Synthesis, properties and supramolecular structure of di(aqua)*bis*(ethylenediamine)nickel(II) *bis*(4-nitrobenzoate)[†]

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Abstract. The reaction of the sodium salt of 4-nitrobenzoic acid (4-nbaH) with $[Ni(H_2O)_6]Cl_2$ or $[Ni(en)_3]Cl_2 \cdot 2H_2O$ (en is ethylenediamine) results in the formation of the known octahedral compound $[Ni(H_2O)_4(\eta^1\text{-}4\text{-}nba)_2] \cdot 2H_2O$ (4-nba = 4-nitrobenzoate) **1** or the title compound di(aqua)*bis*(ethylenediamine)nickel(II) *bis*(4-nitrobenzoate) **2** respectively. Compounds **1** and **2** were characterized by elemental analysis, infrared spectra, DSC thermograms, weight loss studies and the structure of **2** was determined. Both **1** and **2** can be thermally decomposed to green NiO. The title compound $[Ni(H_2O)_2(en)_2](4\text{-}nba)_2$ **2** crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with the Ni(II) situated on an inversion center. The crystal structure of **2** consists of a hexacoordinated Ni(II) complex cation and an uncoordinated 4-nba anion. In the octahedral complex cation, the central metal is linked to two symmetry related bidentate en ligands and two water molecules. In the crystal structure, the cations and anions are linked by three varieties of hydrogen bonding interactions. A comparative study of seven nickel 4-nitrobenzoate compounds is described.

Keywords. Ethylenediamine; 4-nitrobenzoate; octahedral; crystal structure; hydrogen bonding interactions.

1. Introduction

Current efforts in metal-carboxylate research[1,2] are directed towards the development of new methods for the preparation of metal-organic framework materials (MOF's) using benzene based carboxylic acids as the organic part to bind to metal ions and study their properties.[3,4] As part of our metal-carboxylate research program,[5,6] we are investigating the chemistry of metal-nitrobenzoates with the –NO₂ functionality functioning as a hard hydrogen bond acceptor.[7] The ready availability of the isomeric nitrobenzoic acids (nbaH) in pure form, the ability of the –NO₂ group to participate in hydrogen bonding and the relatively little work done on metal-nitrobenzoates[8–10] have been a few factors which prompted us to develop a systematic chemistry of metal-nitrobenzoates to gain more insight on the structure directing effect of the nitro group. The –NO₂ functionality is disposed differently with respect to the –COOH group in the isomeric acids. The structural variation that can arise by altering the position of the nitro group can be evidenced from a recent report on the structural characterization of a barium 2-nitrobenzoate compound.[11] Our recent work has unraveled a rich structural chemistry of alkaline-earth 4-nitrobenzoates.[12–18] The available literature on transition metal 4-nitrobenzoates especially Ni(II) is restricted to a few structure reports.[19–22] In view of this, we have initiated a systematic study of the chemistry of the transition metal 4-nitrobenzoates. In this paper we report on the synthesis, properties and structure of a new Ni(II) compound containing a free 4-nitrobenzoate (4-nba) and a comparative study of seven different nickel 4-nitrobenzoates.

2. Experimental

2.1 *Materials and methods*

All the chemicals used in this study were of reagent grade and were used as received. $[Ni(en)_3]Cl_2 \cdot 2H_2O$ was prepared by a reported procedure.[23] The starting materials and reaction products are air stable and hence were prepared under normal laboratory condi-

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[†]Dedicated to Dr J K Kirtany on the occasion of his 65th birthday.
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tions. Infrared spectra were recorded in KBr matrix on a Shimadzu (IR Prestige-21) TG-DSC measurements were performed in Al_2O_3 crucibles on a STA-409PC (Luxx) thermal analyzer from Netzsch in flowing air. A heating rate of 10 K min^{-1} was employed for the measurements. The insoluble 4-nbaH obtained on acid treatment of the complexes was weighed as described earlier[6] and metal analysis was performed titrimetrically following a standard procedure. Isothermal weight loss studies were performed in an electric furnace fitted with a temperature controller. Single crystal X-ray diffraction study for compound **2** was performed at the National single crystal X-ray facility at School of Chemistry, University of Hyderabad.

2.2 *Preparation of [Ni(H₂O)₄(4-nba)₂]·2H₂O 1*

The sodium salt of 4-nitrobenzoic acid (4-nbaH) was prepared *in situ* by dissolving 4-nbaH (668 mg, 4 mmol) in an aqueous solution of sodium bicarbonate (336 mg, 4 mmol) in water (20 mL). This solution was concentrated to about 10 mL, cooled and then added into $[Ni(H_2O)_6]Cl_2$ (476 mg, 2 mmol) in water (20 mL) to obtain a clear green solution. The reaction mixture was left undisturbed for a few days to obtain green crystalline blocks, which were filtered, washed with cold water (2 mL) followed by ether and dried in air. Yield: (75%). Compound **1** can also be prepared by dissolving freshly prepared $NiCO_3$ in boiling water in the presence of 4-nbaH, followed by crystallization.

Anal. Found (Calcd) for $C_{14}H_{20}NiN_2O_{14}$ (499·01): Ni 11·88 (11·76), 4-nbaH 67·88 (66·98), C 33·76 (33·70), N 5·58 (5·61), H 3·84 (4·04), NiO 14·57 (14·97) IR (in cm^{-1}): 3601 (*s*), 3549 (*s*), 3323 (*s*), 3225 (*s*), 3113 (*s*), 3082 (*s*), 3053 (*s*), 2994 (*s*), 2947 (*s*), 2872 (*s*), 2835 (*s*), 2511 (*s*), 2452 (*s*), 1952 (*w*), 1813 (*w*), 1715 (*w*), 1667 (*m*), 1614 (*m*), 1568 (*s*), 1516 (*s*), 1408 (*s*), 1377 (*s*), 1352 (*s*), 1321 (*s*), 1281 (*m*), 1246 (*w*), 1107 (*m*), 1015 (*m*), 980 (*m*), 957 (*m*), 880 (*s*), 822 (*s*), 797 (*s*), 725 (*s*), 669 (*m*), 567 (*m*), 530 (*s*), 420 (*m*). DSC (in °C): 108 (endo), 390 (exo), 408 (exo).

2.3 *Preparation of [Ni(H₂O)₂(en)₂](4-nba)₂ 2*

The sodium salt of 4-nitrobenzoic acid (4-nbaH) was first prepared by dissolving 4-nbaH (668 mg, 4 mmol) in an aqueous solution of sodium bicarbonate (336 mg, 4 mmol) in water (20 mL) and concen-

trated to ~ 10 mL. To this was added an aqueous solution of $[Ni(en)_3]Cl_2·2H_2O$ (692 mg, 2 mmol) in water (5 mL). The clear purple reaction mixture was filtered and left aside for crystallization. Blue violet blocks of **2**, which separated after a day were filtered, washed with water and dried in air. Yield. 68%. In an alternate method, bis(ethylenediamine-nickel(II) dichloride was prepared *in situ* by reacting $[Ni(en)_3]Cl_2·2H_2O$ (692 mg, 2 mmol) dissolved in water (5 mL) with $[Ni(H_2O)_6]Cl_2$ (238 mg, 1 mmol) in water (10 mL). This resulted in the formation of a blue solution. To this, a solution of freshly prepared sodium salt of 4-nbaH (6 mmol) was added. The reaction mixture was left aside for crystallization to obtain compound **2**, which was isolated as earlier. The IR spectrum of this product is identical to that of the earlier product.

Anal. Found (Calcd) for $C_{18}H_{28}N_6NiO_{10}$ (547·17): Ni 10·95 (10·72), 4-nbaH 60·83 (61·09), C 39·57 (39·51), N 15·23 (15·36), H 5·14 (5·16), NiO 12·76 (13·65).

IR (in cm^{-1}): 3352 (*s*), 3298 (*s*), 3240 (*s*), 3157 (*m*), 3117 (*w*), 3042 (*w*), 2980 (*m*), 2963 (*w*), 2943 (*w*), 2891 (*m*), 2843 (*w*), 2756 (*w*), 2355 (*w*), 2340 (*w*), 1601 (*w*), 1557 (*s*), 1377 (*s*), 1348 (*s*), 1319 (*m*), 1279 (*m*), 1171 (*w*), 1161 (*s*), 1099 (*s*), 1080 (*m*), 1018 (*w*), 1007 (*s*), 974 (*s*), 875 (*m*), 862 (*w*), 825 (*m*), 798 (*m*), 777 (*w*), 719 (*m*), 702 (*w*), 667 (*w*), 513 (*s*), 498 (*w*). DSC (in °C): 129 (endo), 297 (exo), 373 (exo), 418 (exo).

2.4 *X-ray crystallography*

Intensity data for **2** were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. The data integration and reduction were carried out using SAINT.[24] An empirical absorption correction was applied to the collected reflections with SADABS.[24] The structure was solved with direct methods using SHELXS-97[25] and refinement was done against F^2 using SHELXL-97.[25] 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 of the coordinated water molecules were located in the difference map and were refined isotropically using a riding model. The technical details of data acquisition and some selected crystal refinement results for the title compound **2** are summarized in table 1.

Table 1. Technical details of data acquisition and selected refinement results for $[Ni(H_2O)_2(en)_2](4\text{-}nba)_2$ **2**.

Empirical formula	$C_{18}H_{28}N_6NiO_{10}$
Formula weight	547.17 g mol^{-1}
Temperature	$298(2)$ K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 13.3752(9)$ Å
	$b = 6.9571(5)$ Å
	$c = 12.3184(8)$ Å
	$\beta = 93.0050(10)°$
Volume	$1144.68(14)$ Å^3
Z	2
Density (calculated)	1.588 mg/m^3
Absorption coefficient	0.915 mm^{-1}
$F(000)$	572
Crystal size	$0.41 \times 0.32 \times 0.10$ mm^3
Theta range for data collection	1.52 to $25.92°$
Index ranges	$-16 \leq h \leq 16, -8 \leq k \leq 8, -15 \leq l \leq 15$
Reflections collected	11298
Independent reflections	2238 [$R(int) = 0.0276$]
Completeness to theta = $25.92°$	99.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2238/0/166
Goodness-of-fit on F^2	1.040
Final R indices [$I > 2sigma(I)$]	$R1 = 0.0264, wR2 = 0.0713$
R indices (all data)	$R1 = 0.0305, wR2 = 0.0742$
Extinction coefficient	$0.0207(17)$
Largest diff. peak and hole	0.228 and -0.211 eÅ^{-3}

Scheme 1.
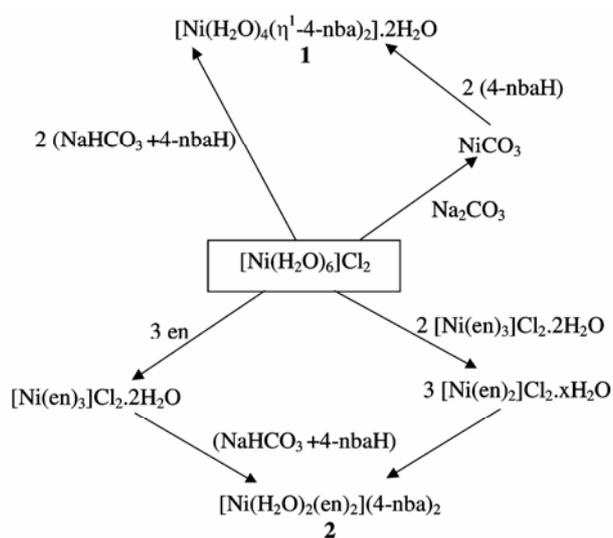
3. Results and discussion

Compounds **1** and **2** which were isolated from aqueous reaction media are insoluble in water but are unstable in dilute HCl and decompose to form the green $[Ni(H_2O)_6]^{2+}$ ion and insoluble 4-nbaH.

The composition of **1** and **2** were arrived at based on elemental analysis and formation of NiO on pyrolysis in a Bunsen flame. The structure of the hexacoordinated Ni(II) compound $[Ni(H_2O)_4(\eta^1\text{-}4\text{-}nba)_2]\cdot 2H_2O$ **1**, has been briefly reported. For the structure determination the crystals were prepared by slowly cooling a boiling solution of nickel nitrate and ammonium 4-nitrobenzoate.[19] In the present work, the protocol employed for the synthesis of compound **1** (scheme 1) by the reaction of $[Ni(H_2O)_6]Cl_2$ with the sodium salt of 4-nbaH or by solubilization of freshly prepared NiCO$_3$ in hot aqueous 4-nbaH is similar to the one, reported by us for the synthesis of several metal carboxylates.[5–7,11–16] The observed analytical characteristics of compound **1** from the different methods are in good agreement for the proposed formula and the infrared spectra are identical. The X-ray powder pattern of **1** is nearly identical with the analogous Co(II) compound[7] $[Co(H_2O)_4(4\text{-}nba\text{-}O)_2]\cdot 2H_2O$ indicating their isostructural nature.

In another structure report, light blue crystals prepared from the reaction of Ni(OH)$_2$ with 4-nbaH in aqueous ammonia have been shown to be a differ-

ently hydrated Ni(II) compound containing a hexa (aqua)nickel(II) cation and free 4-nba anions with the formula $[Ni(H_2O)_6](4\text{-nba})_2 \cdot 2H_2O$.[20] The formation of different products can be attributed to the differing pH of the reaction media. In view of this, it was of interest to investigate the aqueous reactions of Ni(II) with 4-nbaH in the presence of coordinating amines, the use of which can not only affect the pH but the amines can also coordinate to Ni(II). Hence the reaction of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ with sodium 4-nitrobenzoate was investigated, which resulted in the formation of a blue violet compound whose analysis indicated a composition of Ni : en : 4-nba:H$_2$O in a 1 : 2 : 2 : 2 ratio (scheme 1). This observation shows that the coordination sphere of the

Figure 1. TG-DSC thermogram of $[Ni(H_2O)_2(en)_2](4\text{-nba})_2$ **2**.
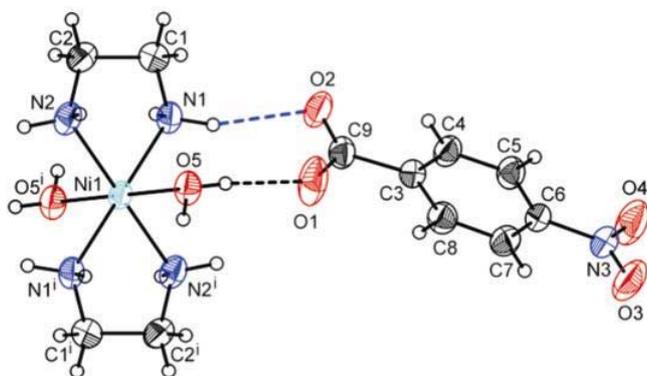
Figure 2. The crystal structure of $[Ni(H_2O)_2(en)_2](4\text{-nba})_2$ **2** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown by broken lines. Symmetry code: (i) $-x + 1, -y, -z + 1$.

$[Ni(en)_3]^{2+}$ undergoes reorganization on reaction with sodium 4-nitrobenzoate, accompanied by anion exchange. A rational synthesis of **2** was achieved by using $[Ni(en)_2]^{2+}$ as the Ni(II) source instead of the *tris* complex. A survey of the literature revealed that the structure of an anhydrous Ni(II) compound containing propane-1,3-diamine (1,3-pn) and 4-nba has been reported.[21] This compound formulated as $[Ni(1,3\text{-pn})_2(\eta^1\text{-4-nba})_2]$ contains a monodentate 4-nba bonded to Ni(II). This was prepared by dispersing a crude product of the nickel salt of 4-nitrobenzoic acid in a 1 : 1 water:ethanol mixture with 1,3-pn and brown crystals were isolated for the structure determination after several weeks. In the present work we have determined the structure of the new compound **2** and have also investigated both **1** and **2** by spectral and thermal studies.

The IR spectra of **1** and **2** exhibit several sharp bands in the mid-infrared region, many of which are due to the vibrations of the organic moieties namely 4-nba in **1** and 4-nba and en in **2**. The IR spectrum of **1** is nearly identical to that of the corresponding Co(II) analogue reported by us earlier.[7] The broad and strong signal in the region 3600–2800 cm^{-1} in both **1** and **2** indicates the presence of water and can be assigned to the O–H stretching vibration. The profile of this signal in both compounds differs and the vibrations of the amino group of en in **2** are masked by the strong –OH signal. The IR spectra of **1** and **2** exhibit the signals due to the vibrations of the carboxylate and nitro groups. However, no definite conclusions can be drawn on the nature of the binding of the carboxylate ligand based only on infrared data.

The TG–DSC thermogram of **1** exhibits an endothermic event at around 108°C followed by exothermic processes at 390 and 408°C. The first enothermic process accompanied by a mass loss of 18·43% can be assigned for the loss of water. The observed weight loss is less than that expected (21·64%) for loss of six moles of water, indicating incomplete dehydration. The two exothermic signals can be assigned for the decomposition of 4-nba leading to the formation of oxide phase. It is to be noted that 4-nba decomposes around 400°C in alkaline-earth compounds.[12,17,18] The observed residue is in good agreement for the formation of NiO. The thermogram of compound **2** is quite different from that of **1** (figure 1) and signals are observed at 129, 297, 373 and 418°C. The first endothermic event at 129°C accompanied by a mass loss of 6·29% is in good agreement for the expected (6·58%) loss of

Table 2. Selected bond distances and bond angles (Å, °) for $[Ni(en)_2(H_2O)_2](4\text{-nba})_2$.

Ni(1)–N(1)	2·1003(13)	Ni(1)–N(2)[i]	2·1015(14)
Ni(1)–N(2)	2·1015(14)	Ni(1)–O(5)	2·1069(12)
Ni(1)–N(1)[i]	2·1003(13)	Ni(1)–O(5)[i]	2·1069(12)
N(1)[i]–Ni(1)–N(1)	180·0	N(2)[i]–Ni(1)–O(5)	92·46(5)
N(1)[i]–Ni(1)–N(2)[i]	82·80(5)	N(2)–Ni(1)–O(5)	87·54(5)
N(1)–Ni(1)–N(2)[i]	97·20(5)	N(1)[i]–Ni(1)–O(5)[i]	88·95(5)
N(1)[i]–Ni(1)–N(2)	97·20(5)	N(1)–Ni(1)–O(5)[i]	91·05(5)
N(1)–Ni(1)–N(2)	82·80(5)	N(2)[i]–Ni(1)–O(5)[i]	87·54(5)
N(2)[i]–Ni(1)–N(2)	180·00(8)	N(2)–Ni(1)–O(5)[i]	92·46(5)
N(1)[i]–Ni(1)–O(5)	91·05(5)	O(5)–Ni(1)–O(5)[i]	180·00(5)
N(1)–Ni(1)–O(5)	88·95(5)		

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

Table 3. Hydrogen-bonding geometry (Å, °) for $[[Ni(H_2O)_2(en)_2](4\text{-nba})_2]$.

D–H···A	d(D–H)	d(H···A)	d(D···A)	<DHA
O5–H5X···O1	0·815	1·825	2·631	172
N1–H1A···O2	0·900	2·179	3·044	161
N1–H1B···O2[ii]	0·900	2·300	3·135	154
N2–H2A···O4[iii]	0·900	2·596	3·267	132
N2–H2A···O3[iii]	0·900	2·663	3·425	143
O5–H5Y···O2[iv]	0·820	1·927	2·738	170
C1–H1D···O5[v]	0·970	2·700	3·387	128
C1–H1C···O3[vi]	0·970	2·655	3·326	127
C2–H2C···O1[v]	0·971	2·601	3·481	151

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

two moles of water. This is followed by all exo-thermic events. The TG curve shows a sharp drop accompanied by the first exothermic peak which can probably be assigned to the decomposition of coor-dinated en ligands and the strong exothermic signal at 418°C can be assigned to the decomposition of 4-nba. As the emitted fragments have not been investigated by mass spectra, the exact nature of these exothermic decomposition processes cannot be unambiguously commented upon. Based on mass loss, as well as its featureless infrared spectrum, the final green residue (12·29%) can be attributed to the formation of NiO. The formation of green NiO as the final residue was also confirmed based on iso-thermal weight loss studies by heating both com-pounds **1** and **2** at 800°C in a temperature controlled furnace.

The structure of compound **1** which crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ has been reported[19] and **1** is isotypic with the corres-ponding Co(II)[7] and Mn(II)[19] analogues. The title compound $[Ni(H_2O)_2(en)_2](4\text{-nba})_2$ **2** crystallizes in

the centrosymmetric monoclinic space group $P2_1/c$ with the Ni(II) situated on an inversion center. In view of the special position for Ni(II), a half of the formula unit of **2** constitutes the asymmetric unit. The structure of **2** consists of a hexacoordinated Ni(II) complex cation and a free uncoordinated 4-nba anion (figure 2). It is interesting to note that the 4-nba functions as an anion for charge balance and is not bonded to Ni(II) unlike in the related hexaco-ordinated compounds $[Ni(H_2O)_4(\eta^1\text{-4-nba})_2]\cdot 2H_2O$ **1** and $[Ni(1,3\text{-pn})_2(\eta^1\text{-4-nba})_2]$ where the an-ion functions as a monodentate (η^1) ligand. The geometric parameters of the anion in **2** are in good agreement with the reported data for compounds containing free uncoordinated 4-nba.[15,26] In the oc-tahedral complex cation the central metal is linked to two symmetry related bidentate en ligands with the nitrogen atoms of en at the corners of an ap-proximate square plane and the coordination of two water molecules *trans* to each other complete the hexacoordination around Ni(II). The *cis* N–Ni–N and N–Ni–O bond angles range from 82·80 to 97·20° indicating a distortion of the octahedron (ta-ble 2). The Ni–N bond distances at 2·1003(13) and 2·1015(14) Å are indistinguishable within experi-mental error and are in agreement with the reported data for $[Ni(1,3\text{-pn})_2(\eta^1\text{-4-nba})_2]$.[21] The Ni–O(H_2O) distance at 2·1069(12) Å is comparable with the re-ported values for $[Ni(H_2O)_6](4\text{-nba})_2]\cdot 2H_2O$.[20]

A scrutiny of the crystal structure of **2** reveals that the cation and anion are linked by three varieties of H-bonding interactions. All the oxygen atoms of the 4-nba and the coordinated water form hydrogen ac-ceptor bonds. The hydrogen atoms of the coordi-nated water, and three hydrogen atoms attached to the amine nitrogen and three of the methylene hy-drogen atoms in en function as H-donors, resulting in nine short O···H contacts comprising of two
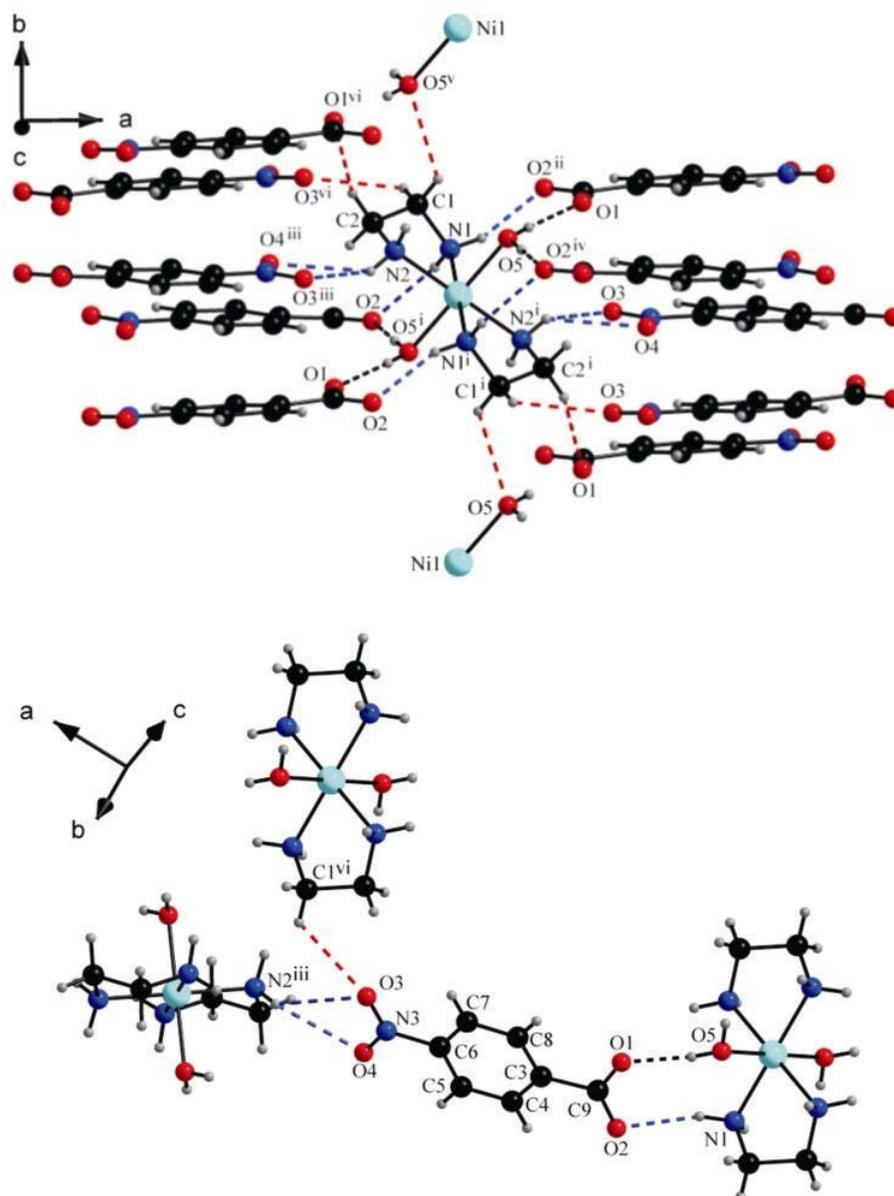
Figure 3. A view of the surroundings of the $[Ni(H_2O)_2(en)_2]^{2+}$ cation along *c* axis show-ing the linking of each cation to ten different 4-nba anions and two symmetry related $[Ni(H_2O)_2(en)_2]^{2+}$ cations via two O–H···O, four N–H···O and three C–H···O hydrogen bonds (top). A view of the surroundings of the 4-nba anion showing the linking of each an-ion to three different $[Ni(H_2O)_2(en)_2]^{2+}$ cations via one O–H···O, three N–H···O and one C–H···O hydrogen bonds (bottom). H-bonds are shown as broken lines. Symmetry codes: (ii) –*x* + 1, *y* – 1/2, –*z* + 1/2; (iii) *x* – 1, –*y* + 1/2, *z* + 1/2; (iv) *x*, –*y* + 1/2, *z* + 1/2; (v) 1 – *x*, 1 – *y*, 1 – *z*; (vi) –1 + *x*, *y*, *z*.

O–H···O, four N–H···O and three C–H···O interac-tions (table 3). All these O···H distances ranging from 1·83 to 2·70 Å are shorter than the sum of their van der Waals radii.[27] An analysis of the crystal structure reveals that each hexacoordinated Ni(II) complex cation is H-bonded to ten different 4-nba anions and two symmetry related cations with the

aid of two O–H···O, four N–H···O and three C–H···O interactions while each 4-nba anion is hydrogen bonded to three different cationic complexes via one O–H···O, one C–H···O and three N–H···O interac-tions (figure 3). The carboxylate oxygen atoms O1 and O2 are involved in strong intramolecular hydro-gen bonds (see figure 2) as evidenced by the short

distances of O5–H5X⋯O1 and N1–H1A⋯O2 interactions accompanied by large bond angles. In contrast, the oxygen atoms of the nitro group O3 and O4 make intermolecular hydrogen bonds. The weak C–H⋯O interactions play a very important role in the supramolecular structure of **2**. The C1–H1D⋯O5 interaction (for symmetry code see table 3) links the hexacoordinated Ni(II) complex cations into an infinite H-bonded chain extending along *b* axis. The other two C–H⋯O interactions (C1–H1C⋯O3 and C2–H2C⋯O1) serve to orient the 4-nba anions parallel to the crystallographic *ac* plane, leading to the stacking of the 4-nba anions. In the crystal structure the stacks of 4-nba anions are organized into pairs such that the –NO$_2$ and –COO groups in

each pair are nearly eclipsed, while they are antiparallel in alternating pairs. The net result is a supramolecular architecture of a one-dimensional chain of cationic complexes situated between stacks of planar 4-nba anions (figure 4). The short ring interactions and distances between the ring centroids (Cg–Cg) in **2** were analysed by using the program PLATON.[28] The Cg–Cg distance between the two aromatic rings is 3·850 Å. The perpendicular distance from the center of the first ring to the second (interplanar distance) at 3·405 Å accompanied by a dihedral angle of 5·62° indicates that the structure of **2** is further stabilized by π–π stacking interactions. The cation and anion are organized into alternating layers and the H-bonding interactions serve to interlink the layers (figure 4).

In addition to compounds **1** and **2**, the structures of five other 4-nitrobenzoate compounds of Ni(II) (table 4) are reported.[19–22,26,29] All these hexacoordinated Ni(II) compounds crystallize in centrosymmetric space groups and the central Ni(II) is situated on an inversion center. In two of the compounds including **1** the metal exhibits a {NiO$_6$} coordination sphere while in [Ni(Im)$_6$](4-nba)$_2$·2H$_2$O (Im = imidazole) the central metal is bound to six N-donor ligands.[26] In the remaining four compounds both O and N donors are present in the form of either {NiN$_4$O$_2$} as in **2** or {NiN$_2$O$_4$}. In addition to coordinating to Ni(II) in a monodentate mode (η^1) via the carboxylate oxygen in four of the seven compounds, the 4-nba moieties act as charge balancing species in all seven Ni(II) compounds. In all the four compounds containing coordinated 4-nba, the monodentate ligands are disposed *trans* to each other in the octahedron, in view of the special position of Ni(II). The Ni–O and Ni–N bond distances in all the seven compounds are in the normal range. The observed secondary interactions in terms of H-bonding in these compounds differ considerably. Compound **1** and [Ni(H$_2$O)$_6$](4-nba)$_2$·2H$_2$O exhibit only O–H⋯O interactions. The title compound **2**, [Ni(Im)$_6$](4-nba)$_2$·2H$_2$O and [Ni(H$_2$O)$_2$(Im)$_2$(η^1-4-nba)$_2$] are involved in three varieties of H-bonding interactions. In contrast, the neutral compound containing the macrocyclic cyclam ligand[29] [Ni(cyclam) (η^1-4-nba)$_2$] exhibits two types of interactions namely N–H⋯O and C–H⋯O. It is interesting to note that the anhydrous compound [Ni(1,3-pn)$_2$(η^1-4-nba)$_2$] is involved in only N–H⋯O interactions with the carboxylate oxygen functioning as H-acceptor. All the compounds are stabilized by π–π stacking interactions as evidenced by the interplanar
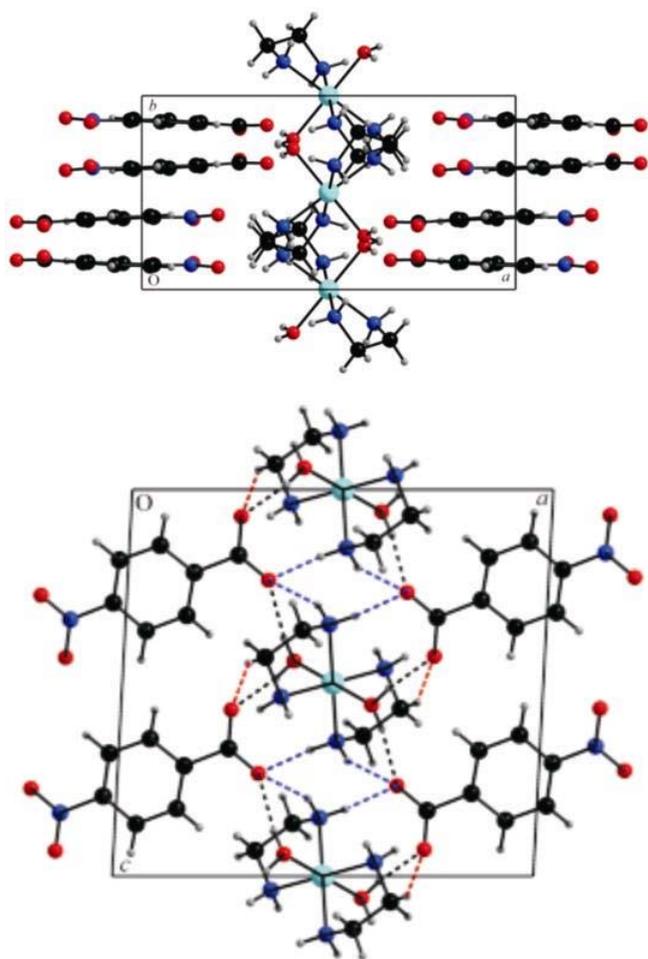
Figure 4. A view along *c* axis showing stacks of 4-nba rings parallel to the *bc* crystallographic plane on either side of a chain of [Ni(H$_2$O)$_2$(en)$_2$]$^{2+}$ cations. For clarity H-bonds are not shown (top). A view along *b* axis of the crystallographic packing of **2** showing the formation of alternating layers of cations and anions. The layers are linked by H-bonds shown as broken lines (bottom).

Table 4. Comparative structural features of known nickel 4-nitrobenzoates.

Compound	Crystal system	Space group	Coordination sphere/colour	Binding mode of 4-nba	Bond lengths (Å)			H-bonding	Cg(1)_Perp	Ref.
					Ni–O	Ni–N				
$[Ni(H_2O)_4(\eta^1\text{-}4\text{-nba})_2]\cdot2H_2O$ **1**	Triclinic	$P\bar{1}$	{NiO$_6$}/green	Monodentate	2·0578(15) 2·0628(13) 2·0768(11)	–		O–H···O	3·384	19
$[Ni(H_2O)_6](4\text{-nba})_2\cdot2H_2O$	Monoclinic	$C2/c$	{NiO$_6$}/light blue	Uncoordinated	2·098(3) 2·117(3) 2·136(2)	–		O–H···O	3·533	20
$[Ni(Im)_6](4\text{-nba})_2\cdot2H_2O$	Monoclinic	$P2_1/c$	{NiN$_6$}/blue	Uncoordinated	–	2·1098(12) 2·1393(12) 2·1508(12)		O–H···O N–H···O C–H···O	3·396	26
$[Ni(H_2O)_2(en)_2](4\text{-nba})_2$ **2**	Monoclinic	$P2_1/c$	{NiN$_4$O$_2$}/blue violet	Uncoordinated	2·1069(12)	2·1003(13) 2·1015(14)		O–H···O N–H···O C–H···O	3·405	This work
$[Ni(1,3\text{-pn})_2(\eta^1\text{-}4\text{-nba})_2]$	Triclinic	$P\bar{1}$	{NiN$_4$O$_2$}/brown	Monodentate	2·129(1)	2·105(1) 2·121(1)		N–H···O	3·542	21
$[Ni(cyclam)(\eta^1\text{-}4\text{-nba})_2]$	Monoclinic	$P2_1/n$	{NiN$_4$O$_2$}/colourless	Monodentate	2·132(2)	2·060(2) 2·080(2)		N–H···O C–H···O	3·501	29
$[Ni(H_2O)_2(Im)_2(\eta^1\text{-}4\text{-nba})_2]$	Triclinic	$P\bar{1}$	{NiN$_2$O$_4$}/green	Monodentate	2·0961(11) 2·1371(10)	2·0602(13)		O–H···O N–H···O C–H···O	3·369	22

In all the compounds Ni(II) is situated on an inversion centre. Cg(1)_Perp is the perpendicular distance of Cg(1) on the second ring. (η^1 – 4-nba) = monodentate 4-nitrobenzoate, Im = imidazole; 1,3-pn = propane-1,3-diamine; cyclam = 1,4,8,11-tetraazacyclotetradecane

distances ranging from 3·369 to 3·542 Å between the planar aromatic rings. The structures of a series of 1,3-pn compounds of Ni(II) has been reported by Klinga[30] and all these compounds have the same general formula with a monodentate carboxylate [Ni(1,3-pn)$_2$(ArCOO)$_2$] (ArCOO is 3-methyl-benzoate, 4-methylbenzoate or 3-nitrobenzoate) indicating that anhydrous compounds are the preferred products with 1,3-pn unlike the hydrated compound **2** obtained using en.

4.   Conclusions

In summary, we have described the synthesis and structural characterization of a new Ni(II) compound di(aqua) *bis*(ethylenediamine)nickel(II)*bis*(4-nitro-benzoate), which exhibits three varieties of H-bonding interactions. A comparative study of seven different nickel(II) compounds containing 4-nitrobenzoate is described.

Supplementary material

Crystallographic data (excluding structure factors) for the structure of compound **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 680912. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

Acknowledgements

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