

Synthesis, spectroscopy and supramolecular structures of two magnesium 4-nitrobenzoate complexes[#]

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Abstract. The aqueous reaction of $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}_2$ with the *in situ* generated sodium salt of 4-nitrobenzoic acid (4-nbaH) and N-methylimidazole (N-MeIm) results in the formation of the dinuclear complex $[\text{Mg}(\text{H}_2\text{O})(\text{N-MeIm})_2(4\text{-nba})_2]_2$ **1** (4-nba = 4-nitro benzoate), while the direct reaction of $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}_2$ with sodium 4-nba leads to the formation of the mononuclear complex, $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **2**. In the centrosymmetric dimer **1**, each Mg atom is coordinated to an aquo ligand, two monodentate N-MeIm ligands and a monodentate 4-nba ligand. The second 4-nba ligand functions as a bridging bidentate ligand, linking the metal centers and completes the hexacoordination around each Mg(II). The dimeric molecules of **1** are linked into a one-dimensional chain along *b* with the aid of intra- as well as intermolecular H-bonding interactions between the coordinated water and the free oxygen atom of the monodentate 4-nba ligand. In the mononuclear complex $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **2**, the Mg(II) is located on an inversion center and its structure consists of an octahedral $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ dication, a free uncoordinated 4-nba anion and a lattice water molecule. One of the H atoms attached of the lattice water is disordered over two positions. The hexaaquamagnesium(II) dication, the 4-nba anion and the lattice water molecule are linked by intra- and intermolecular H-bonding interactions resulting in the formation of alternating layers of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ dications and 4-nba anions in the crystallographic *bc* plane. The lattice water molecules are situated between the cations, while the 4-nba anions are arranged antiparallel to each other along *b*.

Keywords. 4-Nitrobenzoic acid; N-methylimidazole; monodentate; bridging bidentate; H-bonding interactions; hexaaquamagnesium(II).

1. Introduction

Magnesium is a biologically relevant element in view of its widespread occurrence in nature (e.g. Mg in chlorophyll) and in the body. Mg(II) plays an essential role in the activation of enzymes, complexation with nucleic acids, nerve impulse transmission etc. Hence the study of Mg(II) complexes has been undertaken by several research groups in order to understand the mode of binding of Mg(II) *in vivo* and *in vitro*.^{1–3} Many of these studies have focused on the use of carboxylate ligands like aspartate, glutamate, salicylic acid and more recently amino and

mercaptobenzoates.^{4–14} While such studies are important to enhance our understanding of Mg biochemistry, a recent interest in this area is in terms of the rich structural chemistry exhibited by the alkali-earth metal complexes. It is to be noted that the carboxylate group is a versatile ligand and exhibits a variety of binding modes.^{15,16} This property of the carboxylate ligand combined with the fact that many metal-carboxylates are hydrated and contain both coordinated as well as crystal water molecules, which can participate in H-bonding interactions,^{17,18} can be used to construct novel supramolecular metal-organic architectures. The study of crystalline hydrates is an area of current research,¹⁹ as these compounds can function as molecular containers for trapping small water clusters, which exhibit interesting structures of H-bonded water molecules.^{20,21}

[#]Dedicated to Prof. Dr. Werner Weisweiler on the occasion of his 69th birthday

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In the earlier work we have investigated the spectral and thermal characteristics of hydrated Mg(II)-complexes of the isomeric nitrobenzoic acids and had attributed their dehydration characteristics at higher temperatures to the differing nature of H-bonding interactions of the nitro group as compared to the amino analogue.²² As part of this research^{23,24} we are investigating the synthesis and structural aspects of alkali-earth nitrobenzoates with N-donor ligands and have recently reported the structures of the mixed ligand complexes $[\text{Mg}(\text{H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]$ and $[\text{Ca}(\text{H}_2\text{O})_3(\text{Im})(4\text{-nba})_2]\cdot\text{Im}$ (Im = imidazole).²⁵ In continuation of this work, we wish to describe the synthesis, spectral and structural characterization of the dimeric Mg(II) complex obtained by using N-methylimidazole (N-MeIm) as the N-donor ligand. In addition, the crystal structure of $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2\cdot 2\text{H}_2\text{O}$ is 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. The starting materials as well as reaction products are quite stable in air and hence were routinely prepared under normal laboratory conditions. The details of instrumentation were the same as described in our earlier reports.^{24,25} The insoluble 4-nitrobenzoic acid (4-nbaH) obtained on acid treatment of the complexes was weighed as described earlier²² and metal analysis was performed titrimetrically following a standard procedure.²⁶

2.2 Preparation of $[\text{Mg}(\text{H}_2\text{O})(\text{N-MeIm})_2(4\text{-nba})_2]_2$ 1 and $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2\cdot 2\text{H}_2\text{O}$ 2

A mixture of MgCO_3 (0.84 g, 10 mmol) and 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 as evidenced by the 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 reaction mixture was filtered and N-MeIm (3.2 ml, 40 mmol) was added to the hot filtrate. The solution was stirred and concentrated to around 10 ml and left undisturbed for a few days. The pale yellow crystalline blocks that separated were filtered, washed thoroughly with ether and dried in air. Yield 89%. Complex 1

can also be prepared by using magnesium chloride as the Mg source. $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}_2$ (2.03 g, 10 mmol) was dissolved in water (10 ml). Into this, an aqueous solution (40 ml) of sodium salt of 4-nbaH generated *in situ* from 4-nbaH (3.34 g, 20 mmol), NaHCO_3 (1.68 g, 20 mmol) was added, followed by the addition of N-MeIm (3.2 ml, 40 mmol). The reaction mixture was concentrated to about 15 ml, filtered and kept aside for crystallization. The pale yellow crystalline blocks of 1 that separated after a week were filtered, washed with ice-cold water (2 ml), followed by ether and dried in air. Yield: 77%. The IR spectra of the complexes obtained in both the methods are identical. In the absence of any added N-MeIm into the reaction mixture, the mononuclear complex 2 was isolated in 90% yield.

IR data 1 in cm^{-1} 3441 (s), 3129 (s), 3105 (s), 3053 (s), 2884 (w), 2818 (w), 2610 (w), 2444 (w), 2272 (w), 2207 (w), 1944 (w), 1807 (w), 1720 (m), 1645 (s), 1614 (s), 1582 (s), 1516 (s), 1487 (m), 1404 (s), 1346 (s), 1319 (s), 1287 (s), 1238 (s), 1173 (w), 1142 (w), 1107 (s), 1088 (s), 1028 (m), 1015 (m), 968 (w), 939 (s), 880 (s), 868 (s), 827 (s), 802 (s), 781 (s), 758 (s), 725 (s), 702 (s), 667 (s), 621 (s), 563 (s), 517 (s).

Analysis – Found (calcd.) for $\text{C}_{44}\text{H}_{44}\text{Mg}_2\text{N}_{12}\text{O}_{18}$ 1: Mg 4.54 (4.51); 4-nbaH 60.25 (61.65); C 49.09 (49.01); H 4.20 (4.12); N 15.84 (15.59); MgO 7.83 (7.48).

2.3 X-ray crystal structure determination

Intensity data for 1 was collected on a STOE Image Plate Diffraction System and on an AED-II four circle diffractometer for 2, using graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71069\text{\AA}$). The structures were solved with direct methods using SHELXS-97²⁷ and refinement was done against F^2 using SHELXL-97.²⁷ All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were introduced at their calculated positions and included in the refinement riding on their respective parent atoms. In compound 1 the H-atoms attached to the C34 of the methyl group of the N-MeIm ligand are disordered in two orientations rotated by 60° relative to each other. Therefore, they were refined using the HFIX 127 command for disordered methyl groups in SHELXL-97. In compound 2 one of the H atoms (H80) attached to the lattice water (O14) is disordered over two positions and was refined using a split model with site occupation factors of 50 : 50.

Table 1. Technical details of data acquisition and selected refinement results for **1** and **2**.

Compound	[Mg(H ₂ O)(N-MeIm) ₂ (4-nba) ₂] ₂ 1	[Mg(H ₂ O) ₆](4-nba) ₂ 2H ₂ O 2
Formula	C ₄₄ H ₄₄ Mg ₂ N ₁₂ O ₁₈	C ₁₄ H ₂₄ MgN ₂ O ₁₆
Temperature [K]	293(2)	293(2)
Wavelength [pm]	71.073	71.073
Space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> [Å]	8.3235(6)	6.0182(14)
<i>b</i> [Å]	11.1564(8)	7.4098(18)
<i>c</i> [Å]	13.9034(11)	12.3517(17)
α [°]	92.89(1)	98.58(2)
β [°]	97.06(1)	96.81(2)
γ [°]	90.08(1)	91.74(2)
Volume [Å ³]	1279.6(2)	540.2(2)
<i>Z</i>	1	1
μ [mm ⁻¹]	0.132	0.17
<i>F</i> (000)	560	262
Crystal size [mm ³]	0.5 × 0.4 × 0.4	0.2 × 0.1 × 0.1
Molecular weight [g/mol]	1077.53	500.66
Density (calcd.) [g cm ⁻³]	1.398	1.539
<i>hkl</i> Range	-10/10, -14/14, -18/18	0/8, -10/10, -17/17
2 θ range (°)	4.82–56.10	3–60
Reflections collected	14594	3456
Reflections unique	5953	3176
Data (<i>F</i> _o > 2 σ (<i>F</i> _o))	4629	2242
<i>R</i> _{int}	0.0308	0.0220
$\Delta\rho$ [e/Å ³]	0.326/–0.232	0.41/–0.36
Parameters	346	152
<i>R</i> 1[<i>F</i> _o > 2 σ (<i>F</i> _o)]	0.0449	0.0465
<i>W</i> <i>R</i> 2 for all unique data	0.1219	0.1432
Goodness of fit	1.034	1.025

By this disordering alternative hydrogen bonding interactions occur. The H atoms of all the coordinated water molecules of **1** and **2** were located in the difference Fourier maps and refined with fixed isotropic displacement parameters. The technical details of data acquisition and some selected refinement results for both the compounds are summarized in table 1.

3. Results and discussion

3.1 Synthesis

For the synthesis of Mg(II)-carboxylates, two synthetic methods, which differ in terms of the metal source can be used. The syntheses involve either the aqueous reaction of MgCO₃ with 4-nbaH in a 1 : 2 mole ratio or the reaction of MgCl₂ with 4-nbaH in the presence of a weak base like NaHCO₃. Although the metal carbonate route takes a longer reaction time as well as higher temperature (100°C) in order to solubilize the insoluble carbonate in the presence

of the aromatic acid, which is also insoluble, the method is slightly advantageous, in that the carbonate anion is removed in the form of CO₂. In the chloride route performed at room temperature, the chloride anions remain in solution as the highly soluble NaCl and the less soluble carboxylate crystallizes out. It is to be noted that the synthesis of the hexaaquamagnesium(II) bis(4-nitrobenzoate) dihydrate **2** by the carbonate route has been described by us in an earlier report along with its spectral and thermal characteristics.²² But the crystal structure was not reported. In the present work we have investigated the reactions of Mg(II) with 4-nbaH in the presence of excess N-MeIm and this reaction results in the formation of a new complex containing Mg : 4-nbaH : N-MeIm in a 1 : 2 : 2 mole ratio as evidenced by the analytical data. In the absence of the N-donor ligand the previously reported complex **2** was isolated indicating that **2** is a probable intermediate in the formation of **1**. Compound **1** is not stable in acid as evidenced by its decomposition in dilute HCl resulting in the quantitative formation of

insoluble 4-nbaH, which was analyzed as described earlier.²²

3.2 Spectral and thermal studies

The electronic spectrum of **1** exhibits a signal at around 274 nm and is similar to that of the N-MeIm free complex **2**. This signal can be assigned to the intramolecular charge transfer transition of the aromatic acid. The infrared spectrum of **1** exhibits several sharp bands in the mid IR region, indicating the presence of the organic moieties. A comparison of the IR spectrum of **1** with that of **2** reveals the presence of additional bands in **1** as well as a different profile in the region above 3000 cm⁻¹ (see web version). The additional bands in **1** can be attributed to, as originating from the N-MeIm ligand. Further the differing nature of spectra in the carboxylate region (1650 to 1400 cm⁻¹) can probably be due to a differing ligational mode of the 4-nba ligand in the mixed ligand compound. However, no definite conclusions can be drawn on the structure based on IR data alone. The X-ray powder pattern of **1** shows several sharp reflections indicating its crystalline nature and the pattern is quite different from **2** (see web version). The differing nature of the pale yellow complex **1** is also further evidenced from the isothermal mass loss studies. Complex **1** is thermally more stable as compared to **2** and does not exhibit any loss in weight when heated on a water bath unlike **2**, which starts decomposing at 60°C. When heated at a slightly higher temperature of 130°C the observed mass loss of 7.3% is more than twice the expected value (3.35%) for emission of only water. All efforts to prepare the anhydrous compound were not successful. Pyrolysis of **1** in a Bunsen flame or alternatively in a furnace at 800°C resulted in the formation of a white residue, which was identified as the binary metal oxide based on the mass loss as well as metal analysis. The complete loss of organic part could also be evidenced from the featureless IR spectrum. The TG-DTA study of **1** (figure 1) further reinforces these observations. Thus the TG-DTA thermogram exhibits an endothermic event with a DTA peak at 132°C, which can be attributed to the emission of coordinated water. However the observed mass loss of 4.66% is slightly more than the expected value of 3.35% indicating that the removal of water results in further mass loss which is also evidenced by the rapid drop in the TG curve. The TG curve exhibits a second endothermic event at 218°C, which can be

attributed to the possible removal of the neutral N-MeIm ligand. The remaining events at 348, 412, 528 and 554°C are exothermic indicating the decomposition of the complex, resulting in the formation of a white residue. In the absence of associated mass spectral data of the emitted fragments, no definite conclusions can be drawn on the nature of decomposition process. Above 600°C the TG curve is parallel to the X-axis and the observed residue of 7.4% is in good agreement with the expected value of 7.4% for the formation of MgO. The formation of the oxide phase is further confirmed by its X-ray powder pattern. Taken together, the colour as well as the observed yield in the synthesis, analytical data, IR spectra, powder pattern, TG-DTA and weight loss studies, reveal the formation of a new complex containing Mg(II), 4-nba and the N-donor ligand in a 1:2:2 stoichiometry. The results of the crystal structure determination described below, add more credence to the above observations.

3.3 Description of crystal structures

Complex **1** crystallizes in the centrosymmetric triclinic space group P1 and its asymmetric unit consists of half of the dimeric complex molecule. In the centrosymmetric dimer, each Mg atom is coordinated to an aquo ligand, two monodentate N-MeIm ligands and a monodentate 4-nba ligand. The second 4-nitrobenzoate ligand functions as a bridging bidentate ligand, linking the metal centers and completes the hexacoordination around each Mg(II) (figure 2). This binding mode of the 4-nba ligand re-

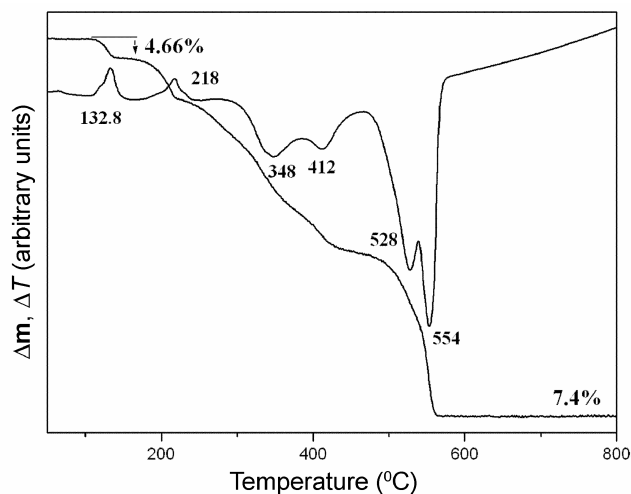


Figure 1. TG-DTA thermogram of complex 1.

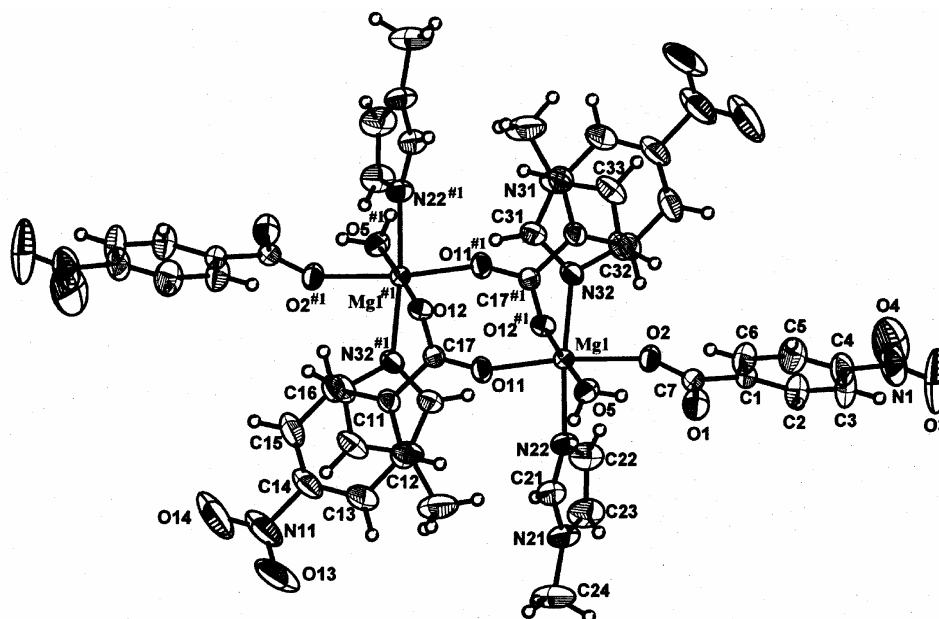


Figure 2. The crystal structure of **1** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the hydrogen atoms, which are shown as circles of arbitrary radius. Symmetry code: #1 $-x, -y + 2, -z + 1$.

Table 2. Selected Bond lengths and angles [\AA , $^\circ$] for $[\text{Mg}(\text{H}_2\text{O})(\text{N-MeIm})_2(4\text{-nba})_2]_2$ **1**.

Mg(1)–O(11)	2.0395(11)	Mg(1)–O(5)	2.1170(11)
Mg(1)–O(12)#1	2.0715(11)	Mg(1)–N(32)	2.1780(13)
Mg(1)–O(2)	2.1105(11)	Mg(1)–N(22)	2.1986(13)
O(11)–Mg(1)–O(12)#1	94.68(4)	O(2)–Mg(1)–N(32)	89.39(5)
O(11)–Mg(1)–O(2)	171.57(4)	O(5)–Mg(1)–N(32)	89.18(5)
O(12)#1–Mg(1)–O(2)	92.47(4)	O(11)–Mg(1)–N(22)	90.75(5)
O(11)–Mg(1)–O(5)	86.54(4)	O(12)#1–Mg(1)–N(22)	89.45(5)
O(12)#1–Mg(1)–O(5)	178.13(4)	O(2)–Mg(1)–N(22)	84.85(5)
O(2)–Mg(1)–O(5)	86.43(4)	O(5)–Mg(1)–N(22)	91.97(5)
O(11)–Mg(1)–N(32)	95.16(5)	N(32)–Mg(1)–N(22)	174.04(5)
O(12)#1–Mg(1)–N(32)	89.29(5)		

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 2, -z + 1$

sults in the formation of the characteristic eight membered ring observed in bridged dinuclear carboxylates, consisting of two Mg atoms, four oxygen atoms and two carbon atoms from the carboxylate moieties of the bridging ligands. The observed bond lengths and bond angles of the organic moieties are in the normal range. The Mg1–O2 bond distance observed for the monodentate 4-nba in **1** is shorter at 2.1105(11) \AA as compared to the Mg–O bond distances of the bridging bidentate 4-nba ligand (table 2). The Mg–N bond lengths in **1** are slightly longer than the reported²⁵ Mg–N bond length of 2.1726(17) \AA in the mononuclear Mg-imidazole

complex $[\text{Mg}(\text{H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]$. The cis O–Mg–O and O–Mg–N angles in **1** range from 84.85(5) to 95.16(5) $^\circ$ with one of the angles close to the ideal value, while the trans bond angles range from 171.51(4) to 178.13(4) $^\circ$ indicating a slight distortion of the $\{\text{MgO}_4\text{N}_2\}$ octahedron. An analysis of the structure reveals that the dimeric Mg(II) complex **1** exhibits two short H-bonding interactions accompanied by large DHA angles (table 3) between a coordinated water and the free oxygen atom of the monodentate 4-nba. Both these O–H \cdots O contacts are much shorter than the sum of their van der Waals radii²⁸ and the coordinated water functions as a

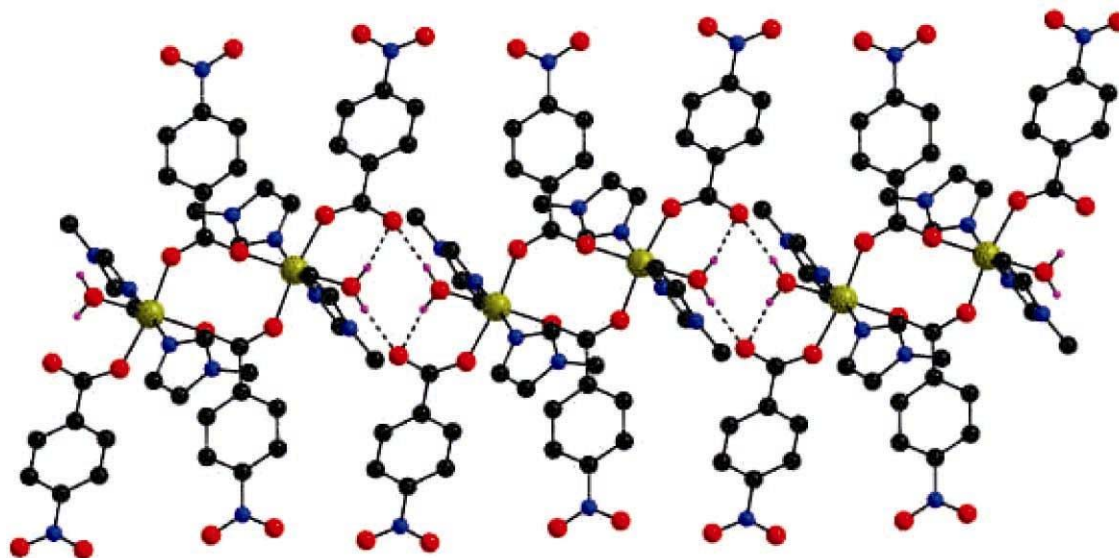


Figure 3. Linking of a dimeric complex **1** with the next unit along *b* by an intermolecular H-bond resulting in the formation of a one-dimensional network. For clarity the H atoms attached to C are not shown.

Table 3. Hydrogen-bonding geometry (Å, °) for $[\text{Mg}(\text{H}_2\text{O})(\text{N-MeIm})_2(4\text{-nba})_2]_2$ **1**.

D–H···A	(D–H)	(H···A)	(D···A)	<DHA
O5–H1O5···O1 ⁱ	0.84	1.987	2.809	166
O5–H2O5···O1	0.84	1.922	2.738	163

Symmetry code: i) $-x, -y + 1, -z + 1$

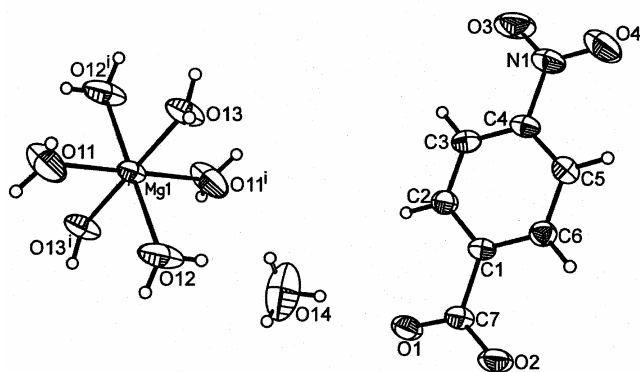


Figure 4. The crystal structure of **2** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the hydrogen atoms, which are shown as circles of arbitrary radius. One of the H atoms attached to the lattice water (O14) is disordered over two positions. Symmetry code: # i $-x, -y, -z + 1$.

singly shared H-donor and the free carboxylate oxygen O1 functions as a H-acceptor. One of these H-bonds, is intramolecular and the other intermolecular, link-

ing a dimeric unit with the next resulting in the formation of a one-dimensional H-bonded network along *b* (figure 3).

Compound **2** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ and the Mg(II) is located on an inversion centre. The structure of **2** consists of a $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cation, a free 4-nba anion and a lattice water molecule (figure 4). The octahedral hexaaquamagnesium(II) cation is a well known unit and has been reported in several Mg(II) complexes.^{9,10,29} The cis O–Mg–O angles in the $\{\text{MgO}_6\}$ octahedron range from 88.6° to 91.5° (table 4). The Mg–O bond distances in the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ unit of **2** range from 2.046(2) to 2.088(2) Å and are shorter than the observed Mg–O (H₂O) bond distance of 2.1170(11) in the dinuclear complex **1**. The observed bond lengths and bond angles of the 4-nba anion are in the normal range and are comparable with those reported for compounds containing the free 4-nba anion.³⁰ An analysis of the crystal structure reveals that the monomeric Mg(II) complex **2** exhibits several H-bonding interactions through all possible sites, with the oxygen atoms of the carboxylate and nitro groups functioning as H-acceptors, while the H atoms of the coordinated waters act as H-donors. The lattice water (O14) functions as H-donor and is linked intramolecularly to the carboxylate oxygen O1 via O14–H70···O1 interaction. As mentioned earlier, one of the H atoms attached to the lattice water is disordered over two positions (H80 and H90). The disordered

Table 4. Selected bond lengths and angles [\AA , $^\circ$] for $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **2**.

Mg(1)–O(11)	2.088(2)	Mg(1)–O(11)#1	2.088(2)
Mg(1)–O(12)	2.066(2)	Mg(1)–O(12)#1	2.066(2)
Mg(1)–O(13)	2.046(2)	Mg(1)–O(13)#1	2.046(2)
O(13)–Mg(1)–O(12)#1	88.6(1)	O(13)#1–Mg(1)–O(12)#1	91.5(1)
O(13)–Mg(1)–O(12)	91.5(1)	O(13)#1–Mg(1)–O(12)	88.6(1)
O(13)–Mg(1)–O(11)	89.9(1)	O(13)#1–Mg(1)–O(11)	90.1(1)
O(12)#1–Mg(1)–O(11)	89.6(1)	O(12)–Mg(1)–O(11)	90.4(1)
O(13)–Mg(1)–O(11)#1	90.1(1)	O(13)#1–Mg(1)–O(11)#1	89.9(1)
O(12)#1–Mg(1)–O(11)#1	90.4(1)	O(12)–Mg(1)–O(11)#1	89.6(1)
O(11)–Mg(1)–O(11)#1	180.0(1)	O(13)–Mg(1)–O(13)#1	180.0
O(12)#1–Mg(1)–O(12)	180.0		

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z + 1$

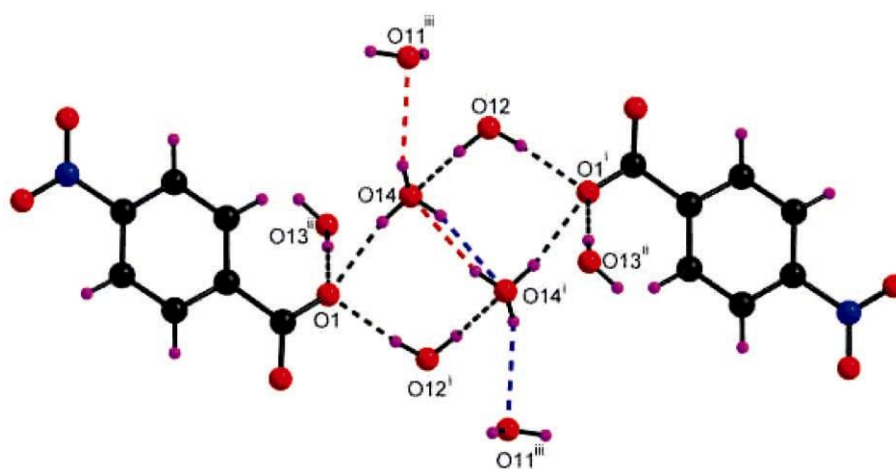


Figure 5. A view of the surroundings of the lattice water showing the H-acceptor bonds with the coordinated waters O11 and O12, a H-donor bond (O14–H7O...O1) to the carboxylate oxygen O1. The H atom involved in the formation of the centrosymmetric cyclic water dimer is disordered over two positions. The red and blue dotted lines indicate the H-bonding of the disordered atoms. Symmetry codes: i) $-x + 1, -y + 1, -z + 1$; ii) $x - y - 1, z$; iii) $-x, -y, -z + 1$.

hydrogen (H80) on O14 is H-bonded to another lattice water through O14–H80...O14 bond, while the H90 is linked to a coordinated water O11 via O14–H90...O11 bond resulting in the formation of a centrosymmetric cyclic water cluster (figure 5). The O14–H80...O14 interaction taken separately constitutes a centrosymmetric cyclic water dimer.

Water oligomers have been extensively investigated by spectroscopic methods^{31,32} and theoretical calculations.^{33–35} In recent years the crystallographic identification of several H-bonded water clusters³⁶ especially linear water dimers in crystalline hydrates has been reported.^{37–39} The patterns of water clusters within the Cambridge Structural Database (CSD Version 5.23 April 2002) have been reviewed by In-

fantes and Motherwell²¹ and classified as discrete chains and rings, infinite chains and tapes, and layer structures. According to this classification many of the reported water clusters fall in the category of discrete chains with water dimers accounting for the majority of the structures. Interestingly there is no mention of a cyclic water dimer in this review.²¹ In a recent paper, Das and coworkers have reported on the identification of a water nonamer, which features an inbuilt cyclic water dimer, in a tetranuclear copper complex.⁴⁰ To the best of our knowledge, there is no other cyclic water dimer crystallographically characterized till date, other than the inbuilt cyclic water dimer mentioned above. The observed O...H and O...O distances of 2.282 and 3.031 \AA in the cyclic

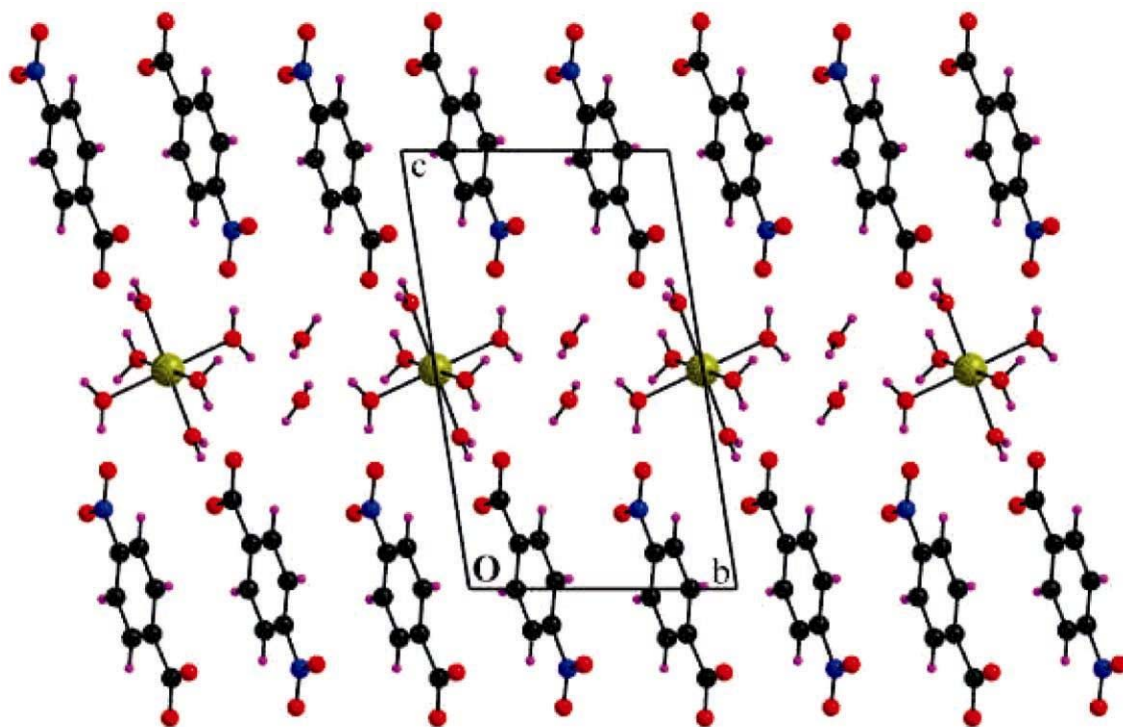


Figure 6. A view of the packing of **2** showing the alternating layers of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations and 4-nitrobenzoate anions in the crystallographic bc plane. The lattice waters are located between the cations, while the anions are arranged antiparallel to each other along b . For clarity H-bonds are not shown.

Table 5. Hydrogen-bonding geometry (\AA , $^\circ$) for $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ **2**.

D–H...A	(D–H)	(H...A)	(D...A)	<DHA
O11–H10...O14 ⁱⁱ	0.82	1.988	2.803	172
O11–H20...O3 ^{iv}	0.82	2.402	3.216	172
O11–H20...O4 ^{iv}	0.82	2.407	3.029	133
O12–H30...O1 ⁱ	0.82	1.830	2.646	174
O12–H40...O14	0.82	2.428	3.103	140
O13–H50...O2 ^v	0.82	1.830	2.648	176
O13–H60...O1 ⁱⁱ	0.82	2.030	2.849	177
O14–H70...O1	0.82	1.994	2.783	161
O14–H80...O14 ⁱ	0.82	2.233	3.031	165
O14–H90...O11 ⁱⁱⁱ	0.82	2.315	2.977	138

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

water dimer in **2** are shorter than the sum of their van der Waals radii but longer than the reported values for nearly linear water dimers identified in other crystalline environments^{37–39} and the inbuilt cyclic water dimer.⁴⁰ Interestingly the OHO angle of 165° which indicates a strong interaction, is more than the reported value of 160° for the inbuilt cyclic water dimer.⁴⁰ The disorder of the hydrogen atom involved

in the formation of the cyclic water dimer can probably account for the observed metric parameters of the O14–H80...O14 interaction. In addition, the lattice water forms H-acceptor bonds with the coordinated waters intra- as well as intermolecularly resulting in the bridging of the cyclic water dimer by four $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations. All H-atoms involved in H-bonding are singly shared donors excepting H20 attached to O11. Unlike the O14 atom of the lattice water and the O1 atom of the carboxylate group, which function as trifurcated acceptors, the oxygen atoms of the nitro group as well as the O2 of the carboxylate act as singly shared acceptors. The observed O–H...O interactions in **2** ranging from 1.830 to 2.428 \AA are shorter than the sum of their van der Waals radii²⁸ and are accompanied by OHO bond angles ranging from 133 to 177° (table 5) These interactions lead to the formation of alternating layers of anions and cations in the crystallographic bc plane and the lattice waters are situated between the dications (figure 6). As a result of the H-bonding pattern in **2**, the 4-nba anions are arranged antiparallel to each other along b . An analysis of the short ring interactions and distances between the ring centroids (Cg–Cg) indicates a nearly overlapped ar-

range of 4-nba anions in the crystal structure of **2** and the perpendicular distance of 3.388 Å accompanied by Cg–Cg distance of 3.674 Å between the 4-nba rings is indicative of π – π stacking interactions.

3.4 Comparative chemistry of magnesium 4-nitrobenzoate complexes:

A comparative study of the structures of **1** and **2** and the recently reported mixed ligand complex²⁵ [Mg(H₂O)₂(Im)₂(4-nba)₂] reveals certain similarities and many differences. In all the three complexes, which contain Mg and 4-nba in a 1 : 2 ratio the central metal is hexacoordinated. However, the 4-nba anion exhibits different ligational behaviour. In complex **1** both monodentate and bridging bidentate modes of 4-nba are observed, and in **2** the 4-nba is uncoordinated while in the imidazole complex it is monodentate. In all the three complexes, which crystallize in the centrosymmetric triclinic $P\bar{1}$ space group the metal ion is differently hydrated. Thus the metal : H₂O ratio is 1 : 1 in the dimeric Mg complex **1** and 1 : 2 in the Mg–Im complex and in both these complexes the waters are coordinated to Mg. In contrast, the Mg : H₂O ratio in **2** is 1 : 8 and **2** contains both coordinated and lattice waters. All the three complexes exhibit intermolecular H-bonding interactions and the resulting H-bonded networks are quite different. The complexes **1** and **2** are H-bonded with the aid of O–H...O interactions, while in [Mg(H₂O)₂(Im)₂(4-nba)₂] two types of interactions namely O–H...O and N–H...O bonds are observed. The N-donor ligand free complex **2** is involved in intermolecular interactions through all its possible sites resulting in the formation of a three dimensional H-bonding network and encapsulating a cyclic water dimer which is further H-bonded to four different hexaaquamagnesium(II) ions. The incorporation of Im as well as 4-nba in the coordination sphere of Mg in [Mg(H₂O)₂(Im)₂(4-nba)₂] results in an intricate three dimensional network with the aid of two varieties of H-bond. In the Im complex only one of the nitro oxygen is H-bonded unlike in **2** where both the oxygen atoms of the –NO₂ functionality are H-bonded to the coordinated waters. The incorporation of N-MeIm as well as 4-nba in the coordination sphere of Mg(II) in **1** results in the formation of a dimeric complex. As expected, the substitution of H atom attached to the amino N in Im by –CH₃ in the N-MeIm ligand not only blocks the H-bonding at this site, which is observed in the Mg–Im complex,

but results in the formation of a one dimensional H-bonded network.

4. Conclusions

The aqueous reaction of MgCl₂ with sodium 4-nba and N-MeIm or alternatively the reaction of MgCO₃ with 4-nbaH and N-MeIm in a 1 : 2 : 4 mole ratio results in the formation of the dimeric Mg complex **1** in good yields. In the absence of any N-donor ligand complex **2** is obtained. Both the compounds are obtained as phase pure solids as evidenced by a comparison of the powder pattern of the bulk sample with that of the calculated pattern from the single crystal data. **1** is thermally more stable as compared to **2** and at elevated temperatures (~800°C), is decomposed to MgO. Both complexes, which crystallize in the triclinic $P\bar{1}$ space group exhibit different binding modes of the 4-nba ligand. An interesting aspect of the structure of complex **2** is the identification of a cyclic water dimer showing that **2** functions as a molecular container for encapsulating a cyclic water dimer. A comparative study of the structures of three magnesium 4-nitrobenzoate complexes reveals that these complexes exhibit a rich structural chemistry in terms of the binding modes of the 4-nba ligand as well as the intermolecular interactions.

Supplementary material

Infrared spectra and X-ray powder pattern of compounds **1** and **2**, are available on the web version of this paper. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 635058 (**1**), CCDC 635059 (**2**). 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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