

# First alkaline earth metal 3-aminobenzoate (3-aba) complex: 1-D polymeric $[\text{Ca}(\text{3-aba})_2(\text{H}_2\text{O})_2]_n$ assembly

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## Abstract

The reaction of  $\text{CaCO}_3$  or  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  with 3-abaH results in the formation of the first alkaline-earth metal complex of 3-abaH  $[\text{Ca}(\text{3-aba})_2(\text{H}_2\text{O})_2]_n$  (**1**) in good yield. The product has been characterized by elemental analysis, IR, UV-vis and  $^1\text{H}$  NMR spectral studies, TGA and single crystal X-ray diffraction studies. The molecular structure of **1** is made up of 1-D polymeric chains that are hydrogen-bonded to each other. The  $\text{Ca}^{2+}$  ion in **1** is surrounded by eight oxygen atoms in a distorted square-antiprismatic geometry.

*Keywords:* Calcium; Aminobenzoate complexes; Coordination polymers; X-ray structure

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## 1. Introduction

Chemistry of alkaline earth metals has remained a largely unexplored area for a long time, in spite of its relevance in various biological processes [1–12]. A range of model complexes containing  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  cations have previously been prepared and used as probes for the better understanding of the modes of binding of these metals in vivo and vitro [13,14]. These studies have focussed in particular on the use of aspartate, glutamate, oronate, pyroglutamate and salicylate ligands [13–17]. Our recent studies in this area are concerned with the complexes formed from the reactions of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  ions with 2- and 4-aminobenzoic acids and 2-mercaptobenzoic acid [18–21]. Schmidbaur and co-workers [22] have obtained crystal structure of  $[\text{Mg}(\text{OH}_2)_6][2\text{-aba}]_2$  in the solid-state and also studied the interaction of 2-abaH with alkali metal ions.

In the series of amino benzoic acids, an important ligand is 3-aminobenzoic acid (3-abaH) which has immense applications in biology [23]. In spite of the biological relevance of this ligand, its coordination

behavior towards group 2 metal ions has not been investigated. Thus, to understand the complexation chemistry of 3-abaH with s-block metal ions we have studied the reaction of  $\text{Ca}^{2+}$  ion with 3-abaH under a variety of conditions. Preliminary results of these studies are reported herein.

## 2. Experimental section

Starting materials have been procured from commercial sources and used as received. Methods used for purification of solvents and starting materials and the details of the instrumentation used in the present study are similar to those described previously [25].

### 2.1. Preparation of complex **1**

(a)  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (3.6 mmol, 0.54 g) and 3-abaH (7.2 mmol, 1 g) are dissolved in  $\text{H}_2\text{O}$  (25 ml)/MeOH (30 ml) and warmed to  $50^\circ\text{C}$  for 30 min. Aq.  $\text{NH}_3$  (25%) (20 ml) is added dropwise under constant stirring and the resulting solution is heated at  $80^\circ\text{C}$  for 2 h on a water bath. The resultant turbid solution is filtered and allowed to stand at room temperature to obtain large, needle-shaped red crystals of **1** after several days.

(b)  $\text{CaCO}_3$  (0.25 g, 2.5 mmol) is dissolved in water (15 ml) to form a milky suspension and 3-abaH (0.685 g, 5 mmol) is dissolved in MeOH (30 ml). The two solutions are mixed together and heated on water bath till the volume becomes half of the original solution. The solution is filtered and crystallized to obtain analytically pure crystals of **1** in 80% yield after several days. M.p.  $>250$  °C. Elemental analysis for  $[\text{Ca}(3\text{-aba})_2(\text{H}_2\text{O})_2]$ , Calcd: C, 48.27; H, 4.63; N, 8.04; Found: C, 47.77; H, 4.51; N, 7.91. IR (KBr,  $\text{cm}^{-1}$ ): 3407s, 3322s, 1558s, 1459m, 1420s, 1314m, 1268m.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz)  $\delta$  6.79 (ddd, 2H), 7.08 (dd, 2H), 7.38 (ddd, 2H), 7.39 (dd, 2H) ppm.

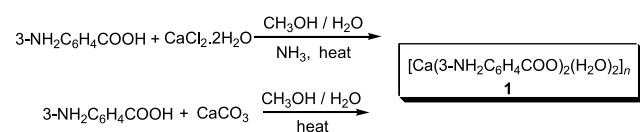
## 2.2. X-ray diffraction studies

The data collection for **1** has been carried out on an STOE-AED2 diffractometer. Intensity data collection and cell determination protocols are carried out using a monochromatized  $\text{MoK}\alpha$  radiation. Structure solution is achieved by direct methods using SHELXS-97 [26a] software. Further structural refinement and identification of lighter atoms have been carried out using SHELXL-97 [26b]. The final *R* factors and other details pertaining to data collection, structure solution and final refinement for **1** are given in Table 3.

## 3. Results and discussion

Synthesis of the title compound **1** is accomplished by the reaction of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  with 3-abaH under basic conditions ( $\text{pH} \approx 10$ ) (Scheme 1). Addition of aqueous  $\text{NH}_3$  was necessary for the complete neutralization of the amino acid. Compound **1** is also synthesized by the carbonate route, which involved the addition of a milky suspension of calcium carbonate in water to a clear solution of the amino acid and then heating the resulting mixture on a water bath. Compound **1** is freely soluble in water, methanol, and ethanol but only moderately soluble in dimethyl sulfoxide.

The 3-aminobenzoate complex **1** has been obtained in good yield in an analytically pure form. The compound shows high thermal stability and does not melt or decompose until 250 °C. The empirical formula and composition of **1** could be established from elemental analysis, which corresponds to the formulation  $[\text{Ca}(3\text{-aba})_2(\text{H}_2\text{O})_2]$ . The aqueous solution of **1** is found to be almost neutral ( $\text{pH} = 7.3$ ) and not significantly



Scheme 1.

basic due to the possible involvement of  $-\text{NH}_2$  group in coordination or hydrogen bonding (vide infra).

Complex **1** is also further characterized by UV, IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral studies. The IR spectrum of complex **1** as KBr disc shows strong absorptions in the region  $3200\text{--}3500$   $\text{cm}^{-1}$  indicating the presence of water molecules with varying degrees of hydrogen bonding. The expected  $-\text{NH}_2$  absorption of the 3-aba is masked by the much broader absorption of water molecules. The  $\Delta\nu$  between asymmetric and symmetric stretching vibrations of the carboxylate group is indicative of the role of the carboxylate group as a multidentate ligand probably through chelating and bridging modes of coordination to calcium ions (vide infra). The UV-vis spectrum of **1** in methanol contains two ligand-based strong absorptions at 227 and 309 nm.

The  $^1\text{H}$  NMR chemical shifts of the aromatic protons of **1** are almost comparable to those reported for the free ligand [24]. The aromatic region of the  $^1\text{H}$  NMR spectrum of **1** recorded at room temperature as  $\text{CD}_3\text{OD}$  solution and the spectral assignment is shown in Fig. 1. The  $\text{H}_b$  proton, which is adjacent to the amino group, resonates as a doublet of doublet of doublet (ddd) around 6.79 ppm due to its strong three-bond coupling with  $\text{H}_c$  and weak four-bond coupling with  $\text{H}_d$  and  $\text{H}_e$  protons. The expected doublet of doublet pattern for  $\text{H}_c$

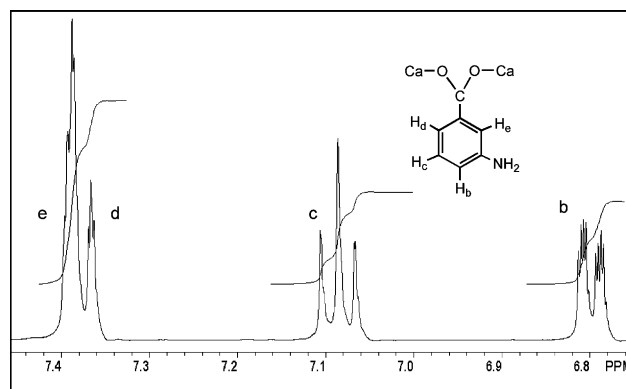


Fig. 1.  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{OD}$ , 400 MHz) of the aromatic region of **1**.

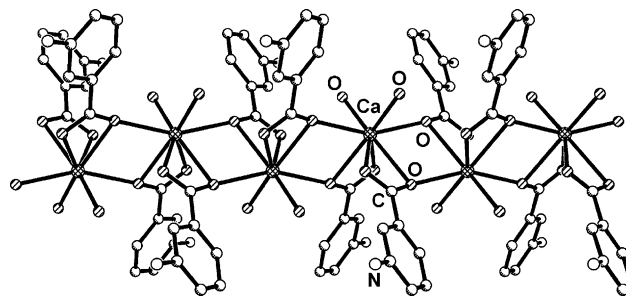


Fig. 2. Ball and stick model of 1-D polymeric chain formed in the crystal structure of **1**.

Table 1  
Selected structural parameters observed in **1**

<i>Bond distances</i> (Å)				
Ca(1)–O(3)	2.4049(9)	Ca(1)–Ca(1)#2	4.0034(5)	
Ca(1)–O(2)	2.4163(8)	O(1)–C(7)	1.2596(14)	
Ca(1)–O(1)	2.4713(8)	C(7)–O(2)#3	1.2583(13)	
Ca(1)–O(2)#2	2.5771(9)	N(1)–C(3)	1.4049(15)	
Ca(1)–C(7)	2.8722(11)			
<i>Bond angles</i> (°)				
O(3)#1–Ca(1)–O(2)#2	157.14(3)	O(3)–Ca(1)–O(2)#1	93.04(3)	
O(2)#1–Ca(1)–O(2)	156.05(4)	O(3)–Ca(1)–O(2)#2	89.83(3)	
O(3)#1–Ca(1)–O(1)#1	147.41(3)	O(2)#2–Ca(1)–O(2)#3	83.97(4)	
O(2)#1–Ca(1)–O(2)#2	126.38(3)	O(3)#1–Ca(1)–O(1)	81.87(3)	
O(2)–Ca(1)–O(1)#1	118.85(3)	O(1)–Ca(1)–O(2)#2	77.00(3)	
O(1)#1–Ca(1)–O(1)	110.85(4)	O(2)#1–Ca(1)–O(1)#1	75.70(3)	
O(3)#1–Ca(1)–O(3)	103.68(5)	O(2)–Ca(1)–O(2)#2	73.45(3)	
C(7)–O(1)–Ca(1)	95.12(6)	O(3)–Ca(1)–O(2)	71.98(3)	
<i>Hydrogen bonds</i>				
D–H⋯A (Å)	D–H (Å)	H⋯A (Å)	D⋯A (Å)	D–H⋯A (°)
N(1)–H(1A)⋯N(2)	0.900	2.184	3.072	169
N(1)–H(1B)⋯O(2)	0.900	2.187	3.020	154
O(1)–H(4B)⋯N(3)	0.900	1.801	2.685	167
C(3)–H(3A)⋯O(2)	0.960	2.424	3.232	142

#1  $-x + 1, y, -z + 1/2$ ; #2  $-x + 1, -y, -z$ ; #3  $x, -y, z + 1/2$ .

due to its unequal three-bond coupling with  $H_b$  and  $H_d$ , however appears as a triplet centered at  $\sim 7.09$  ppm due to the merging of the two inner lines. The resonances of  $H_d$  and  $H_e$  are downfield shifted. One-half of the expected ddd pattern for  $H_d$  proton ( $\sim 7.38$  ppm) coincides with the multiplet due to  $H_e$  proton which appears at around 7.39 ppm due to its four-bond coupling with both  $H_d$  and  $H_e$  protons.

The TGA curve of complex **1** shows the first weight loss in the region 90–150 °C corresponding to the loss of one coordinated water molecule. The weight loss observed in the range 200–440 °C is due to the loss of second coordinated water molecule. The weight loss observed above 450 °C could be attributed to the decomposition of the organic moiety. The residue remaining above 750 °C corresponds to the formation of calcium oxide.

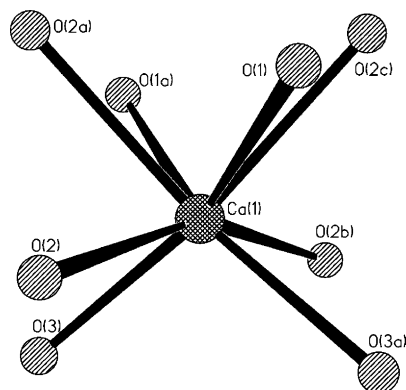


Fig. 3. Coordination geometry of calcium ions in crystal of **1**.

Although the information available from the analytical, spectroscopic and thermal analysis data provide clue about the exact composition and to some extent the structural formula, to establish the three-dimensional solid-state structure of **1**, a single crystal X-ray diffraction study has been carried out. The compound crystallizes in the centrosymmetric orthorhombic group *Pbcn*. The molecular structure of  $[\text{Ca}(\text{3-aba})_2(\text{OH}_2)_2]_n$  (**1**) showing the immediate coordination environment around the central metal ion and the formation of a linear 1-D coordination polymer is shown in Fig. 2. Selected bond lengths and angles around the calcium ions are listed in Table 1. The Ca–O distances observed in **1** are comparable to those found for the related aminobenzoate complexes [19,20].

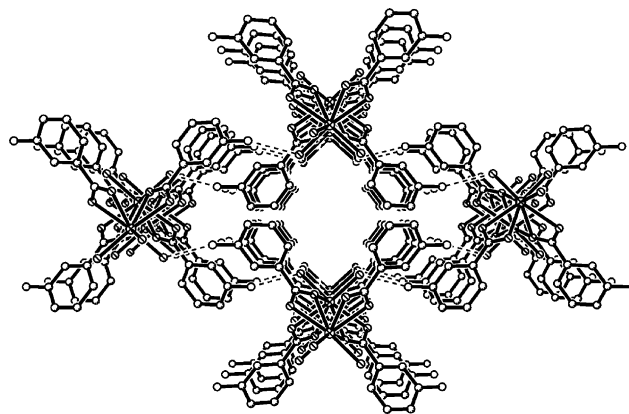


Fig. 4. Packing diagram of **1** showing the supramolecular assembly formed by the hydrogen bonds between coordination polymers.

Table 2  
Comparison of structural features in **1** and **2**

Complex	<b>1</b>	<b>2</b> <sup>a</sup>
Formula	[Ca(3-aba) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sub>∞</sub>	[Ca(2-aba) <sub>2</sub> (OH <sub>2</sub> ) <sub>3</sub> ] <sub>∞</sub>
Space group	Pbcn	Pbcn
Cell parameters	<i>a</i> = 20.369(4) <i>b</i> = 10.668(2) <i>b</i> = 10.668(2)	28.373(6) Å 7.318(2) Å 7.915(2) Å
Ca ion co-ordination number	Eight	Seven
Co-ordination geometry around calcium ion	Distorted square anti-prism	Distorted pentagonal bipyramid
Role of aminobenzoate ligand	Tridentate through both bridging and chelating modes	Bidentate through only bridging mode
Hydrogen bonds-distinctive features	O–H···O interactions absent	N–H···N interactions absent
Bond lengths/angles with respect to calcium	The angles around calcium vary from 51.8° to 167.1°. The Ca–O distances range from 2.405 to 2.872 Å	The angles around calcium vary from 73.7° to 163.9°. The Ca–O distances range from 2.326 to 2.485 Å

<sup>a</sup> From [19].

Table 3  
Crystal data and structure refinement for **1**

Empirical formula	C <sub>14</sub> H <sub>16</sub> CaN <sub>2</sub> O <sub>6</sub>
Formula weight	348.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbcn
Unit cell dimensions	<i>a</i> = 20.369(4) Å <i>b</i> = 10.668(2) Å <i>c</i> = 7.490(1) Å
Volume	1627.7(4) Å <sup>3</sup>
<i>Z</i>	4
Density (calculated)	1.422 mg/m <sup>3</sup>
Absorption coefficient	0.417 mm <sup>-1</sup>
<i>F</i> (000)	728
Crystal size	0.4 × 0.25 × 0.25 mm <sup>3</sup>
Theta range for data collection	3.6–27.5°
Index ranges	–26 ≤ <i>h</i> ≤ 26, –13 ≤ <i>k</i> ≤ 13, –9 ≤ <i>l</i> ≤ 9
Reflections collected	7444
Independent reflections	1862 [ <i>R</i> (int) = 0.044]
Completeness to $\theta = 27.51^\circ$	99.8%
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	1862/0/137
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.072
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0244, <i>wR</i> 2 = 0.0655
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0274, <i>wR</i> 2 = 0.0678
Largest diff. peak and hole	0.327 and –0.160 eÅ <sup>-3</sup>

The calcium ions in **1** are octa-coordinated in an approximate square antiprismatic coordination environment (Fig. 3). Four of the coordination sites in **1** are occupied by bridging carboxylate oxygen atoms (O(2), O(2a), O(2b), O(2c)), two are by chelating oxygen atoms (O(1), O(1a)) and the rest two by the two coordinated water molecules (O(3), O(3a)). Each of the carboxylate ligand is chelating as well as bridging. The amino group does not directly take part in the coordination to the metal but forms a hydrogen bond with the oxygen atom of the coordinated water molecule from a neighboring polymeric chain. In addition, O–H···O hydrogen

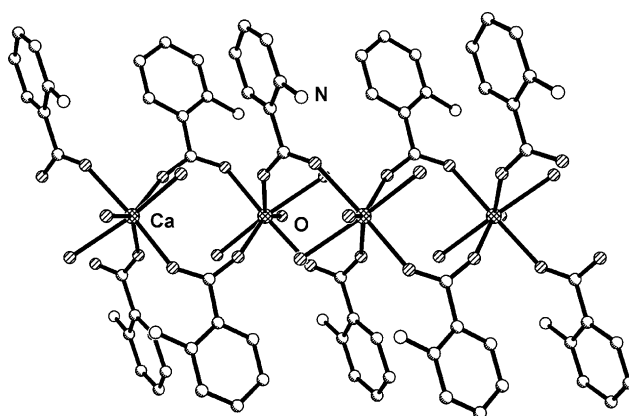


Fig. 5. Ball and stick model of 1-D polymeric chain formed in the crystal structure of the related 2-aminobenzoate complex **2** [19].

bonds exist between the polymeric chains that originate from either the coordinated water molecules or the carboxylate oxygen atoms. Thus, the one-dimensional polymeric chains are connected to each other, resulting in the formation of a supramolecular metal-organic framework as shown in Fig. 4.

It is of interest to compare the structural features of **1** with those found for the calcium 2-aminobenzoic acid complex [Ca(2-aba)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**2**) (see Table 2) [19]. Although both these compounds essentially form a 1-D chain structure, there are some essential differences. While the calcium ion is eight-coordinate in **1**, a hepta-coordination has been found for **2**. More interestingly, the 2-aba ligand in **2** acts only as a bidentate ligand by symmetrically bridging two adjacent calcium ions (Fig. 5) compared to the observed chelating-bridging tridentate mode of coordination (Fig. 2) for the 3-aba ligand in **1**.

In summary, we have described, in this communication, the synthesis and unambiguous structural characterization of the first alkaline earth metal 3-aminobenzoate complex. The formation of complex **1**

is pH dependent and the complex that is formed exhibits almost neutral pH. The complex exists as a 1-D coordination polymer in the solid-state due to the chelating and bridging ability of the 3-aminobenzoate ligand. The 1-D polymeric chains are further held together by hydrogen bonding. The presence of additional  $\pi$ - $\pi$  stacking of aromatic ligands (Fig. 4), stabilizes the final supramolecular structure.

### Supplementary material

X-ray crystallographic information and thermogravimetric analysis for **1** are available as supplementary material.

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