

On the distorted $\{\text{NiN}_6\}$ octahedron in hexakis(imidazole)nickel(II) bis(4-nitrobenzoate) dihydrate

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The reaction of $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ with the sodium salt of 4-nitrobenzoic acid (4-nbaH) in the presence of imidazole results in the formation of the title compound hexakis(imidazole)nickel(II) bis(4-nitrobenzoate) dihydrate (**1**). Compound (**1**) is dehydrated to hexakis(imidazole)nickel(II) bis(4-nitrobenzoate) (**2**) by heating at 100°C. Both compounds are characterized by elemental analysis, infrared spectra, X-ray powder pattern and thermal studies. The title compound $[\text{Ni}(\text{Im})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ (**1**) crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with the Ni(II) situated on an inversion center. The structure of (**1**) consists of a distorted octahedral hexakis(imidazole)nickel(II) cation, a free uncoordinated 4-nba anion and a lattice water with half of the molecule accounting for the asymmetric unit. In the complex cation the central metal is bonded to six neutral terminal Im ligands. The distortion of the $\{\text{NiN}_6\}$ octahedron in (**1**) is discussed in terms of the difference between the longest and shortest Ni-N bonds. A comparative study of several $[\text{Ni}(\text{Im})_6]^{2+}$ compounds in different structural environments is described. In the crystal structure, the cation, anion and lattice water are linked by three types of H-bonding interactions comprising two O-H...O, three N-H...O and three C-H...O interactions. Each hexacoordinated Ni(II) complex cation is linked to eight symmetry related 4-nba anions and four different lattice water molecules via N-H...O and C-H...O interactions, while each 4-nba anion is H-bonded to four complex cations and two symmetry related lattice water molecules. Pairs of $[\text{Ni}(\text{Im})_6]^{2+}$ cations and 4-nba anions are linked to lattice water molecules via O-H...O and C-H...O interactions. As a result of the hydrogen bonding interactions, the cations and anions are organized into alternating layers.

Keywords: Coordination chemistry, Hydrogen bonding interactions; Crystal structure, Imidazoles, Nitrobenzoates, Nickel

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Compounds containing imidazole and carboxylate are of considerable interest in view of their biological and medicinal applications¹⁻³. Imidazole (Im) can function as a neutral monodentate, bridging bidentate or in certain cases as an anionic imidazolate ligand⁴. The octahedral $[\text{M}(\text{Im})_6]^{2+}$ unit (M=bivalent metal) has been structurally characterized for several metals⁵⁻⁸. The availability of Im in very pure form, its solubility in a variety of solvents, its ability to function as a ligand for metals, the importance of metal-imidazole compounds in biological applications etc. are some reasons for the study of metal-imidazole compounds. An extensive chemistry of metal-carboxylates has been developed demonstrating the versatile ligational behavior of the carboxylate anion towards metal ions⁹⁻¹¹. The study of metal-carboxylates and mixed ligand metal carboxylates continues to attract the attention of several research groups. A few years ago we initiated a study of metal carboxylates¹²⁻¹³ and as

part of this research we are currently investigating the synthesis, reactivity characteristics, and structural aspects of nitrobenzoate compounds of transition and s-block metals¹⁴⁻²².

We report herein the synthesis and characterization of a new Ni(II) compound, namely, hexakis(imidazole)nickel(II) bis(4-nitrobenzoate) dihydrate (**1**), with a distorted $\{\text{NiN}_6\}$ octahedron.

Materials and Methods

All the chemicals were of reagent grade and were used as received. The starting materials and reaction products are air stable and hence were prepared under normal laboratory conditions. MIR spectra of both compounds were recorded in a KBr matrix on a Shimadzu (IR Prestige-21) FT-IR spectrometer while far IR spectrum of (**1**) was measured on a Bruker IFS-66 infrared spectrometer in a pressed polyethylene disc. TG-DTA measurements were

performed in Al_2O_3 crucibles on a STA-409CD simultaneous thermal analyzer from Netzsch in flowing air. A heating rate of 4 K min^{-1} was employed for the measurements. The insoluble 4-nbaH obtained on acid treatment of the complexes was weighed as described earlier¹³ and metal analysis was carried out 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 was performed at the National Single Crystal X-ray facility at School of Chemistry, University of Hyderabad.

Preparation of hexakis(imidazole)nickel(II) bis(4-nitrobenzoate) dehydrate (1)

Sodium salt of 4-nitrobenzoic acid (4-nbaH) was generated *in situ* by dissolving 4-nbaH (1.67 g, 10 mmol) in an aqueous solution of sodium bicarbonate (0.84 g, 10 mmol) in water (40 ml). This solution was then added to $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (1.190 g, 5 mmol) in water (60 ml) to obtain a clear green solution. To this green reaction mixture, imidazole (2.04 g, 30 mmol) dissolved in water (30 ml) was added, resulting in the immediate formation of a blue solution. The reaction mixture was filtered and left aside for crystallization. After 3-4 days the blue crystalline blocks that separated, were filtered and air dried. (Yield 80 %). Anal.: Calc. for $\text{C}_{32}\text{H}_{36}\text{N}_{14}\text{NiO}_{10}$ (1): Ni, 7.03; NiO, 8.94, 4-nbaH, 40.06; C, 46.01; H, 4.34; N, 23.47. Found: Ni, 7.11; NiO, 8.88; 4-nbaH 40.4; C 45.69; H 4.30; N, 23.59 %. IR data (cm^{-1}): 3532 $\nu_s(\text{OH})$, 3154 $\nu_s(\text{NH})$, 2947, 2841, 2708, 2610, 2384, 2272, 2207, 2108, 1954, 1815, 1614 $\nu_s(\text{OH})$, 1574 $\nu_{\text{as}}(\text{COO})$, 1539, 1519 $\nu_{\text{as}}(\text{NO}_2)$, 1487, 1440, 1385 $\nu_s(\text{COO})$, 1344 $\nu_s(\text{NO}_2)$, 1323, 1281, 1256, 1256, 1167, 1144, 1069, 1011, 976, 939, 883, 831, 797, 779, 756, 745, 725, 667, 621, 513, 410, 315, 259 $\nu(\text{Ni-N})$, 214, 178.

In another method, a solution of Na_2CO_3 (0.265 g, 2.5 mmol) in water (~5 ml) was added into $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (0.595 g, 2.5 mmol), resulting in the immediate precipitation of NiCO_3 . To this solution containing NiCO_3 generated *in situ*, 4-nbaH (0.835 g, 5 mmol) in 50 ml water was added. The reaction mixture was heated on a water bath to obtain a green solution with a small quantity of insoluble matter, which was filtered. An aqueous solution of imidazole (1.02 g, 15 mmol) was added to the clear green filtrate resulting in the immediate formation of a blue coloured solution. At this stage, the blue solution was quickly filtered and left undisturbed for

crystallization. Blue crystals obtained after 3-4 days were filtered, washed with ice-cold water and air dried. The crystals obtained by this method were employed for single crystal study (Yield 66.5%).

Dehydration of hexakis(imidazole)nickel(II) bis(4-nitrobenzoate) dihydrate

A powdered sample of $[\text{Ni}(\text{Im})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ (1) (0.315 g) was heated on a water bath for 30 minutes. The hot mass was cooled in a desiccator and weighed to obtain 0.3025 g of anhydrous hexakis(imidazole)nickel(II) bis(4-nitrobenzoate) (2). The observed mass loss of 3.97 % is in close agreement with the expected value (4.3 %) for the loss of two moles of water. Anal.: Calc. for $\text{C}_{32}\text{H}_{32}\text{N}_{14}\text{NiO}_8$ (2): Ni, 7.34; NiO, 9.34; 4-nbaH, 41.82; C, 48.08; H, 4.03; N, 24.53. Found: Ni, 7.28; NiO, 9.15; 4-nbaH 40.4; C 48.22; H 4.23; N, 24.71 %. IR data (cm^{-1}): 3132 $\nu_s(\text{NH})$, 3107, 3046, 3028, 2941, 2837, 2722, 2631, 2480, 2390, 2286, 2208, 1922, 1582 $\nu_{\text{as}}(\text{COO})$, 1547, 1518 $\nu_{\text{as}}(\text{NO}_2)$, 1454, 1379 $\nu_s(\text{COO})$, 1344 $\nu_s(\text{NO}_2)$, 1305, 1258, 1148, 1099, 1072, 1015, 839, 876, 856, 826, 795, 752, 721, 667, 621, 552, 552, 523.

X-ray crystallographic studies

Intensity data for (1) were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo- K_α radiation. The data integration and reduction were processed with SAINT software²³. An empirical absorption correction was applied to the collected reflections with SADABS²⁴. The structure was solved with direct method using SHELXS-97²⁵ and refinement was done against F^2 using SHELXL-97²⁵. The carbon atoms C7, C8 and C9 in one of the imidazole rings were disordered over two positions and were refined using a split model. 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 lattice water 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 (1) are summarized in Table 1.

Results and Discussion

The reaction of $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ with the sodium salt of 4-nbaH in a 1:2 mole ratio followed by the addition of six moles of Im results in the formation of the blue title compound (1). In the absence of imidazole,

Table 1 — Crystallographic data and selected refinement results for $[\text{Ni}(\text{Im})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ (**1**)

Empirical formula	$\text{C}_{32}\text{H}_{36}\text{N}_{14}\text{NiO}_{10}$
Formula weight	835.46 g mol ⁻¹
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 8.0081(6)$ Å $\alpha = 95.6820(10)^\circ$ $b = 9.2029(6)$ Å $\beta = 101.3200(10)^\circ$ $c = 13.5542(9)$ Å $\gamma = 103.8570(10)^\circ$
Volume	939.72(11) Å ³
Z	1
Density (cal.)	1.476 mg/m ³
Absorption coefficient	0.592 mm ⁻¹
F(000)	434
Crystal size	0.42 × 0.26 × 0.18 mm ³
Theta range for data collection	1.55 to 26.03°
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16
Reflections collected	9803
Independent reflections	3684 [R(int) = 0.0212]
Completeness to theta = 26.03°	99.5 %
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	3684/4/287
Goodness-of-fit on F ²	1.051
Final R indices [$I > 2$ sigma (I)]	R1 = 0.0330, wR2 = 0.0848
R indices (all data)	R1 = 0.0346, wR2 = 0.0858
Extinction coefficient	0.018(2)
Largest diff. peak and hole	0.246 and -0.258 (e.Å ⁻³)

a green compound $[\text{Ni}(\text{H}_2\text{O})_4(4\text{-nba})_2] \cdot 2\text{H}_2\text{O}$ crystallizes from the solution²⁶ while the use of reduced amounts of Im (Ni : Im = 1 : 2) leads to the formation of the bis(imidazole) compound $[\text{Ni}(\text{H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]$ ²⁷. Both the neutral compounds, $[\text{Ni}(\text{H}_2\text{O})_4(4\text{-nba})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]$, contain monocoordinated 4-nba ligands. Compound (**1**) can also be prepared by solubilising NiCO_3 generated *in situ* in hot aqueous 4-nbaH followed by reaction with excess Im. The observed analytical characteristics of compound (**1**) from both methods are in good agreement with the proposed formula containing Ni : Im : 4-nba : H₂O in

a 1 : 6 : 2 : 2 ratio. The infrared spectra of the blue compound obtained from both methods were identical.

The formation of solid compound (**1**) from the reaction medium can be visualised as follows in terms of soluble molecular species²⁸. In aqueous solution all six water ligands of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ are replaced by the N-donor ligand resulting in $[\text{Ni}(\text{Im})_6]^{2+}$. Further aggregation is dictated by weak H-bonding interactions. The stability is provided by H-bonding between -COO groups of two adjacent molecules mediated by two lattice water molecules (*vide supra*) resulting in the formation of a dihydrate. It is interesting to note that the above explanation for the formation of compound (**1**), which contains $[\text{Ni}(\text{Im})_6]^{2+}$ unit and uncoordinated 4-nba ligands, is in accordance with the known chemistry of Ni(II) in terms of its affinity for N-donor ligands. It is to be noted that the reaction of $\text{Ni}(\text{OH})_2$ with 4-nbaH in the presence of ammonia (alkaline medium) has been reported to result in the formation of $[\text{Ni}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ containing free 4-nba ligands²⁹. Heating of (**1**) at 100°C on a water bath resulted in the formation of the anhydrous compound (**2**). Treatment of (**1**) or (**2**) with dilute HCl resulted in the quantitative formation of 4-nbaH. The insoluble carboxylic acid was weighed and analysed as described earlier¹³. The filtrate obtained from this procedure was analysed gravimetrically for Ni(II) content. Pyrolysis of both compounds over a Bunsen flame resulted in the formation of NiO. The compounds were further characterized by elemental analysis, infrared spectra and X-ray powder diffraction. The composition of (**1**) and (**2**) was arrived at based on these data. The X-ray powder pattern of (**1**) and (**2**) (See Supplementary Data) exhibit several sharp signals in their powder diffractograms indicating their crystalline nature.

The IR spectra of both compounds exhibit several sharp bands in the mid-infrared region, many of which are due to the vibrations of the organic moieties, namely, 4-nba and Im. The assignments of the vibrations, i.e., $\nu_s(\text{OH})$ of the lattice water, $\nu_s(\text{NH})$ of the imidazole, $\nu_s(\text{Ni-N})$ of $[\text{Ni}(\text{Im})_6]^{2+}$ unit, and the vibrations of the nitro and -COO functionalities of 4-nba have been given in the experimental section. The peak at 259 cm⁻¹ is assigned for the Ni-N vibration⁶. The assignments for the signals due to the vibrations of the carboxylate and nitro groups of the 4-nba anion are made based on a recent report³⁰. The

strong signals at 3532 and 3154 cm^{-1} in (**1**) may be assigned to O-H and N-H stretching vibrations respectively. The stretching and bending vibrations of -OH at 3532 and 1614 cm^{-1} respectively are not observed in the IR spectrum of the anhydrous compound (**2**) (See Supplementary Data). But for this difference, the IR spectrum of the anhydrous compound is very similar to that of (**1**).

Thermal studies

The TG-DTA thermogram of (**1**) (Fig. 1) exhibits two endothermic events at 95 and 217°C followed by two closely related exothermic processes at 375 and 396°C respectively. The first endothermic process accompanied by a mass loss of 4.43 % is in very good agreement for the expected (4.3%) loss of two lattice water molecules. The formation of the anhydrous compound $[\text{Ni}(\text{Im})_6](4\text{-nba})_2$ can also be evidenced from the IR spectrum of the anhydrous compound obtained by heating (**1**) at 100°C. Further, the X-ray powder pattern of the anhydrous compound is different from (**1**), indicating the formation of a new phase. The second endothermic signal can be assigned to the loss of the neutral imidazole ligand. The TG curve shows a steep drop after about 210°C indicating that the removal of imidazole results in further decomposition as evidenced by the two exothermic events at 375 and 396°C. The profile of the DTA curve indicates that this process is a complex one involving the decomposition of 4-nba leading to the formation of oxide phase. The assignment of the exothermic events for the decomposition of 4-nba gains credence based on reported thermal studies of other bivalent metal 4-nitrobenzoates^{21,22}. The observed residue of 8.36 % is in good agreement with

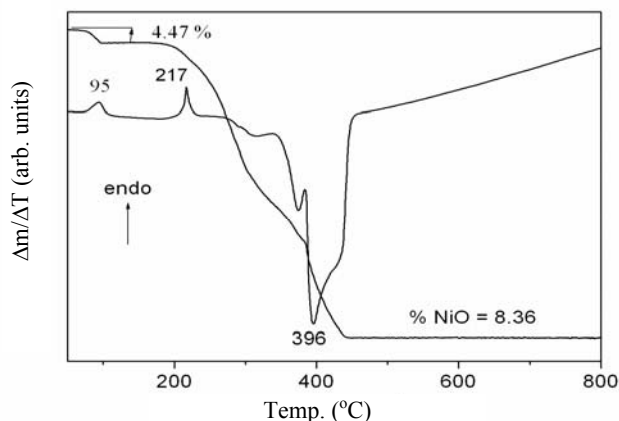


Fig. 1 — TG-DTA thermogram of $[\text{Ni}(\text{Im})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ (**1**). [Heating rate 4K min^{-1} ; air atmosphere].

the formation of NiO. The formation of NiO as the final residue was further confirmed based on isothermal weight loss studies by heating compound (**1**) at 800°C in a temperature controlled furnace.

Description of crystal structure of $[\text{Ni}(\text{Im})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ (**1**)

The title compound $[\text{Ni}(\text{Im})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ (**1**) crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with the Ni(II) situated on an inversion center. In view of the special position for Ni(II), one half of the formula unit constitutes the asymmetric unit. The structure of (**1**) consists of a distorted octahedral hexakis(imidazole)nickel(II) cation, a free uncoordinated 4-nba anion and a lattice water (Fig. 2). It is to be noted that 4-nba functions as an anion for charge balance and is not bonded to Ni(II), unlike in the reported bis(imidazole) compound $[\text{Ni}(\text{H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]$ where the carboxylate anion functions as a monodentate ligand²⁷. The geometric parameters of the anion in (**1**) are in good agreement with the reported data²² for compounds containing free uncoordinated 4-nba. In the octahedral $[\text{Ni}(\text{Im})_6]^{2+}$ complex cation the central metal is linked to six symmetry related Im ligands with the N atoms of Im at the corners of an octahedron. The three *trans* N-Ni-N bond angles exhibit the ideal value while the *cis* N-Ni-N bond angles range from 88.81(5) to 91.19(5)° indicating a slight distortion of the octahedron (Table 2). The Ni-N bond distances range from 2.1098(12) to 2.1508(13) Å and the difference Δ between the longest and shortest Ni-N bonds is 0.041 Å.

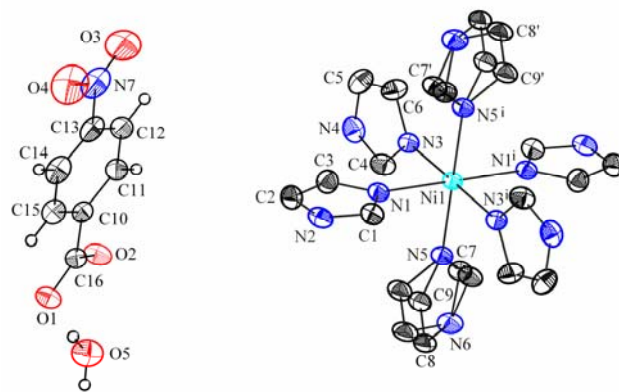


Fig. 2 — The asymmetric unit of $[\text{Ni}(\text{Im})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ (**1**) showing the atom-labeling scheme. The carbon atoms C7, C8 and C9 are disordered over two positions. Displacement ellipsoids are drawn at the 30% probability level except for the H atoms, which are shown as circles of arbitrary radius. For clarity H atoms of the coordinated imidazole ligand are not shown. [Symmetry code: (i) $-x, -y, -z+1$].

Comparative study of [Ni(Im)₆]²⁺ compounds in different environments

The octahedral [Ni(Im)₆]²⁺ dication has been structurally characterized with many other counter anions^{6,31-40} indicating its flexibility to exist in different environments. The availability of geometric parameters of the [Ni(Im)₆]²⁺ unit in many environments (Table 3) permits a comparative study. Of all the known [Ni(Im)₆]²⁺ compounds studied, the compound [Ni(Im)₆](NO₃)₂·4H₂O³¹, which

crystallizes in the hexagonal space group *P*6₃ showing the longest and the shortest Ni-N bond distances of 2.059 and 2.204 Å respectively, is an exception. Here the {NiN₆} unit is a trigonally distorted polyhedron and it is noted that for this compound (CCDC Refcode AJOSOH) the H-atom coordinates of the Im ligand are not available. In the other compounds listed in Table 3 excepting [Ni(Im)₆](ODA)₂·EtOH (for abbreviations see Table 3), the Ni(II) is located on an inversion center³⁸. Although the shortest and the longest reported values for Ni-N bonds in these compounds are 2.108 and 2.1682 Å respectively, the average Ni-N distance for all compounds is scattered in a very narrow range between 2.1245 to 2.1435 Å. The difference Δ between the longest and shortest Ni-N bonds ranges from zero to a maximum value of 5.91 pm in the recently reported [Ni(Im)₆](HCOO)₂ complex⁶. For compound **(I)** the observed Δ value is 4.1 pm. The value of Δ can be considered as a measure of distortion of the {NiN₆} octahedron in these compounds.

The geometric distortion of an octahedron can be characterized by two asymmetry parameters⁴¹, namely, the axial distortion, *D*, and the rhombic distortion, *E*. The axial distortion can result in either a compression or elongation (four short and two long bonds) of the octahedron along the *z* axis. Positive values of *D* indicate elongation while negative values denote the occurrence of four long and two short

Table 2 — Selected bond distances (Å) and angles (°) of [Ni(Im)₆](4-nba)₂·2H₂O (**I**)

Bond lengths (Å)			
Ni(1)-N(5)	2.1098(12)	Ni(1)-N(3) ⁱ	2.1393(13)
Ni(1)-N(5) ⁱ	2.1098(12)	Ni(1)-N(1)	2.1508(13)
Ni(1)-N(3)	2.1393(13)	Ni(1)-N(1) ⁱ	2.1508(13)
Bond angles (°)			
N(5) ⁱ -Ni(1)-N(5)	180.0	N(3) ⁱ -Ni(1)-N(1)	91.19(5)
N(5) ⁱ -Ni(1)-N(3) ⁱ	89.84(5)	N(3)-Ni(1)-N(1)	88.81(5)
N(5)-Ni(1)-N(3) ⁱ	90.16(5)	N(5) ⁱ -Ni(1)-N(1) ⁱ	90.36(5)
N(5) ⁱ -Ni(1)-N(3)	90.16(5)	N(5)-Ni(1)-N(1) ⁱ	89.64(5)
N(5)-Ni(1)-N(3)	89.84(5)	N(3) ⁱ -Ni(1)-N(1) ⁱ	88.81(5)
N(3) ⁱ -Ni(1)-N(3)	180.0	N(3)-Ni(1)-N(1) ⁱ	91.19(5)
N(5) ⁱ -Ni(1)-N(1)	89.64(5)	N(1)-Ni(1)-N(1) ⁱ	180.00(6)
N(5)-Ni(1)-N(1)	90.36(5)		

Symmetry transformations used to generate equivalent atoms:
(i) -*x*, -*y*, -*z*+1

Table 3 — Structural parameters of [Ni(Im)₆]²⁺ unit with different counter anions

Compound	Space group	Ni-N1 (Å)	Ni-N2 (Å)	Ni-N3 (Å)	Ni-N(av) (Å)	Δ (pm)	<i>D</i> (pm)	<i>E</i> (pm)	Ref.
[Ni(Im) ₆](NO ₃) ₂ ·4H ₂ O ^a	<i>P</i> 6 ₃	2.059 × 3	2.204 × 3		2.132	14.5	---	---	31
[Ni(Im) ₆](NO ₃) ₂	<i>R</i> -3	2.129	2.129	2.129	2.129	0.00	0.00	0.00	32
[Ni(Im) ₆]CO ₃ ·5H ₂ O	<i>P</i> 6 ₃ / <i>m</i>	2.126	2.126	2.126	2.126	0.00	0.00	0.00	33
[Ni(Im) ₆](ClOAc) ₂	<i>P</i> $\bar{1}$	2.130	2.132	2.133	2.132	0.3	-0.25	0.05	6
[Ni(Im) ₆](BF ₄) ₂	<i>P</i> 2 ₁ / <i>n</i>	2.125	2.127	2.131	2.128	0.6	+0.45	0.15	34
[Ni(Im) ₆](ClO ₄) ₂	<i>P</i> 2 ₁ / <i>n</i>	2.128	2.131	2.134	2.131	0.6	-0.50	0.10	35
[Ni(Im) ₆]Cl ₂ ·4H ₂ O	<i>P</i> $\bar{1}$	2.122	2.129	2.133	2.128	1.1	-0.90	0.20	36
[Ni(Im) ₆](Met-Benz) ₂	<i>P</i> $\bar{1}$	2.127	2.140	2.141	2.136	1.4	-1.35	0.05	37
[Ni(Im) ₆](ODA) ₂ ·EtOH ^b	<i>P</i> $\bar{1}$	2.113, 2.129	2.118, 2.121	2.134, 2.139	2.126	1.7	+1.62	0.07	38
[Ni(Im) ₆](Sal) ₂	<i>P</i> $\bar{1}$	2.1199	2.1241	2.1408	2.1283	2.09	+1.90	0.20	39
[Ni(Im) ₆](2-Cl-Pro) ₂	<i>P</i> $\bar{1}$	2.1146	2.1277	2.1414	2.1245	2.68	+2.03	0.66	6
[Ni(Im) ₆](DIP-DTP) ₂	<i>C</i> 2/ <i>c</i>	2.108	2.126	2.140	2.125	3.2	-2.40	0.70	40
[Ni(Im) ₆](4-nba) ₂ ·2H ₂ O	<i>P</i> $\bar{1}$	2.1098	2.1393	2.1508	2.1333	4.1	-3.52	0.57	This work
[Ni(Im) ₆](HCOO) ₂	<i>P</i> 2 ₁ / <i>c</i>	2.1091	2.1533	2.1682	2.1435	5.91	-5.17	0.75	6

Abbreviations used: *D* = $d_z - (d_x + d_y)/2$; *E* = $(d_x - d_y)/2$ where d_x , d_y , d_z are the Ni-N distances along *x*, *y*, and *z*; Δ = (Ni-N3)-(Ni-N1);

^a trigonally distorted {NiN₆} polyhedron; ClOAc = chloroacetate; Met-Benz = 4-methoxybenzoate; ODA = oxydiacetate;

^b Ni(II) is located in a general position; Sal = 2-hydroxybenzoate; DIP-DTP = diisopropyldithiophosphate

bonds due to compression. The values of these parameters for the $\{\text{NiN}_6\}$ octahedron for several $[\text{Ni}(\text{Im})_6]^{2+}$ compounds calculated from their structural data are listed in Table 3. It is to be noted that the rhombic component of the geometric distortion is relatively less and is less than 1 pm for all compounds. However the axial distortion varies from a high value of +2.03 pm in $[\text{Ni}(\text{Im})_6](2\text{-Cl-Pro})_2$ to -5.17 pm in $[\text{Ni}(\text{Im})_6](\text{HCOO})_2$ through -3.52 pm in compound (**1**). The D value is zero in two compounds containing nitrate or carbonate as counter anions indicating a perfect octahedron. It is to be noted that Δ and D exhibit a direct relationship, i.e., with increase in Δ , the value of D also increases. However the magnitude of D is always less than the corresponding Δ value. While increasing Δ values point to more distortion, the positive or negative sign of the D parameter describes the distortion in terms of elongation or compression. As expected, compound (**1**) with four long and two short bonds exhibits a D value of -3.52 pm indicating compression of the $\{\text{NiN}_6\}$ octahedron. The central metal atom is surrounded not only by six N-donor atoms of the imidazole but also by six N-H groups each of which is hydrogen bonded to the carboxylate oxygen, resulting in very long $\text{Ni}\cdots\text{O}$ separations ranging from 6.818(6) to 7.033(3) Å. In addition, there are also other H-bonding interactions (see below). The different type, strength and number of these secondary interactions in the $[\text{Ni}(\text{Im})_6]^{2+}$ compounds listed in Table 3 can probably explain the structural anisotropy as well as the observation of different Δ or D values in these compounds.

Secondary interactions in $[\text{Ni}(\text{Im})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ (**1**)

In the crystal structure of (**1**) the cation, anion and crystal water are linked by three types of H-bonding

Table 4 — Hydrogen-bonding geometry for $[\text{Ni}(\text{Im})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$ (**1**)

D-H \cdots A	$d(\text{D-H})$ (Å)	$d(\text{H}\cdots\text{A})$ (Å)	$d(\text{D}\cdots\text{A})$ (Å)	$\angle \text{DHA}$ ($^\circ$)
N2-H1N2 \cdots O2 ⁱⁱ	0.860	1.948	2.750	155
N4-H1N4 \cdots O1 ⁱⁱⁱ	0.860	2.051	2.887	164
N6-H1N6 \cdots O2 ^{iv}	0.860	2.006	2.816	157
O5-H1O5 \cdots O1	0.820	2.167	2.977	169
O5-H2O5 \cdots O1 ^v	0.820	2.123	2.932	169
C7-H7 \cdots O5 ^{vi}	0.930	2.472	3.230	139
C5-H5 \cdots O5 ^{vii}	0.930	2.631	3.309	130
C4-H4 \cdots O3 ^{viii}	0.929	2.446	3.206	139

Symmetry code: ii) $x, y, z+1$; iii) $-x+1, -y+1, -z$; iv) $-x, -y+1, -z$; v) $-x+1, -y+2, -z$; vi) $x+1, y+1, z$; vii) $x, y+1, z$; viii) $x+1, y, z$

interactions resulting in eight short $\text{O}\cdots\text{H}$ contacts comprising two $\text{O-H}\cdots\text{O}$, three $\text{N-H}\cdots\text{O}$ and three $\text{C-H}\cdots\text{O}$ interactions (Table 4). The $\text{O}\cdots\text{H}$ distances ranging from 1.948 to 2.631 Å are shorter than the sum of their van der Waals radii⁴². An analysis of the crystal structure reveals that each hexacoordinated Ni(II) complex cation is H-bonded to eight different 4-nba anions via $\text{N-H}\cdots\text{O}$ bonds with the amine N atoms functioning as H donors and the carboxylate O atoms O1 and O2 functioning as H-acceptors. Further, the cation is linked to four symmetry related water molecules with the aid of weak $\text{C-H}\cdots\text{O}$ interactions. The carboxylate oxygen atoms of 4-nba function as trifurcated (O1) or bifurcated H-acceptors, with the nitro oxygen O3 involved in $\text{C-H}\cdots\text{O}$ bonding, resulting in the linking of each 4-nba anion, to four symmetry related cationic complexes via three $\text{N-H}\cdots\text{O}$ and one $\text{C-H}\cdots\text{O}$ interactions and to two

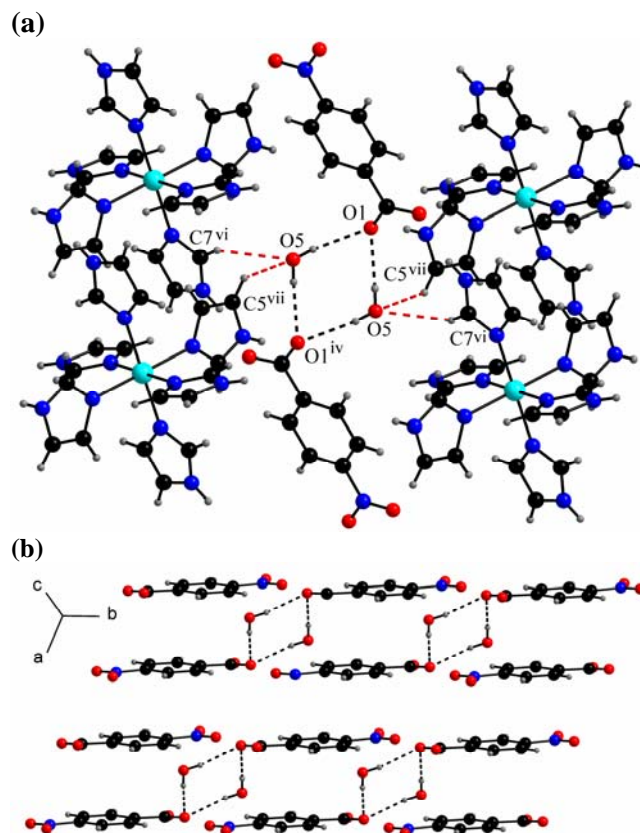


Fig. 3 — (a) A view of the surroundings of the lattice water molecule showing the linking of each water to two symmetry related $[\text{Ni}(\text{Im})_6]^{2+}$ cations via two $\text{C-H}\cdots\text{O}$ and two 4-nba anions with the aid of two $\text{O-H}\cdots\text{O}$ hydrogen bonds. (b) A view showing the H-bonding of crystal water with only 4-nba anions resulting in antiparallel organization of the aromatic rings of 4-nba. For clarity the cations are not shown. [Symmetry code: (iv) $-x, -y+1, -z$; (vi) $x+1, y+1, z$; (vii) $x, y+1, z$].

different water molecules via O-H···O interactions. The lattice water molecule functions both as H-donor and H-acceptor and serves to link pairs of cations and anions with the aid of hydrogen bonds (Fig. 3). Each lattice water molecule is linked to two different cationic complexes via C7-H7···O5 and C5-H5···O5 interactions resulting in tetracoordination around the water oxygen O5. The intramolecular O5-H1O5···O1 and intermolecular O5-H2O5···O1 interactions at shorter distances (2.167 and 2.123 Å respectively), connect two different 4-nba anions with the lattice water. The O-H···O interactions are responsible for the organisation of 4-nba anions in antiparallel manner (Fig. 3) perpendicular to the crystallographic *ac* plane. Analysis of the short ring interactions and distances between the ring centroids (Cg-Cg) of the 4-nba anions in **(1)** reveals that the Cg-Cg distance between the two six-membered rings is 3.7490 Å and the perpendicular distance from the center of the first ring to the second (interplanar distance) is 3.396 Å indicating that the structure is further stabilized

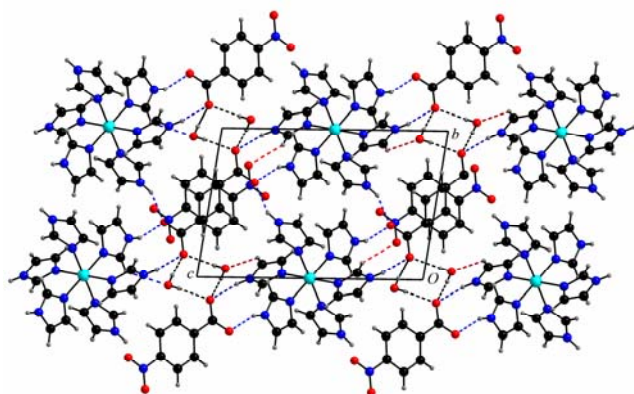


Fig. 4 — A view along *a* axis of the crystallographic packing of [Ni(Im)₆](4-nba)₂·2H₂O (**1**) showing the formation of alternating layers of cations and anions with the lattice water molecules serving to link the layers. The three varieties of H-bonds (O-H···O; N-H···O; C-H···O) are shown as broken lines.

by π - π stacking interactions. Finally, as a result of the three types of hydrogen bonding interactions in **(1)** the cations and anions are organised into alternating layers (Fig. 4) with the lattice water molecules providing the interlayer interactions.

In addition to the title compound **(1)**, the structures of several other 4-nitrobenzoate compounds of Ni(II) are known^{27,29,43-45}. The mode of binding of 4-nba, and the secondary interactions in terms of H-bonding differ considerably in these compounds (Table 5). All these hexacoordinated Ni(II) compounds crystallize in centrosymmetric space groups and the central Ni(II) is situated on an inversion center. In the title compound, the metal contains a {NiN₆} coordination sphere and in two compounds the metal exhibits a {NiO₆} coordination sphere. In the remaining compounds both O and N donors are present in the form of either {NiN₄O₂} or {NiN₂O₄}. In addition to coordinating to Ni(II) in a monodentate mode via the carboxylate oxygen, the 4-nba moieties act as charge balancing species in all these Ni(II) compounds. The differently hydrated 4-nba compounds, [Ni(H₂O)₄](4-nba-O)₂·2H₂O and [Ni(H₂O)₆](4-nba)₂·2H₂O exhibit O-H···O interactions while the mixed ligand compound [Ni(1,3-pn)₂](4-nba-O)₂ involves only N-H···O interactions. Two types of interactions, namely, N-H···O and C-H···O, are observed in the neutral compound containing the macrocyclic cyclam ligand [Ni(cyclam)(4-nba-O)₂]. The Im containing compounds **(1)** and [Ni(H₂O)₂](Im)₂(4-nba-O)₂ are involved in three types of H-bonding interactions.

Supplementary Data

The X-ray powder pattern and the infrared spectra of compounds **(1)** and **(2)** may be obtained from the authors. Crystallographic data (excluding structure factors) for the structure of compound **(1)** reported in this paper have been deposited with the

Table 5 — Comparative structural features of nickel(II) 4-nitrobenzoate compounds

Compound	Space group	Coord sphere / colour	Binding mode of 4-nba	Type of H-bonds	Ref.
[Ni(H ₂ O) ₄](4-nba-O) ₂ ·2H ₂ O	<i>P</i> $\bar{1}$	{NiO ₆ } / green	Monodentate	O-H···O	43
[Ni(H ₂ O) ₆](4-nba) ₂ ·2H ₂ O	<i>C</i> 2/ <i>c</i>	{NiO ₆ } / light blue	Uncoordinated	O-H···O	29
[Ni(1,3-pn) ₂](4-nba-O) ₂	<i>P</i> $\bar{1}$	{NiN ₄ O ₂ } / brown	Monodentate	N-H···O	44
[Ni(cyclam)(4-nba-O) ₂]	<i>P</i> 2 ₁ / <i>n</i>	{NiN ₄ O ₂ } / colourless	Monodentate	N-H···O C-H···O	45
[Ni(H ₂ O) ₂](Im) ₂ (4-nba-O) ₂	<i>P</i> $\bar{1}$	{NiN ₂ O ₄ } / green	Monodentate	O-H···O N-H···O C-H···O	27
[Ni(Im) ₆](4-nba) ₂ ·2H ₂ O	<i>P</i> $\bar{1}$	{NiN ₆ } / blue	Uncoordinated	O-H···O N-H···O C-H···O	This work

In all the compounds Ni(II) is situated on an inversion centre. 4-nba-O = monocoordinated 4-nitrobenzoate; 1,3-pn = propane-1,3-diamine Im=imidazole cyclam=1,4,8,11-tetraazacyclotetradecane.

Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 684343. 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).

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