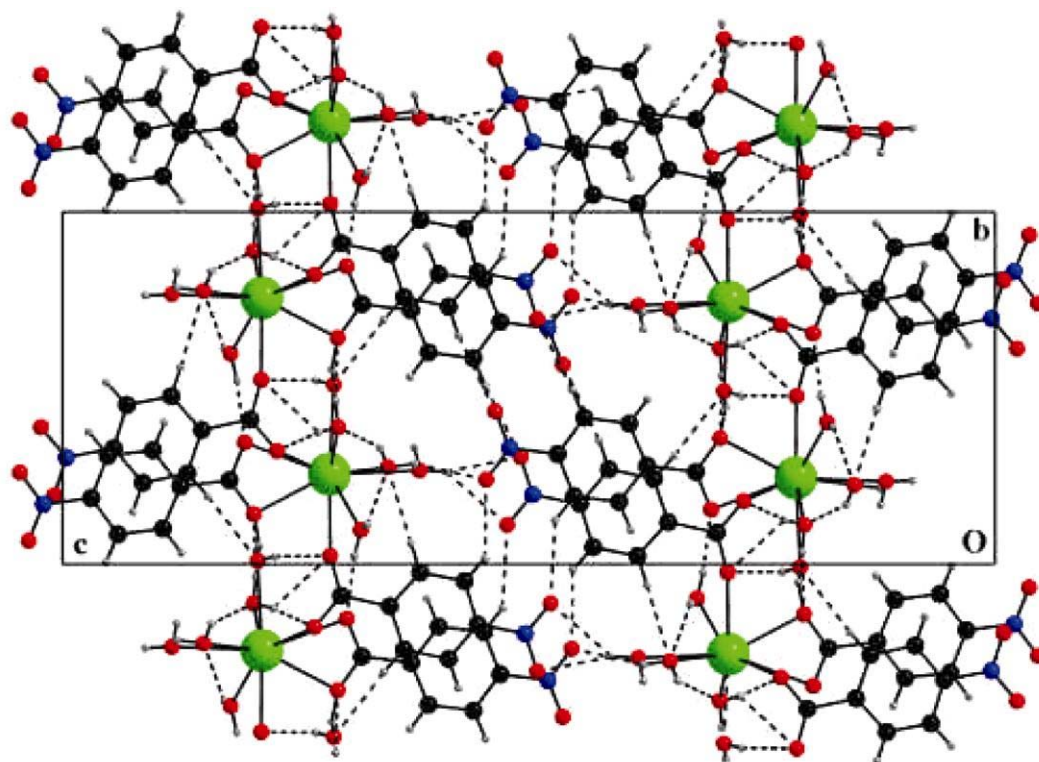


Figure 4. Packing diagram of **1** viewed along *a* axis showing the intrachain and interchain H-bonding interactions.

atoms of the nitro groups function as H-bond acceptors and are linked to the H-atoms attached to C13, C15, C3, C5, O22 and O24 on a neighbouring chain. These interchain interactions serve to link the parallel polymeric chains resulting in a two dimensional H-bonded network (figure 4).

The short ring interactions and distances between the ring centroids (Cg–Cg) in **1** were analysed by using the program Platon.³³ The Cg–Cg distance between the two 4-nba ligands is 3.684 Å and the perpendicular distance from the center of the first ring to the second (interplanar distance) is 3.358 Å accompanied by a dihedral angle of 2.68°. Although these values indicate that the rings do not overlap, the magnitude of the values is suggestive of π – π interactions.

Heating of **1** at 100°C on a water bath showed a mass loss of 11.3%. This value is less than the expected value (12.86%) for the loss of four moles of water. The IR spectrum of this product still showed the presence of O–H signal in the complex. When the weight loss studies were performed at higher temperatures in an oven at 200°C the observed weight loss of 14.64% is more than the value required for 4 moles of water but less than that for the removal

of all the water molecules. All our efforts to prepare the anhydrous barium(II) *bis*(4-nitrobenzoate) complex by employing different temperatures were not fruitful. Calcination of **1** at a higher temperature of 800°C results in the formation of BaCO₃. The amount of the observed final residue as well as its chemical and metal analysis are in good agreement for carbonate formation. The DSC thermogram of **1** exhibits an endothermic event at around 80°C assignable for the dehydration process, followed by a weak endothermic signal at around 125°C and two strong exothermic signals at 391 and 488°C respectively which can be attributed to the decomposition of the complex.

The availability of structural information of the 4-nitrobenzoates of the lighter congeners Mg, Ca and Sr namely [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 permits a comparative study of the alkali earth 4-nitrobenzoates. The comparison reveals certain similarities and many differences. All the compounds can be synthesized by an aqueous reaction of the corresponding metal carbonate with 4-nbaH and contain metal:4-nba in 1 : 2 mole ratio but are differently hydrated. The structures demonstrate the ver-

satellite ligational behaviour of the 4-nba ligand towards the bivalent alkali-earth metal ions. In the Mg(II) complex¹⁶ [Mg(H₂O)₆](4-nba)₂·2H₂O, the 4-nitrobenzoate is free and uncoordinated and forms an outer-sphere complex with the inner sphere being occupied by six water ligands, while the two ligands are linked in monodentate (4-nba-O) and bidentate (4-nba-O,O') manner in the seven coordinated neutral Ca(II) complex¹⁷ [Ca(H₂O)₄(4-nba-O)(4-nba-O,O)] which contains only coordinated water. In the higher congeners, the 4-nba complex of strontium contains both coordinated and lattice waters and one of the 4-nba anions function as a bidentate ligand while the other is free and uncoordinated, while in the title Ba complex which contains only coordinated water molecules one of the 4-nba is a bidentate ligand with the other bonded in a bridging bidentate fashion leading to a polymeric structure. All the compounds exhibit several weak hydrogen bonding interactions resulting in novel extended structures.

4. Conclusions

In summary, we have described the synthesis, and structural characterization of a Ba(II) coordination polymer using 4-nba as ligand. The observed Ba...Ba distance of 6.750(1) Å between adjacent metal atoms in **1** is much longer than the sum of their van der Waals radii. The present results taken together with our recent work of 4-nba complexes of Ca(II), Mg(II) and Sr(II) reveal a rich and variable structural chemistry of the alkali-earths with 4-nitrobenzoate. The title Ba(II) complex exhibits several O–H...O and C–H...O interactions. It will be of interest to investigate the structural features of Ba(II) complexes of the other isomeric nitrobenzoates to see how the positioning of the –NO₂ substituent can affect the properties. Efforts in this direction are underway.

Supplementary material

Illustration describing the H-bonding situation around the nine coordinated polymeric Ba(II) complex **1** is available on the web version of this paper. Crystallographic 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 639044. 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 e-mail: deposit@ccdc.cam.ac.uk).

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