



# Tetraaquabis(pyridine-3-carbonitrile- $\kappa N^1$ )nickel(II) benzene-1,4-dicarboxylate tetrahydrate

Monsumi Gogoi<sup>a\*</sup> and Birinchi Kumar Das<sup>b</sup><sup>a</sup>Department of Chemistry, Gauhati University, Guwahati-781014, Assam, India, and <sup>b</sup>Bhattacharjee University, Bajali, Pathsala-781325, Assam, India. \*Correspondence e-mail: monsumigogoi@gmail.com

Received 6 October 2020

Accepted 3 December 2020

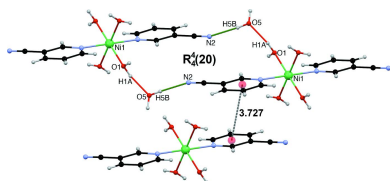
Edited by V. Jancik, Universidad Nacional Autónoma de México, México

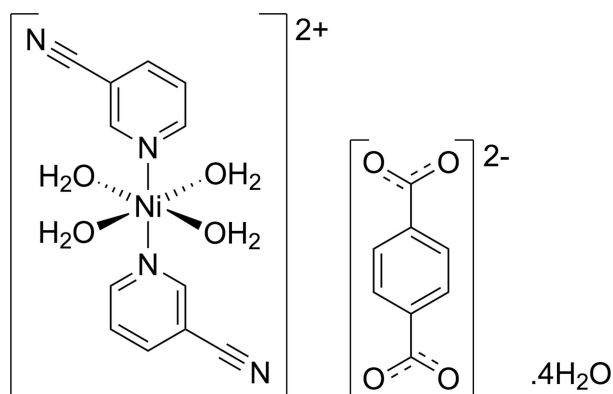
**Keywords:** Ni<sup>II</sup> complex; terephthalate; pyridine-3-carbonitrile;  $\pi$ - $\pi$  interaction; graph set; crystal structure.**CCDC reference:** 1538307**Supporting information:** this article has supporting information at journals.iucr.org/e

A nickel(II) terephthalate complex, *viz.*  $[\text{Ni}(\text{C}_6\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_4](\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2) \cdot 4\text{H}_2\text{O}$ , has been synthesized and studied by single-crystal X-ray diffraction. It crystallizes in the triclinic space group  $P\bar{1}$ . The crystal structure shows an approximately octahedral coordination environment of the complex with the  $[\text{Ni}(\text{H}_2\text{O})_4(3\text{-NCpy})_2]^{2+}$  (3-NCpy is pyridine-3-carbonitrile) cation associated with four free water molecules and hydrogen bonded to a terephthalate dianion [graph set  $R_2^2(8)$ ]. The supramolecular structure of the compound is stabilized by a three-dimensional array of O—H $\cdots$ O and O—H $\cdots$ N hydrogen bonds, along with  $\pi$ - $\pi$  stacked pyridine-3-carbonitrile rings and C—H $\cdots$ O interactions.

## 1. Chemical context

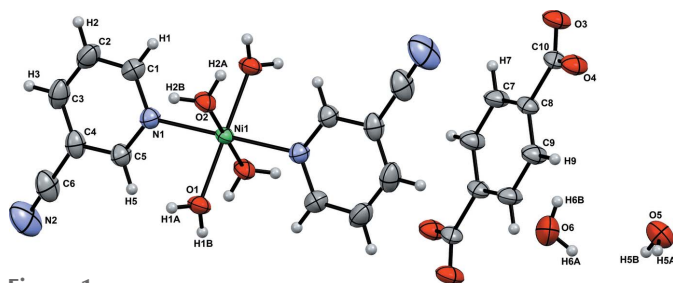
Multi-carboxylate ligands with suitable spacers, especially benzene-multicarboxylate ligands, are frequent choices for coordination chemistry as they feature a broad range of coordination modes and can result in the formation of systems with variable complexity ranging from molecular complexes to metal-organic frameworks of different dimensionality (Janiak & Vieth, 2010; Kim *et al.*, 2001). Benzene-1,4-dicarboxylate (terephthalate) ligands have received increased attention in the field of coordination chemistry, especially as building blocks for coordination polymers, mainly with porous networks with varied metal ions (Kim *et al.*, 2003). As a result of the presence of conjugation, the terephthalate anion can provide an electronic pathway for delocalization of electrons belonging to the *d*-orbitals of the metal ion, thus changing its magnetic properties. The most important factor that affects magnetic exchange pathways between two metal centres is the proper choice of bridging ligands since they influence the magnetic strength and behaviour of the molecule (Massoud *et al.*, 2006; Mukherjee *et al.*, 2003; Rogan *et al.*, 2000). Coordinated ligand systems containing electron-donor as well as acceptor sites also give rise to metallosupramolecular assemblies. Hence, pyridine-3-carbonitrile (3-NCpy) with the electron-withdrawing nitrile group as the acceptor along with the pyridyl nitrogen atom as the donor stands as a suitable ligand in this regard. Despite the availability of two potentially coordinating sites, not many compounds having pyridine-3-carbonitrile as a bidentate bridging ligand are known (Heine *et al.*, 2018). The nitrile group may also be expected to take part in hydrogen bonding and  $\pi$ - $\pi$  interactions. In this work, we describe our results on the synthesis and crystal structure of a pyridine-3-carbonitrile-based Ni<sup>II</sup>-terephthalate complex, *viz.*  $[\text{Ni}(\text{H}_2\text{O})_4(3\text{-NCpy})_2][\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2] \cdot 4\text{H}_2\text{O}$ .





## 2. Structural commentary

The title compound,  $[\text{Ni}(\text{H}_2\text{O})_4(3\text{-NCpy})_2][\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2]\cdot 4\text{H}_2\text{O}$  is a discrete coordination complex and it crystallizes in the triclinic system with space group  $P\bar{1}$ . An ORTEP view is shown in Fig. 1. The compound consists of a complex dication, which is in association with four free water molecules and an uncoordinated terephthalate dianion, where the asymmetric unit contains half of these quantities. The  $\text{Ni}^{2+}$  centre is situated on an inversion centre and coordinates to two axial pyridine-3-carbonitrile ligands and four equatorial water molecules forming the cationic complex  $[\text{Ni}(\text{H}_2\text{O})_4(3\text{-CNpy})_2]^{2+}$ . The bond angles in the cationic part suggest that the complex contains an  $\text{Ni}^{2+}$  ion in an approximately octahedral coordination environment [*cis* angles in the range of  $88.66(4)\text{--}91.33(4)^\circ$ ]. The free terephthalate anion is also located on an inversion centre and has an angle of  $14.54(7)^\circ$  between the planes of the aromatic ring and of the carboxylate group. Furthermore, it does not coordinate to the  $\text{Ni}^{2+}$  ion and remains fully deprotonated for charge balance. It also acts as a secondary acceptor to the cationic complex unit. The Ni–O bond lengths are 2.0381 (11) and 2.0519 (9) Å and are in agreement with similar complexes reported (Xiao *et al.*, 2003; Ma & Xu, 2010; Ju *et al.*, 2016). The Ni–N bond length of 2.1481 (11) Å is slightly longer than those in the similar complexes reported by Zukerman-Schpector *et al.* (2000) and Heine *et al.* (2018).



**Figure 1**  
ORTEP diagram of  $[\text{Ni}(\text{H}_2\text{O})_4(3\text{-NCpy})_2][\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2]\cdot 4\text{H}_2\text{O}$  showing the atom-labelling scheme (ellipsoids drawn at the 50% probability level; unlabelled atoms generated by the symmetry operations  $2 - x, 2 - y, -z$  for the cation and  $1 - x, 1 - y, 1 - z$  for the anion).

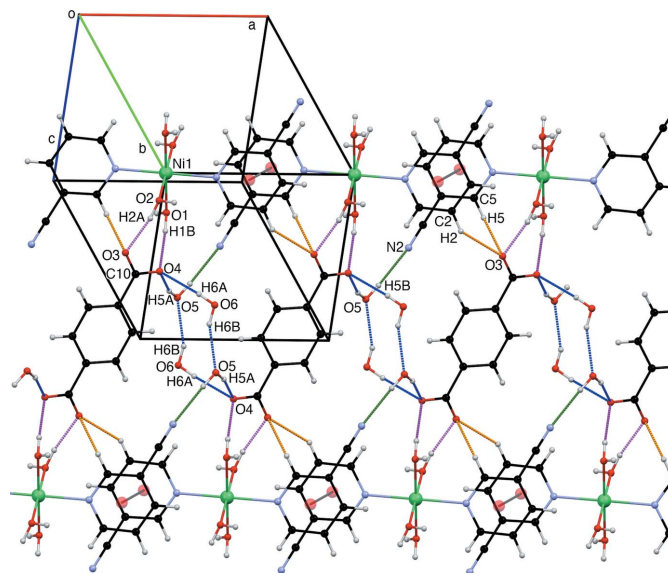
**Table 1**  
Hydrogen-bond geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{O2--H2A}\cdots\text{O3}^{\text{i}}$	0.84 (1)	1.80 (1)	2.6301 (14)	171 (2)
$\text{C5--H5}\cdots\text{O3}^{\text{i}}$	0.93	2.46	3.1832 (17)	135
$\text{O1--H1A}\cdots\text{O5}^{\text{ii}}$	0.83 (1)	1.94 (1)	2.7591 (17)	171 (2)
$\text{O2--H2B}\cdots\text{O6}^{\text{iii}}$	0.83 (1)	1.86 (1)	2.6710 (17)	168 (2)
$\text{O1--H1B}\cdots\text{O4}^{\text{iv}}$	0.84 (1)	1.87 (1)	2.7050 (14)	176 (2)
$\text{O6--H6A}\cdots\text{O4}^{\text{v}}$	0.82 (1)	2.01 (1)	2.8240 (17)	174 (2)
$\text{O6--H6B}\cdots\text{O5}^{\text{vi}}$	0.84 (1)	2.07 (1)	2.855 (2)	156 (2)
$\text{O5--H5A}\cdots\text{O4}^{\text{v}}$	0.83 (1)	1.95 (1)	2.7645 (17)	167 (2)
$\text{O5--H5B}\cdots\text{N2}^{\text{vii}}$	0.83 (1)	2.12 (1)	2.950 (2)	176 (2)

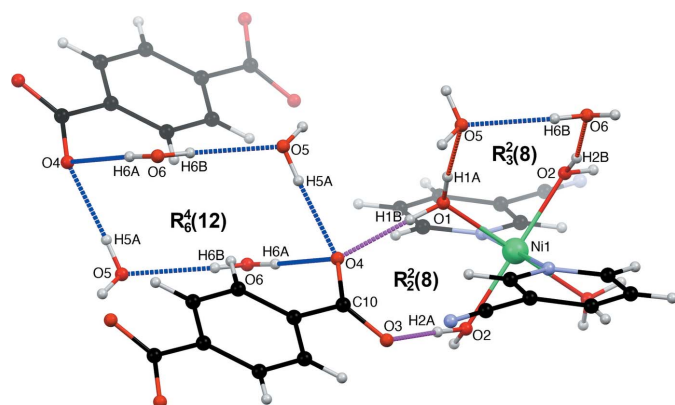
Symmetry codes: (i)  $x, y + 1, z$ ; (ii)  $x + 1, y + 1, z - 1$ ; (iii)  $-x + 1, -y + 2, -z$ ; (iv)  $-x + 2, -y + 1, -z$ ; (v)  $x - 1, y, z$ ; (vi)  $-x, -y + 1, -z + 1$ ; (vii)  $x, y - 1, z$ .

## 3. Supramolecular features

The supramolecular structure of the title compound is consolidated by several  $\text{O--H}\cdots\text{O}$  and  $\text{O--H}\cdots\text{N}$  hydrogen bonds that involve all the possible hydrogen-bond acceptors and donors, which result in the formation of a three-dimensional hydrogen-bonded array in the crystal (Table 1, Figs. 2–4). The two-dimensional hydrogen-bonded layers featured in Fig. 2 are connected together *via* hydrogen bonds described by the  $R_3^2(8)$  graph set depicted in Fig. 3. The cationic complex and the terephthalate dianion are hydrogen bonded *via* the  $\text{O1--H1B}\cdots\text{O4}$  and  $\text{O2--H2A}\cdots\text{O3}$  interactions within the  $R_2^2(8)$  graph set and form infinite chains (Fig. 3). Neighbouring chains are interconnected by  $\text{O1--H1A}\cdots\text{O5}$  and  $\text{O5--H5B}\cdots\text{N2}$  hydrogen bonds described by an  $R_4^4(20)$  graph set,  $\pi\text{--}\pi$  interactions arising from stacking of the 3-NCpy rings [centroid–centroid distance of  $3.727(8)$  Å, with a slippage of  $1.067$  Å, Fig. 4]. The cavity formed is filled by the four solvent water molecules (O5, O6) interconnecting two neighbouring terephthalate dianions by a cooperative  $\text{O--H}\cdots\text{O}$  ring



**Figure 2**  
Packing structure of the complex showing the hydrogen bonds and  $\text{C--H}\cdots\text{O}$  and  $\pi\text{--}\pi$  interactions.

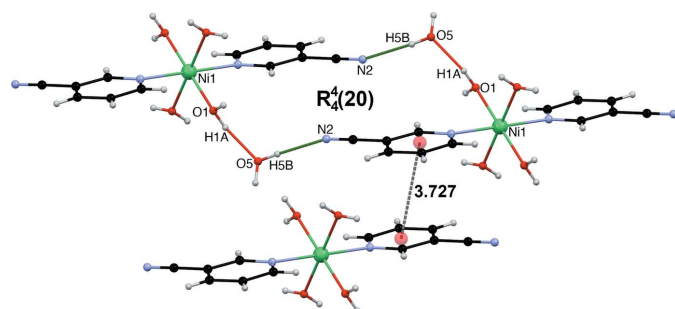


**Figure 3** Hydrogen-bonding pattern associated with the  $R_2^2(8)$ ,  $R_3^2(8)$  and  $R_6^4(12)$  graph sets.

network with an  $R_6^4(12)$  motif, forming infinite chains in a zigzag fashion along the  $a$ -axis direction (Fig. 3). Finally, the three-dimensional network is further accomplished among others by the  $D_2^2(7)$   $O2-H2B \cdots O6$  hydrogen bonds and  $C2-H2 \cdots O3$  and  $C5-H5 \cdots O3$  interactions (Table 1, Fig. 2). A comprehensive list of first and second level graph sets can be found in Table 2.

#### 4. Database survey

A survey of the Cambridge Structural Database (CSD version 2020.2; Groom *et al.*, 2016) for  $Ni^{II}$  complexes involving an uncoordinated terephthalate dianion led us to a few results, some of which are as follows. In the complex  $[Ni(2,2'-bipy)(H_2O)_4](C_8H_4O_4)$  ( $2,2'$ -bipy =  $2,2'$ -bipyridyl) (CSD refcode: WUWZET) reported by Xiao *et al.* (2003), the terephthalate anion acts as a synthon to generate a supramolecular network. The hydrogen bonds between the terephthalate anions and the  $[Ni(2,2'-bipy)(H_2O)_4]^{2+}$  cations produce a two-dimensional hydrogen-bonded architecture with double sheets. A similar compound, tetraaquabis(dimethylformamide)nickel(II) tetrachloroterephthalate, (QAMDUF; Ma & Xu, 2010) has a nearly ideal octahedral structure with the metal ion lying on an inversion center along with an uncomplexed and fully deprotonated terephthalate dianion. Another  $Ni^{II}$ -terephthalate complex (AJUPEC; Ju *et al.*, 2016) with 4,7-di(4-



**Figure 4** Hydrogen-bonded pattern associated with the  $R_4^4(20)$  graph set and  $\pi$ - $\pi$  interactions between two 3-NCpy rings.

**Table 2** Graph-set descriptions.

Graph set	Level	Period	No. of Molecules
$D_1^1(2) a$	1		2
$D_2^2(7) <a>a$	1		3
$D_1^1(2) b$	1		2
$C_2^2(13) >b<b$	1	2	3
$D_1^1(2) c$	1		2
$C_2^2(13) >c<c$	1	2	3
$D_1^1(2) d$	1		2
$D_2^2(7) <d>d$	1		3
$D_1^1(2) e$	1		2
$D_2^2(10) >e<e$	1		3
$D_1^1(2) f$	1		2
$D_2^2(13) >f<f$	1		3
$D_1^1(2) g$	1		2
$D_2^2(10) >g<g$	1		3
$D_3^3(2) h$	1		2
$C_2^2(10) >a>f$	2	2	3
$R_2^2(8) >b<c$	2	2	2
$R_4^4(20) >a>f>a>f$	2	2	4

$a = H1A \cdots O5$ ,  $b = H1B \cdots O4$ ,  $c = H2A \cdots O3$ ,  $d = H2B \cdots O6$ ,  $e = H5A \cdots O4$ ,  $f = H5B \cdots N2$ ,  $g = H6A \cdots O4$  and  $h = H6B \cdots O5$ .

pyridyl)-2,1,3-benzothiadiazole as auxiliary ligand crystallizes in the monoclinic  $P2_1/c$  space group. The terephthalate dianion remains uncoordinated and the  $Ni^{II}$  ion sits in the centre of an octahedron constituted by two pyridyl N atoms in the apical positions and four water oxygen atoms constructing the equatorial plane. The independent cationic units are held together by  $\pi$ - $\pi$  stacking interactions and  $O-H \cdots O$  hydrogen bonding, generating a compact packing structure. A pyrazine-based  $Ni^{II}$ -terephthalate complex (AGIWOC; Groeneman & Atwood, 2000) is a one-dimensional zigzag coordination polymer, where each nickel centre has two *cis*  $\mu$ -pyrazine ligands along with four coordinated water molecules, giving rise to a distorted octahedral coordination environment. A survey of  $Ni^{II}$  complexes involving pyridine-3-carbonitrile as ligand led us to some other related structures. Heine *et al.* (2018) investigated the ability of pyridine-3-carbonitrile to act as a mono- or bidentate ligand in complexes of the type  $[M^{II}Br_2(3-CNpy)_x]_n$  with  $M^{II} = Mn, Fe, Co, Ni$  and  $x = 1, 2$  and 4, (CSD refcodes XOSNUR, XOSPAZ, XOSPAZ02) and found that the pyridine-3-carbonitrile ligand acted as bridging ligand in complexes with a metal:ligand ratio of 1:1 and as a terminal ligand with ratios of 1:2 and 1:4. In an adduct of  $Ni^{II}$  acetylacetonate chelating with pyridine-3-carbonitrile (MASTUV; Zukerman-Schpector *et al.*, 2000), the  $Ni^{II}$  atom is situated on a centre of symmetry and is octahedrally bonded to two equatorial AcAc groups and two pyridine-3-carbonitrile groups, which are axially coordinated in a *trans* configuration.

#### 5. Synthesis and crystallization

All reagents were purchased from E. Merck and used without further purification. A mixture of nickel(II) sulfate heptahydrate,  $NiSO_4 \cdot 7H_2O$  (1.120 g, 4 mmol) and disodium terephthalate,  $Na_2C_8H_4O_4$  (0.840 g, 4 mmol) was dissolved in 20 mL of water in a 100 mL round-bottomed flask. To this,

0.832 g (8 mmol) of pyridine-3-carbonitrile was added and the resulting reaction mixture was stirred mechanically for 2 h. A light-green precipitate was formed. It was filtered, washed with water under suction and dried in a vacuum desiccator over fused CaCl<sub>2</sub>. Green prism-shaped single crystals of the title compound suitable for X-ray diffraction studies were obtained from the undisturbed aqueous reaction solutions after 24 h, yield 73% (1.675 g). The compound is air stable and insoluble in common organic solvents. The crystals remained indefinitely stable against dehydration under ambient conditions. IR spectroscopic data (KBr disc, cm<sup>-1</sup>):  $\nu_{\text{asym}}(\text{OCO}^-)$  1568,  $\nu_{\text{sym}}(\text{OCO}^-)$  1365,  $\nu(\text{C}=\text{N})$  1602,  $\nu(\text{CN}_{\text{py}})$  2243,  $\delta_{\text{asym}}(\text{OCO}^-)$  810,  $\delta_{\text{sym}}(\text{OCO}^-)$  748. Decomposition point 270°C.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The non-hydrogen atoms were refined with anisotropic displacement parameters. C-bound hydrogen atoms were placed in idealized positions with C–H = 0.95–0.99 Å, and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{C-methyl})$ .

## Acknowledgements

The authors thank USIC, Gauhati University, Guwahati for recording the X-ray crystallographic data for the crystals.

## Funding information

Funding for this research was provided by: UGC, India .

## References

- Bruker (2004). *APEX2* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groeneman, R. H. & Atwood, J. L. (2000). *Supramol. Chem.* **11**, 251–254.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Heine, M., Fink, L. & Schmidt, M. U. (2018). *CrystEngComm*, **20**, 7556–7566.
- Janiak, C. & Vieth, J. K. (2010). *New J. Chem.* **34**, 2366–2388.
- Ju, Z., Yan, W., Gao, X., Shi, Z., Wang, T. & Zheng, H. (2016). *Cryst. Growth Des.* **16**, 2496–2503.
- Kim, J. C., Cho, J. & Lough, A. J. (2001). *Inorg. Chim. Acta*, **317**, 252–258.
- Kim, J. C., Jo, H., Lough, A. J., Cho, J., Lee, U. & Pyun, S. Y. (2003). *Inorg. Chem. Commun.* **6**, 5, 474–477.
- Ma, J. Q. & Xu, S. Y. (2010). *Z. Kristallogr. New Cryst. Struct.* **225**, 791–792.

**Table 3**

Experimental details.

Crystal data	
Chemical formula	[Ni(C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )·4H <sub>2</sub> O
$M_r$	575.17
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
$a, b, c$ (Å)	8.5709 (17), 8.6760 (17), 9.2644 (19)
$\alpha, \beta, \gamma$ (°)	77.26 (3), 81.99 (3), 77.34 (3)
$V$ (Å <sup>3</sup> )	652.6 (3)
$Z$	1
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.81
Crystal size (mm)	0.34 × 0.32 × 0.19
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 2016)
$T_{\text{min}}, T_{\text{max}}$	0.752, 0.826
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	12067, 3762, 3635
$R_{\text{int}}$	0.026
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.704
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.026, 0.074, 1.05
No. of reflections	3762
No. of parameters	194
No. of restraints	14
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.33, -0.40

Computer programs: *APEX* and *SAINTE* (Bruker, 2004), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2017/1* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2020) and *pubCIF* (Westrip, 2010).

- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- Massoud, S. S., Mautner, F. A., Vicente, R. & Rodrigue, B. M. (2006). *Inorg. Chim. Acta*, **359**, 3321–3329.
- Mukherjee, P. S., Konar, S., Zangrando, E., Mallah, T., Ribas, J. & Chaudhuri, N. R. (2003). *Inorg. Chem.* **42**, 2695–2703.
- Rogan, J., Poleti, D., Karanovic, L., Bogdanovic, G., Bire, A. S. & Petrovic, D. M. (2000). *Polyhedron*, **19**, 11, 1415–1421.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Sheldrick, G. M. (2016). *SADABS*. University of Göttingen, Germany.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Xiao, H. P., Shi, Z., Zhu, L. G., Xu, R. R. & Pang, W. Q. (2003). *Acta Cryst.* **C59**, m82–m83.
- Zukerman-Schpector, J., Trindade, A. C. & Dunstan, P. O. (2000). *Acta Cryst.* **C56**, 763–765.

## supporting information

*Acta Cryst.* (2021). E77, 14–17 [https://doi.org/10.1107/S2056989020015832]

## Tetraaquabis(pyridine-3-carbonitrile- $\kappa N^1$ )nickel(II) benzene-1,4-dicarboxylate tetrahydrate

Monsumi Gogoi and Birinchi Kumar Das

### Computing details

Data collection: *APEX* (Bruker, 2004); cell refinement: *S SAINT* (Bruker, 2004); data reduction: *S SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2017/1* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Tetraaquabis(pyridine-3-carbonitrile- $\kappa N^1$ )nickel(II) benzene-1,4-dicarboxylate tetrahydrate

#### Crystal data

$[\text{Ni}(\text{C}_6\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_4](\text{C}_8\text{H}_4\text{O}_4) \cdot 4\text{H}_2\text{O}$

$M_r = 575.17$

Triclinic,  $P\bar{1}$

$a = 8.5709$  (17) Å

$b = 8.6760$  (17) Å

$c = 9.2644$  (19) Å

$\alpha = 77.26$  (3)°

$\beta = 81.99$  (3)°

$\gamma = 77.34$  (3)°

$V = 652.6$  (3) Å<sup>3</sup>

$Z = 1$

$F(000) = 300$

$D_x = 1.463$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4157 reflections

$\theta = 3.4$ – $28.3$ °

$\mu = 0.81$  mm<sup>-1</sup>

$T = 293$  K

Prism, green

$0.34 \times 0.32 \times 0.19$  mm

#### Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.333 pixels mm<sup>-1</sup>

phi and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 2016)

$T_{\min} = 0.752$ ,  $T_{\max} = 0.826$

12067 measured reflections

3762 independent reflections

3635 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 30.0$ °,  $\theta_{\min} = 2.3$ °

$h = -11 \rightarrow 12$

$k = -12 \rightarrow 12$

$l = -12 \rightarrow 12$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.074$

$S = 1.05$

3762 reflections

194 parameters

14 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.1177P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL2017/1

(Sheldrick 2015b),

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.213 (7)

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	1.000000	1.000000	0.000000	0.02537 (8)
O1	0.98267 (11)	0.96951 (11)	-0.21023 (9)	0.03464 (18)
H1A	0.990 (2)	1.0424 (15)	-0.2842 (15)	0.052*
H1B	1.025 (2)	0.8825 (13)	-0.2376 (19)	0.052*
O2	0.85605 (10)	1.22212 (10)	-0.04411 (9)	0.03425 (17)
H2A	0.8004 (19)	1.262 (2)	0.0256 (14)	0.051*
H2B	0.894 (2)	1.2951 (17)	-0.1021 (16)	0.051*
O3	0.66032 (11)	0.32360 (13)	0.17543 (10)	0.0441 (2)
O4	0.86703 (10)	0.30492 (11)	0.30301 (10)	0.0407 (2)
O5	0.03827 (14)	0.21002 (14)	0.54999 (11)	0.0508 (2)
H5A	-0.026 (2)	0.237 (3)	0.4851 (19)	0.076*
H5B	0.1233 (16)	0.160 (3)	0.514 (2)	0.076*
O6	0.03774 (18)	0.55747 (17)	0.26293 (14)	0.0633 (3)
H6A	-0.011 (3)	0.484 (2)	0.268 (3)	0.095*
H6B	-0.006 (3)	0.610 (3)	0.328 (2)	0.095*
N1	0.78988 (11)	0.89668 (11)	0.07505 (11)	0.03167 (19)
N2	0.33024 (18)	1.0277 (3)	0.4103 (2)	0.0778 (5)
C1	0.75634 (16)	0.78588 (15)	0.00979 (14)	0.0390 (2)
H1	0.832785	0.744160	-0.060450	0.047*
C2	0.61331 (19)	0.73082 (19)	0.04213 (17)	0.0493 (3)
H2	0.594395	0.654339	-0.006152	0.059*
C3	0.49961 (17)	0.79021 (19)	0.14618 (17)	0.0483 (3)
H3	0.401786	0.756363	0.168663	0.058*
C4	0.53433 (14)	0.90164 (16)	0.21666 (14)	0.0394 (3)
C5	0.68038 (13)	0.95226 (15)	0.17811 (13)	0.0350 (2)
H5	0.702508	1.027604	0.225918	0.042*
C6	0.42063 (16)	0.9712 (2)	0.32545 (18)	0.0533 (4)
C7	0.44154 (14)	0.43845 (16)	0.39715 (14)	0.0383 (3)
H7	0.401890	0.397181	0.328307	0.046*
C8	0.60607 (13)	0.42491 (13)	0.39660 (12)	0.0322 (2)
C9	0.66387 (14)	0.48662 (16)	0.49989 (14)	0.0388 (3)
H9	0.773958	0.477732	0.500156	0.047*
C10	0.71845 (14)	0.34553 (13)	0.28278 (13)	0.0334 (2)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.02417 (11)	0.02844 (11)	0.02502 (11)	-0.00512 (7)	0.00326 (6)	-0.01197 (7)
O1	0.0414 (4)	0.0360 (4)	0.0276 (4)	-0.0048 (3)	0.0005 (3)	-0.0138 (3)
O2	0.0352 (4)	0.0318 (4)	0.0329 (4)	-0.0020 (3)	0.0064 (3)	-0.0108 (3)
O3	0.0389 (5)	0.0569 (6)	0.0407 (5)	-0.0020 (4)	0.0028 (3)	-0.0297 (4)
O4	0.0332 (4)	0.0468 (5)	0.0435 (5)	0.0005 (3)	0.0029 (3)	-0.0242 (4)
O5	0.0513 (6)	0.0591 (6)	0.0366 (5)	-0.0033 (5)	-0.0014 (4)	-0.0071 (4)
O6	0.0782 (8)	0.0595 (7)	0.0548 (7)	-0.0331 (6)	0.0061 (6)	-0.0049 (5)
N1	0.0283 (4)	0.0326 (4)	0.0354 (5)	-0.0073 (3)	0.0000 (3)	-0.0097 (4)
N2	0.0392 (7)	0.1149 (15)	0.0757 (10)	-0.0070 (8)	0.0116 (7)	-0.0295 (10)
C1	0.0431 (6)	0.0373 (6)	0.0400 (6)	-0.0124 (5)	-0.0033 (5)	-0.0110 (5)
C2	0.0564 (8)	0.0489 (7)	0.0515 (8)	-0.0271 (6)	-0.0113 (6)	-0.0084 (6)
C3	0.0382 (6)	0.0576 (8)	0.0513 (7)	-0.0239 (6)	-0.0087 (5)	0.0017 (6)
C4	0.0263 (5)	0.0468 (6)	0.0406 (6)	-0.0077 (4)	-0.0013 (4)	0.0004 (5)
C5	0.0281 (5)	0.0376 (5)	0.0397 (6)	-0.0077 (4)	0.0019 (4)	-0.0105 (4)
C6	0.0286 (6)	0.0724 (10)	0.0542 (8)	-0.0096 (6)	0.0030 (5)	-0.0075 (7)
C7	0.0347 (6)	0.0467 (6)	0.0391 (6)	-0.0053 (5)	0.0019 (4)	-0.0262 (5)
C8	0.0324 (5)	0.0323 (5)	0.0323 (5)	-0.0020 (4)	0.0044 (4)	-0.0162 (4)
C9	0.0297 (5)	0.0487 (7)	0.0414 (6)	-0.0035 (5)	0.0031 (4)	-0.0245 (5)
C10	0.0348 (5)	0.0312 (5)	0.0341 (5)	-0.0033 (4)	0.0071 (4)	-0.0160 (4)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ni1—O2 <sup>i</sup>	2.0381 (11)	N1—C1	1.3409 (15)
Ni1—O2	2.0381 (11)	N2—C6	1.136 (2)
Ni1—O1 <sup>i</sup>	2.0519 (9)	C1—C2	1.3828 (19)
Ni1—O1	2.0519 (9)	C1—H1	0.9300
Ni1—N1 <sup>i</sup>	2.1481 (11)	C2—C3	1.372 (2)
Ni1—N1	2.1481 (11)	C2—H2	0.9300
O1—H1A	0.829 (9)	C3—C4	1.381 (2)
O1—H1B	0.839 (9)	C3—H3	0.9300
O2—H2A	0.838 (9)	C4—C5	1.3909 (16)
O2—H2B	0.828 (9)	C4—C6	1.438 (2)
O3—C10	1.2396 (15)	C5—H5	0.9300
O4—C10	1.2735 (15)	C7—C9 <sup>ii</sup>	1.3873 (16)
O5—H5A	0.830 (9)	C7—C8	1.3885 (17)
O5—H5B	0.830 (9)	C7—H7	0.9300
O6—H6A	0.822 (9)	C8—C9	1.3864 (17)
O6—H6B	0.837 (9)	C8—C10	1.5035 (15)
N1—C5	1.3342 (15)	C9—H9	0.9300
O2 <sup>i</sup> —Ni1—O2	180.00 (5)	N1—C1—H1	118.5
O2 <sup>i</sup> —Ni1—O1 <sup>i</sup>	89.76 (5)	C2—C1—H1	118.5
O2—Ni1—O1 <sup>i</sup>	90.24 (5)	C3—C2—C1	119.30 (13)
O2 <sup>i</sup> —Ni1—O1	90.24 (5)	C3—C2—H2	120.4
O2—Ni1—O1	89.76 (5)	C1—C2—H2	120.4

O1 <sup>i</sup> —Ni1—O1	180.0	C2—C3—C4	118.21 (12)
O2 <sup>i</sup> —Ni1—N1 <sup>i</sup>	89.33 (4)	C2—C3—H3	120.9
O2—Ni1—N1 <sup>i</sup>	90.67 (4)	C4—C3—H3	120.9
O1 <sup>i</sup> —Ni1—N1 <sup>i</sup>	88.66 (4)	C3—C4—C5	119.42 (12)
O1—Ni1—N1 <sup>i</sup>	91.33 (4)	C3—C4—C6	121.56 (12)
O2 <sup>i</sup> —Ni1—N1	90.67 (4)	C5—C4—C6	118.98 (13)
O2—Ni1—N1	89.33 (4)	N1—C5—C4	122.40 (12)
O1 <sup>i</sup> —Ni1—N1	91.33 (4)	N1—C5—H5	118.8
O1—Ni1—N1	88.67 (4)	C4—C5—H5	118.8
N1 <sup>i</sup> —Ni1—N1	180.0	N2—C6—C4	179.2 (2)
Ni1—O1—H1A	122.0 (12)	C9 <sup>ii</sup> —C7—C8	120.18 (11)
Ni1—O1—H1B	121.0 (12)	C9 <sup>ii</sup> —C7—H7	119.9
H1A—O1—H1B	106.7 (15)	C8—C7—H7	119.9
Ni1—O2—H2A	120.0 (12)	C9—C8—C7	119.43 (10)
Ni1—O2—H2B	118.1 (12)	C9—C8—C10	121.09 (10)
H2A—O2—H2B	107.6 (15)	C7—C8—C10	119.47 (10)
H5A—O5—H5B	107.4 (17)	C8—C9—C7 <sup>ii</sup>	120.39 (11)
H6A—O6—H6B	107.9 (18)	C8—C9—H9	119.8
C5—N1—C1	117.63 (10)	C7 <sup>ii</sup> —C9—H9	119.8
C5—N1—Ni1	120.87 (8)	O3—C10—O4	124.25 (10)
C1—N1—Ni1	121.17 (8)	O3—C10—C8	117.83 (11)
N1—C1—C2	123.01 (13)	O4—C10—C8	117.92 (10)

Symmetry codes: (i)  $-x+2, -y+2, -z$ ; (ii)  $-x+1, -y+1, -z+1$ .

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2A $\cdots$ O3 <sup>iii</sup>	0.84 (1)	1.80 (1)	2.6301 (14)	171 (2)
C5—H5 $\cdots$ O3 <sup>iii</sup>	0.93	2.46	3.1832 (17)	135
O1—H1A $\cdots$ O5 <sup>iv</sup>	0.83 (1)	1.94 (1)	2.7591 (17)	171 (2)
O2—H2B $\cdots$ O6 <sup>v</sup>	0.83 (1)	1.86 (1)	2.6710 (17)	168 (2)
O1—H1B $\cdots$ O4 <sup>vi</sup>	0.84 (1)	1.87 (1)	2.7050 (14)	176 (2)
O6—H6A $\cdots$ O4 <sup>vii</sup>	0.82 (1)	2.01 (1)	2.8240 (17)	174 (2)
O6—H6B $\cdots$ O5 <sup>viii</sup>	0.84 (1)	2.07 (1)	2.855 (2)	156 (2)
O5—H5A $\cdots$ O4 <sup>vii</sup>	0.83 (1)	1.95 (1)	2.7645 (17)	167 (2)
O5—H5B $\cdots$ N2 <sup>ix</sup>	0.83 (1)	2.12 (1)	2.950 (2)	176 (2)

Symmetry codes: (iii)  $x, y+1, z$ ; (iv)  $x+1, y+1, z-1$ ; (v)  $-x+1, -y+2, -z$ ; (vi)  $-x+2, -y+1, -z$ ; (vii)  $x-1, y, z$ ; (viii)  $-x, -y+1, -z+1$ ; (ix)  $x, y-1, z$ .