

First alkaline earth 2-carbamoyl-4-nitrobenzoate: Synthesis and supramolecular structure

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2-Carbamoyl-4-nitrobenzoic acid (2-ca-4nbaH) has been prepared by alkaline hydrolysis of 4-nitrophthalimide. Aqueous reaction of MgCO_3 with 2-ca-4nbaH results in the formation of $[\text{Mg}(\text{H}_2\text{O})_6](2\text{-ca-4nba})_2$, which crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $\text{Mg}(\text{II})$ situated on an inversion center. The crystal structure consists of a distorted octahedral hexaaquamagnesium(II) cation and a free uncoordinated 2-ca-4nba anion. The cation and anion are involved in three varieties of H-bonding interactions, resulting in a supramolecular bilayer of 2-ca-4nba anions sandwiched between layers of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations.

Keywords: Coordination chemistry, Magnesium, Crystal structure, Supramolecular bilayer

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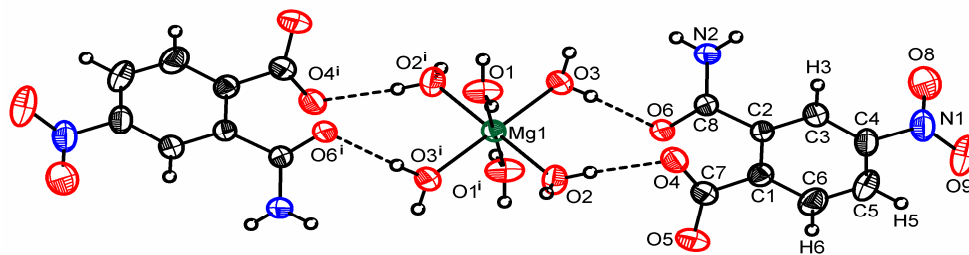
Chemistry of *s*-block elements is a topical area of research¹⁻⁶. Non-toxic and water soluble nature, variable structural chemistry⁶, affinity for O-donor ligands⁷, relevance in biology⁸ are some factors responsible for the growing interest in the chemistry of *s*-block elements. As part of our longstanding research interest^{9,10}, we are investigating the coordination chemistry of the amino- (aba) and nitro- (nba) benzoates of *s*-block elements. In earlier work, we have reported the spectral characteristics, structural aspects and thermal properties and have unraveled a rich structural chemistry of alkaline earth nitro-(nba) benzoates^{5,11-14}. A comparison of the structural features of alkaline earth nitrobenzoates with those of the aminobenzoates¹⁵⁻¹⁷ reveals that in the case of $\text{Mg}(\text{II})$, the compounds contain the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ unit charge balanced by the corresponding carboxylate anion^{14,15,17} while the aminobenzoates of the heavier alkaline earths exhibit

M-N (M = Sr or Ba) bonding¹⁶. In the nitrobenzoates, no metal to N bonding is observed, excepting in $[\text{Ba}(\text{H}_2\text{O})_3(2\text{-nba})_2]$ which shows coordination of Ba to the nitro oxygen¹¹. In terms of secondary interactions, the amino group acts as H-donor while the oxygen atom of the nitro moiety functions as a hard H-bond acceptor leading to novel supramolecular assemblies. It is of interest to investigate the structural aspects of metal-carboxylates, containing both H-acceptor and H-donor groups in the same ligand, in addition to the carboxylate. Herein, we report the synthesis of 2-carbamoyl-4-nitrobenzoic acid (2-ca-4nbaH) (**1**) in which an amide (H-donor) and a nitro group (H-acceptor) are disposed *ortho* and *trans* respectively with respect to the carboxylate group. The presence of such substituents in (**1**) results in an interesting supramolecular architecture in $[\text{Mg}(\text{H}_2\text{O})_6](2\text{-ca-4nba})_2$ (**2**), which constitutes the first example of a structurally characterized alkaline earth 2-carbmoyl-4-nitrobenzoate.

Experimental

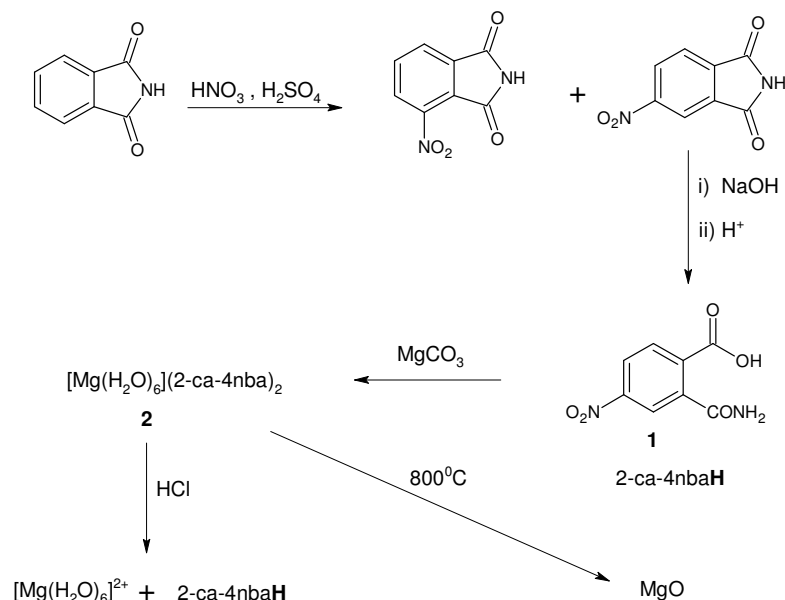
Nitration of phthalimide by a literature method¹⁸ afforded a mixture of the isomeric 3- and 4-nitrophthalimide. After separation from the soluble 3-nitro isomer (minor product), the insoluble 4-nitrophthalimide (10 g, 0.052 mol) was taken in water (50 mL) containing NaOH (2.08 g, 0.052 mol) at room temperature and stirred for 15 min to obtain a clear brown solution. To this, dilute HCl was added in drops ($\text{pH} = 4\text{-}5$) resulting in the separation of the crude product. The solid was filtered and washed well with water till free of chloride and recrystallized from alcohol to obtain (**1**) in 8 g yield. (m.pt.: 144-145 °C)

UV-vis: $\lambda_{\text{max}} = 293 \text{ nm}$ ($\epsilon = 5210 \text{ L mol}^{-1} \text{ cm}^{-1}$); IR (cm^{-1}): 3396, 3268, 3219, 3116, 3093, 2872, 2778, 2596, 2480, 1725 $\nu_{\text{as}}(-\text{COO})$, 1667 $\nu_{\text{CO}}(\text{amide})$, 1611, 1572 $\nu_{\text{as}}(-\text{NO}_2)$ 1502, 1485, 1441, 1380, 1354 $\nu_{\text{s}}(-\text{NO}_2)$, 1306, 1267, 1246, 1120, 1068, 977, 910, 861, 807, 777, 737, 685, 643, 620, 547, 429; ^1H NMR ($\text{DMSO}-d_6$) δ (in ppm) 7.64 (d, $J = 8.4 \text{ Hz}$, H3), 8.20 (dd, $J = 2.4 \text{ Hz}$, $J = 8.4 \text{ Hz}$, H5), 8.36 (d, $J = 2.4 \text{ Hz}$, H6), 8.94 (br s, $J = 2.4 \text{ Hz}$, -N-H). For assignment, the numbering for H-atom is same as the crystallographic labeling in Fig. 1.



Intensity data for (2) were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo-K α radiation. Data integration and reduction were processed with SAINT software¹⁹ and an empirical absorption correction was applied to the collected reflections with SADABS¹⁹. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were introduced on calculated positions and included in the refinement riding on their respective carbon atoms. The hydrogen atoms attached to the O and N atoms of water and amide were located in the difference map and were refined

Compound (**2**) was also prepared by the reaction of an aqueous solution of MgCl_2 with the Na-salt of 2-ca-4nbaH (**1**). Our synthetic methodology is very similar to the one employed for the synthesis of several Mg(II) carboxylates (Table 1) wherein MgCO_3 or Mg(OH)_2 is reacted with the carboxylic acid or alternatively the water soluble MgCl_2 is reacted with the Na or K salt of the acid generated



Scheme 1

Table 1 – Synthesis^a and structural aspects^b of some Mg(II) carboxylates

Compound	Mg source	Base	Space group	Secondary interaction	Ref.
$[\text{Mg}(\text{H}_2\text{O})_6](\text{2-ca-4nba})_2$	MgCO_3	----	$P2_1/c$	O-H...O,	This work
	MgCl_2	NaHCO_3		N-H...O, C-H...O	
$[\text{Mg}(\text{H}_2\text{O})_6](\text{2-aba})_2 \cdot 2\text{H}_2\text{O}^c$	MgCl_2	KOH	$P2_1/c$	O-H...O, N-H...O	17
$[\text{Mg}(\text{H}_2\text{O})_6](\text{4-aba})_2 \cdot 2\text{H}_2\text{O}$	MgCl_2	NH_4OH	$Pbca$	O-H...O, N-H...O	15
$[\text{Mg}(\text{H}_2\text{O})_6](\text{4-nba})_2 \cdot 2\text{H}_2\text{O}$	MgCO_3	----	$P\bar{1}$	O-H...O	14
$[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_7\text{H}_4\text{NO}_5)_2$	MgCl_2	NaOH	$P\bar{1}$	O-H...O	3
$[\text{Mg}(\text{H}_2\text{O})_4(\text{C}_7\text{H}_3\text{NO}_5)]^d$	$\text{Mg}(\text{OH})_2$	---	$P\bar{1}$	O-H...O	3
$[\text{Mg}(\text{H}_2\text{O})_6](\text{H}_2\text{PMA})_2$	MgCO_3	----	$P2/m$	O-H...O	21

^a In a typical synthesis MgCO_3 or $\text{Mg}(\text{OH})_2$ is reacted with the acid in aqueous medium. Alternatively MgCl_2 can be reacted with the acid in the presence of a base.

^b All compounds listed in Table are six coordinated and contain a $\{\text{MgO}_6\}$ octahedron with Mg(II) situated on an inversion centre.

^c For an alternate synthesis see Ref. 9

^d $(\text{C}_7\text{H}_3\text{NO}_5)$ functions as a bidentate ligand binding through a phenolate O and a nitro O.

Abbr.: 2-abaH = 2-aminobenzoic acid; 4-abaH = 4-aminobenzoic acid; 4-nbaH = 4-nitrobenzoic acid; $\text{C}_7\text{H}_4\text{NO}_5$ = 3-hydroxy-4-nitrobenzoate; H_4PMA = benzene-1,2,4,5-tetracarboxylic acid.

in situ by use of NaOH, KOH or NaHCO_3 ^{3,14,15,17,21}. In all reactions, a Mg(II) carboxylate product containing a minimum of six moles of water per Mg(II) is obtained. However, with 3-hydroxy-4-nitrobenzoic acid a compound having Mg:H₂O in a 1:4 ratio has been reported using $\text{Mg}(\text{OH})_2$ as Mg source³. Coordination polymers having one or two moles of water per Mg or no water, are obtained under hydrothermal conditions^{1,2}. Reaction of (2) with dilute HCl resulted in its decomposition leading to the quantitative formation of 2-ca-4nbaH, while pyrolysis of (2) at 800°C resulted in the formation of MgO.

Both compounds analyzed satisfactorily and exhibit identical NMR and UV spectra. The observed chemical shifts in the NMR spectra of the free acid

(1) and the Mg(II) compound (2) are in the normal range and are nearly identical. The strong absorption at 293 nm in the UV spectra of both compounds can be attributed to an internal charge transfer of the aromatic acid. Compound (2) exhibits a broad and strong signal centered around 3300 cm^{-1} which can be assigned for the O-H vibration of the coordinated water and the profile of the IR spectrum in this region is different for both compounds. The vibrations of the nitro group are observed around 1560 and 1350 cm^{-1} . The TG-DSC thermogram of (2) exhibits three endothermic processes at 94, 136, and 245 °C followed by two exothermic events at 433 and 545 °C respectively. The mass loss of 19 % for the first two processes is in good agreement for the expected

(19.63 %) loss of six water molecules. The third endothermic signal above 200 °C is indicative of a slow decomposition of 2-ca-4nba moiety leading to further decomposition as evidenced by the two exothermic events at 433 and 545 °C. Above this temperature, MgO is formed as a final decomposition product. The formation of MgO as the final residue was further confirmed based on isothermal weight loss studies by heating compound (**2**) at 800 °C in a temperature controlled furnace.

[Mg(H₂O)₆](2-ca-4nba)₂ (**2**) crystallizes in the centrosymmetric monoclinic space group *P*2₁/*c* and is the first structurally characterized alkaline earth salt of 2-ca-4nbaH. In (**2**) the Mg(II) is located on an inversion center, and the structure consists of an octahedral [Mg(H₂O)₆]²⁺ cation and a 2-ca-4nba anion (Fig 1). The centrosymmetric [Mg(H₂O)₆]²⁺ unit is a well-known structural motif in several Mg(II) compounds (Table 1). The Mg-O bond distances scatter in a narrow range between 2.0566(11) and 2.0735(11) Å and are in agreement with reported values^{3,14,15,17,21}. The trans O-Mg-O angles exhibit ideal values, while the cis O-Mg-O angles range between 85.03(5) and 94.97(5)° indicating a slight distortion of the {MgO₆} octahedron. The geometric parameters of the anion are in the normal range.

A scrutiny of the crystal structure of (**2**) reveals that the cations and anions are involved in three varieties of H-bonding interactions, comprising six O-H...O, two N-H...O and two C-H...O bonds (Table 2). The O...H distances ranging from 1.915 to 2.677 Å are accompanied by DHA angles ranging from 143 to 178°. An analysis of the crystal structure reveals that each hexacoordinated Mg(II) complex cation is H-bonded to eight different 2-ca-4nba anions via O-H...O interactions (Fig. 2). The H atoms attached to water function as H-donors and the oxygen atoms of the carboxylate (O4, O5) and the amide (O6) function as H-acceptors. In view of the

O-H...O interactions the cations always point towards the carboxylate end of the anion and thus play an important role in the supramolecular organization of compound (**2**).

In the 2-ca-4nba anion, all H-atoms excepting H6 act as H-donors and the oxygen atoms of the carboxylate and amide function as H-acceptors. An oxygen (O9) of the nitro group functions as a bifurcated H-acceptor forming a C-H...O bond, a

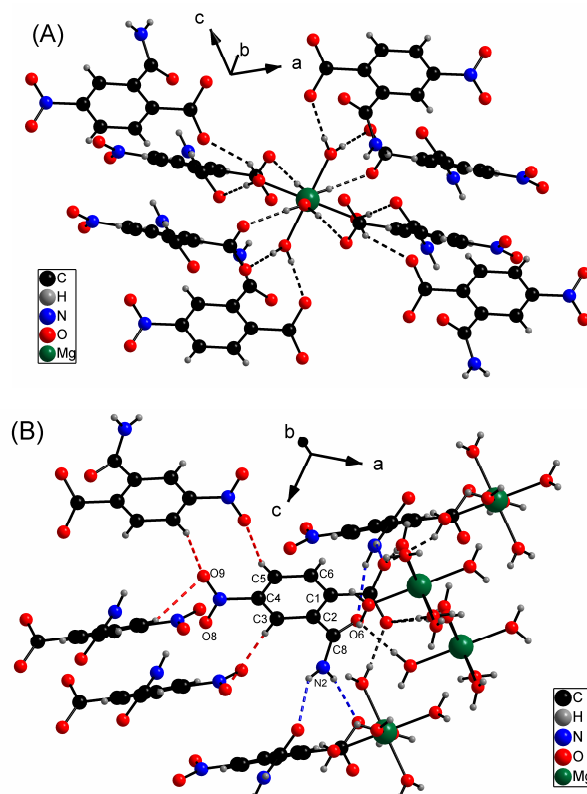


Fig. 2 – (A) View of the surroundings of the [Mg(H₂O)₆]²⁺ cation in (**2**) showing its linking with eight different 2-ca-4nba anions via O-H...O hydrogen bonds. (B) View of the surroundings of the 2-ca-4nba anion in [Mg(H₂O)₆](2-ca-4nba)₂ (**2**) showing its linking with four symmetry related [Mg(H₂O)₆]²⁺ cations and five different 2-ca-4nba anions with the aid of three varieties of H-bonding interactions shown as dashed lines.

Table 2—Hydrogen-bonding geometry for [Mg(H₂O)₆](2-ca-4nba)₂ (**2**)

D-H...A	D(D-H) (Å)	D(H...A) (Å)	D(D...A) (Å)	<DHA (°)	Symmetry code
O1-H1O1...O5	0.820	1.950	2.770	178	-x+2, -y+1, -z+1
O1-H2O1...O4	0.820	1.915	2.717	166	-x+2, y-1/2, -z+3/2
O2-H1O2...O4	0.820	2.007	2.826	177	-x+2, -y+1, -z+1
O2-H2O2...O4	0.820	1.992	2.807	172	x, y, z
O3-H1O3...O6	0.820	1.919	2.738	177	x, y, z
O3-H2O3...O5	0.820	2.259	2.99	149	x, -y+1/2, z+1/2
N2-H1N2...O5	0.860	2.118	2.921	155	x, -y+1/2, z+1/2
N2-H2N2...O6	0.860	2.176	2.907	143	x, -y+1/2, z+1/2
C3-H3...O9	0.930	2.677	3.508	149	-x+1, y-1/2, -z+3/2
C5-H5...O9	0.930	2.420	3.321	163	-x+1, -y+2, -z+1

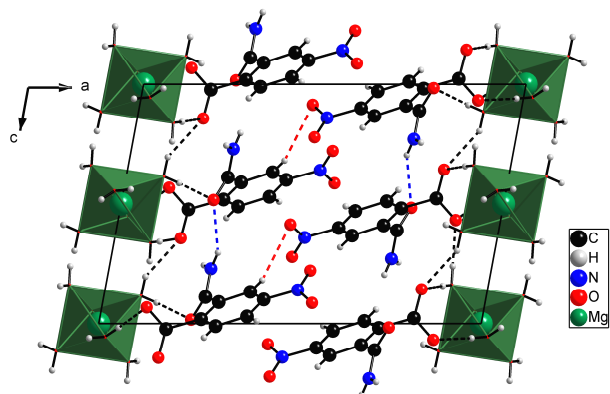


Fig. 3—Crystallographic packing of $[\text{Mg}(\text{H}_2\text{O})_6](2\text{-ca-4nba})_2$ (2) viewed along b axis showing the supramolecular bilayer of 2-ca-4nba anions sandwiched between layers of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ (open polyhedra) cations.

feature observed in several nitrobenzoates^{11-14,22}. Each anion is H-bonded to four different $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations at the carboxylate end and to five symmetry related anions via O-H...O, N-H...O (amide hydrogen atoms linked to carboxylate oxygen and amide oxygen) and C-H...O interactions (Fig. 2). The intramolecular C-H...O interactions involving nitro oxygen result in a head (nitro) to head (nitro) alignment of anions. Since the cations always point towards the carboxylate oxygen atoms due to the O-H...O interactions, a bilayer of anions sandwiched between layers of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations is formed (Fig. 3). The net result is the organization of cations and anions in the following sequence $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ (2-ca-4nba)⁻ (2-ca-4nba)⁻ $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ along a axis.

Supplementary data

Crystallographic data (excluding structure factors) for the structure of $[\text{Mg}(\text{H}_2\text{O})_6](2\text{-ca-4nba})_2$ (2) reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 720527. 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). IR and thermal data of compound (2) may be obtained from the authors on request.

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