



Syntheses and structural characterizations of the first coordination polymers assembled from the Ni(cyclam)²⁺ cation and the benzene-1,3,5-tricarboxylate linker

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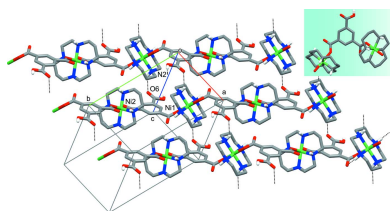
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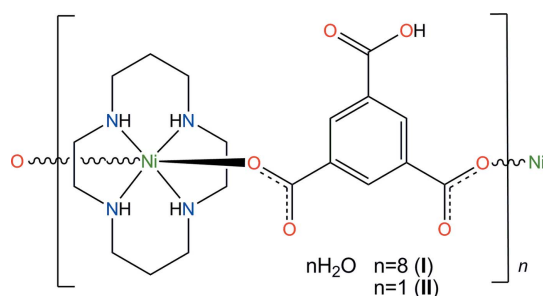
The asymmetric unit of *catena*-poly[[[(1,4,8,11-tetraazacyclotetradecane-κ⁴N¹,N⁴,N⁸,N¹¹)nickel(II)]-μ₂-5-carboxybenzene-1,3-dicarboxylato-κ²O¹:O³] octahydrate], {[Ni(C₉H₄O₆)(C₁₀H₂₄N₄)]·8H₂O}_n (**I**), consists of a macrocyclic Ni²⁺ cation, a carboxylate dianion and eight highly disordered water molecules of crystallization. The components of the compound *catena*-poly[[[(1,4,8,11-tetraazacyclotetradecane-κ⁴N¹,N⁴,N⁸,N¹¹)nickel(II)]-μ₂-5-carboxybenzene-1,3-dicarboxylato-κ²O¹:O³] monohydrate], {[Ni(C₉H₄O₆)(C₁₀H₂₄N₄)]·H₂O}_n (**II**), are two crystallographically unique centrosymmetric macrocyclic dications, a carboxylate dianion and one water molecule of crystallization. In each compound, the metal ion is coordinated in the equatorial plane by the four secondary N atoms of the macrocyclic ligand, which adopts the most energetically stable *trans*-III conformation, and two mutually *trans* O atoms of the carboxylate anions in a slightly tetragonally distorted *trans*-NiN₄O₂ octahedral geometry. The crystals of both compounds are composed of parallel coordination polymeric chains running along the [010] direction in **I** and the [110] and [1 $\bar{1}$ 0] directions in **II**. The bridging carboxylate anions display different modes of coordination connected with the relative orientation of coordinated O atoms, *i.e.*, remote in **I** and intermediate in **II**, thus resulting in essentially different distances between the Ni atoms in the chains [11.0657 (4) and 8.9089 (2) Å in **I** and **II**, respectively]. As a result of hydrogen-bonding interactions, the chains are joined together in sheets oriented parallel to the (10 $\bar{1}$) and (001) planes in **I** and **II**, respectively.

1. Chemical context

Azamacrocyclic complexes of transition metals are widely used for the construction of metal–organic frameworks (MOFs) – crystalline porous materials displaying many promising properties connected with the possibilities of their practical applications (Lampeka & Tsybmal, 2004; Suh & Moon, 2007; Suh *et al.*, 2012; Stackhouse & Ma, 2018). Complexes of the 14-membered tetraaza cyclam ligand (cyclam = 1,4,8,11-tetraazacyclotetradecane, C₁₀H₂₄N₄, *L*), which is the most suitable for binding of 3*d* transition-metal ions, in particular, Ni²⁺, are among popular metal-containing nodes in the formation of MOFs. Their interactions with different oligocarboxylates as the most common bridging ligands (Rao *et al.*, 2004) usually result in coordination polymers, the dimensionalities of which are dependent on the number of carboxylic groups present in the linker. As was shown formerly for a number of macrocyclic Ni²⁺ complexes



of aza- and diazacyclam derivatives, which are the closest structural analogues of *L* (azacyclam = 1,3,5,8,12-pentatetraazacyclotetradecane, diazacyclam = 1,3,5,8,10,12-hexaazacyclotetradecane), the coordination of the simplest tridentate aromatic ligand benzene-1,3,5-tricarboxylate (btc^{3-}) in the *trans*-axial coordination positions of the metal ion leads to the formation of two-dimensional coordination polymers with hexagonal nets of 6^3 topology (Choi *et al.*, 2001; Meng *et al.*, 2011; Choi & Suh, 1998; Ryoo *et al.*, 2010; Lu *et al.*, 2001; Lu *et al.*, 2002; Lampeka *et al.*, 2012). Surprisingly, for the $\text{Ni}(\text{L})^{2+}$ cation itself, only ionic compounds built on the *trans*-diaqua $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]^{2+}$ cation and the non-coordinated btc^{3-} anion have been described to date (Choi *et al.*, 1999; Parsons *et al.*, 2006; Tadokoro *et al.*, 2015).



The present work describes the preparation and structural characterization of the first representatives of polymeric complexes formed by $\text{Ni}(\text{L})^{2+}$ and the benzene-1,3,5-tricarboxylate anion, namely, *catena*-poly[[[(1,4,8,11-tetraazacyclotetradecane- $\kappa^4\text{N}^1, \text{N}^4, \text{N}^8, \text{N}^{11}$)nickel(II)]- μ_2 -5-carboxybenzene-1,3-dicarboxylato- $\kappa^2\text{O}^1: \text{O}^3$] octahydrate], $\{[\text{Ni}(\text{C}_9\text{H}_4\text{O}_6)(\text{C}_{10}\text{H}_{24}\text{N}_4)] \cdot 8\text{H}_2\text{O}\}_n$ (**I**) and *catena*-poly[[[(1,4,8,11-tetraazacyclotetradecane- $\kappa^4\text{N}^1, \text{N}^4, \text{N}^8, \text{N}^{11}$)nickel(II)]- μ_2 -5-carboxybenzene-1,3-dicarboxylato- $\kappa^2\text{O}^1: \text{O}^3$] monohydrate], $\{[\text{Ni}(\text{C}_9\text{H}_4\text{O}_6)(\text{C}_{10}\text{H}_{24}\text{N}_4)] \cdot \text{H}_2\text{O}\}_n$ (**II**).

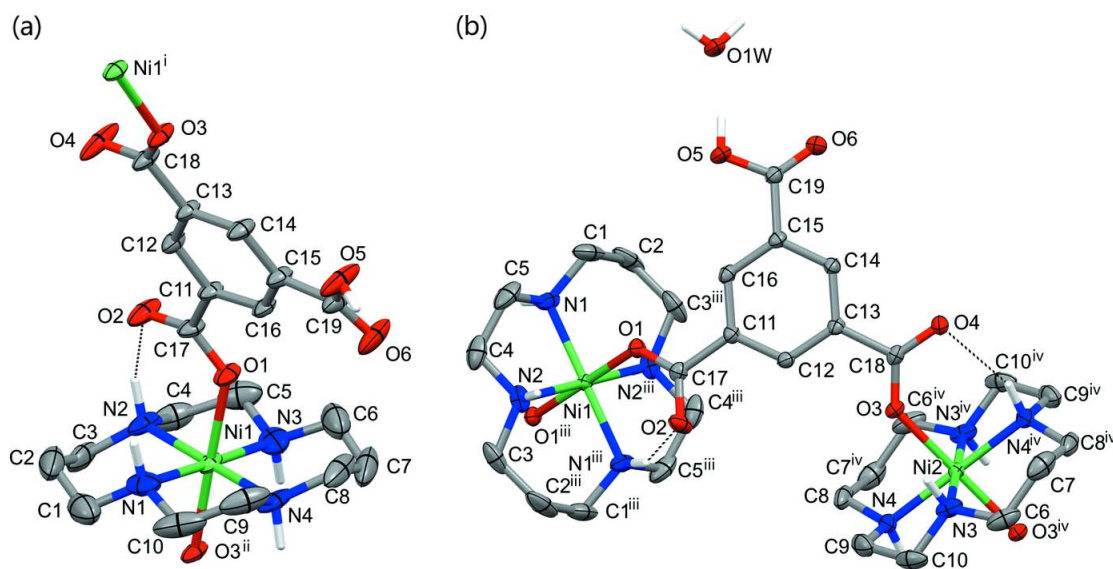


Figure 1

The extended asymmetric unit in (a) **I** and (b) **II** showing the coordination environment of the Ni atoms and the atom-labeling scheme (displacement ellipsoids are drawn at the 30% probability level). C-bound H atoms are omitted for clarity. Intramolecular hydrogen bonds are shown as dotted lines. Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, -y, -z + 1$; (iv) $-x, -y + 1, -z + 1$.

Table 1

Selected geometric parameters (\AA , $^\circ$).

I		II	
Ni1—N1	2.056 (3)	Ni1—N1	2.051 (2)
Ni1—N2	2.066 (2)	Ni1—N2	2.064 (3)
Ni1—N3	2.053 (3)	Ni2—N3	2.063 (2)
Ni1—N4	2.046 (3)	Ni2—N4	2.050 (3)
Ni1—O1	2.1106 (18)	Ni1—O1	2.1242 (19)
Ni1—O3i	2.1377 (18)	Ni2—O3	2.1129 (18)
N1—Ni1—N4	85.55 (15)	N1—Ni1—N2	85.31 (11)
N2—Ni1—N3	84.92 (14)	N3—Ni2—N4	85.38 (11)
N1—Ni1—N2	93.13 (14)	N1—Ni1—N2ii	94.69 (11)
N3—Ni1—N4	96.41 (15)	N3—Ni1—N4iii	94.62 (11)

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x, -y + 1, -z + 1$.

2. Structural commentary

The molecular structures of **I** and **II** are shown in Fig. 1. The asymmetric unit of **I** consists of a macrocyclic $[\text{Ni}(\text{L})]^{2+}$ dication, a monoprotonated carboxylate Hbtc^{2-} dianion and eight water molecules of crystallization, while the components of **II** are the same dianion, two crystallographically unique centrosymmetric dications and one water molecule of crystallization. The coordination polyhedra of the metal ions in both complexes are very similar: the Ni^{2+} ions are coordinated by the four secondary N atoms of the macrocycle *L*, which adopt the most energetically stable *trans*-III (*R,R,S,S*) conformation (Bosnich *et al.*, 1965a; Barefield *et al.*, 1986) in which the five-membered (N—Ni—N bite angles $\simeq 85^\circ$) and six-membered (N—Ni—N bite angles $\simeq 95^\circ$) chelate rings are in *gauche* and *chair* conformations, respectively (Table 1). The O atoms of the carboxylate ligands occupy the axial positions in the coordination spheres of the metal ions, resulting in a tetragonally elongated *trans*- NiN_4O_2 coordination octahedra

Table 2
Hydrogen-bond geometry (Å, °) for **I**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O5—H5···O4 ⁱ	0.82	1.83	2.604 (3)	157
N2—H2···O2	0.98	2.08	2.969 (3)	150
N4—H4···O4 ⁱⁱ	0.98	2.00	2.891 (3)	151
N4—H4···O6 ⁱⁱⁱ	0.98	2.59	3.226 (4)	123

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 2, -y + 1, -z + 2$.

with the Ni—N bond lengths (average value 2.063 Å) slightly shorter than the Ni—O ones (average value 2.121 Å) (Table 1). The axial Ni—O bonds are nearly orthogonal to the NiN₄ planes (deviations of the angles N—Ni—O from 90° do not exceed 5°). The deviations of the Ni and N atoms from the mean N₄ plane in **I** are 0.011 Å and ±0.009 Å, respectively, while the NiN₄ coordination moieties in **II** are strictly planar because of the location of the metal ions on crystallographic inversion centers. As in other complexes of the Ni²⁺ macrocyclic cations and carboxylate ligands (Tsymbal *et al.*, 2021) the Ni—O bonds in **I** and **II** are reinforced by the intramolecular hydrogen bonds between the secondary NH atoms and the non-coordinated O atoms of each coordinated carboxylic group (Fig. 1, Tables 2 and 3).

The C—O bond lengths in the deprotonated carboxylate groups are nearly equal, thus indicating essential electron delocalization, while protonated carboxylic groups remain non-delocalized [the lengths of the C—OH and C=O bonds in **I** and **II** are 1.305 (4) and 1.200 (3) Å and 1.314 (4) and 1.205 (3) Å, respectively]. The mean planes of the carboxylate groups are slightly tilted relative to the mean plane of their attached aromatic rings (average angle equals 7.0° in **I** and 16.0° in **II**).

In both complexes, the monoprotonated carboxylate ligands display a μ₂-bis-monodentate bridging function of the isophthalate type, resulting in the formation of one-dimensional coordination polymers (Figs. 2 and 3). The Ni—O coordination bonds of the Hbtc²⁻ bridge are characterized by the *syn/syn* orientation. Since the carboxylate groups are

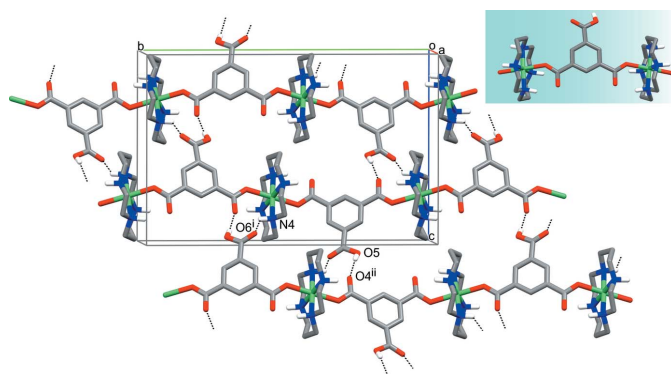


Figure 2
The hydrogen-bonded (dashed lines) sheet in **I**. C-bound H atoms have been omitted; the intramolecular hydrogen bonds are not shown. The mode of coordination of carboxylate ligand is shown as an inset. Symmetry codes: (i) $-x + 2, -y + 1, -z + 2$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 3
Hydrogen-bond geometry (Å, °) for **II**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O5—H5···O1W	0.82	1.72	2.531 (3)	170
N2—H2···O6 ⁱ	0.98	2.38	3.199 (4)	141
N4—H4···O4 ⁱⁱ	0.98	2.09	2.959 (3)	147
N1—H1···O2 ⁱⁱⁱ	0.98	1.97	2.872 (3)	153
O1W—H1WA···O2 ^{iv}	0.85	1.83	2.664 (3)	168
O1W—H1WB···O4 ^v	0.85	1.92	2.747 (3)	165

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x + 1, -y, -z + 1$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

nearly coplanar with the aromatic rings, the possibility arises for appearance of different modes of ligand coordination, depending on the mutual spatial arrangement of coordinated O atoms (Tsymbal *et al.*, 2021). In the complexes under consideration, these modes can be recognized as remote (rm) in **I** and intermediate (im) in **II** (see insets in Figs. 2 and 3).

Such peculiarities lead to several differences in the structures of the polymeric chains. In particular, the angle between the mean NiN₄ planes of the macrocyclic cations in **I** is 40.62 (1)°, while they are nearly orthogonal in **II** [85.49 (1)°]. Therewith, the chains of the Ni atoms in **I** are non-linear [the angle Ni···Ni···Ni is 169.590 (9)°], in contrast to strictly linear metal atom chains in **II**. The most important difference is connected with the mode of the carboxylate coordination and consists of essentially different distances between the Ni atoms in the chains formed by the *rm-syn/syn* coordinated ligand in **I** [Ni···Ni = 11.0657 (4) Å], as compared to the *im-syn/syn* coordinated one in **II** [8.9089 (2) Å].

3. Supramolecular features

Both compounds are characterized by lamellar structures as the result of linking of the polymeric chains into sheets due to hydrogen-bonding interactions (Tables 2 and 3). The key role in the formation of sheets oriented parallel to the (10 $\bar{1}$) plane from the chains running along the [010] direction in the crystals of **I** is played by the protonated carboxylic group of

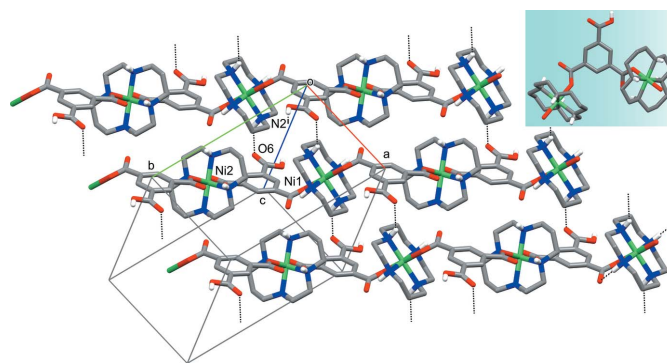


Figure 3
The hydrogen-bonded (dashed lines) sheet in **II**. C-bound H atoms and water molecule of crystallization have been omitted; the intramolecular hydrogen bonds are not shown. The mode of coordination of carboxylate ligand is shown as an inset. Symmetry code: (i) $x - 1, y, z$.

the Hbtc^{2-} dianion, which forms two $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds acting both as the proton donor in a strong interaction with the O atom of the coordinated carboxylic ligand on neighboring chain $[\text{O}5-\text{H}5\cdots\text{O}4(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})]$ and as the proton acceptor in a weak interaction with the secondary amino group of the macrocyclic cation belonging to the same neighboring chain $[\text{N}4-\text{H}4\cdots\text{O}6(-x + 2, -y + 1, -z + 2)]$ (Fig. 2). There are no hydrogen-bonding contacts between the sheets and the three-dimensional coherence of the crystal is provided by van der Waals interactions.

In the crystal of **II**, polymeric chains with different orientations are present, namely, running along the [110] or $[\bar{1}\bar{1}0]$ directions. As a result of the weak hydrogen bond between the carbonyl O6 atom of the protonated carboxylic group of the acid as the acceptor and the secondary N2–H2 amino group of the macrocyclic cation of a neighboring chain as the donor (Fig. 3), they form alternating sheets oriented parallel to the (001) plane. At the same time, the hydroxyl group of the protonated carboxylate group as the donor interacts strongly with the water molecule of crystallization as acceptor, and this interaction together with two additional hydrogen bonds with participation of O1W molecule results in a three-dimensional network in **II**.

As estimated by *PLATON* (Spek, 2020), the volume of the solvent-accessible voids in **I** in the form of parallel one-dimensional channels equals 1111 \AA^3 (37.5% of the unit-cell volume) and according to *SQUEEZE* calculations it is filled with eight highly disordered water molecules of crystallization. The crystals of **II** are non-porous.

4. Database survey

The Cambridge Structural Database (CSD, Version 5.43, last update March 2022; Groom *et al.*, 2016) contains descriptions of several polymorphs of compounds containing the $\text{Ni}(L)$ moiety and the benzene-1,3,5-tricarboxylate anion (refcodes GOQTIP, Choi *et al.*, 1999; PELCOZ, Parsons *et al.*, 2006; GOQTIP01, SABLEP, SABLOZ and SABLOZ01, Tadokoro *et al.*, 2015). All of them are highly hydrated (18–29 water molecules of crystallization) ionic complexes containing the *trans*-diaqua $[\text{Ni}(L)(\text{H}_2\text{O})_2]^{2+}$ dication and non-coordinated btc^{3-} trianions. At the same time, a number of two-dimensional coordination polymers built on parent 14-membered derivatives of Ni(azacyclam) (CAXMIZ, Lampeka *et al.*, 2012) and Ni(diazacyclam) (IPOZIWI, Choi *et al.*, 2001; IWESIN and IWESOT, Meng *et al.*, 2011; JEDQIS and JEDQOY, Choi & Suh, 1998; UJUHUD, Ryoo *et al.*, 2010; VOQSAV, Lu *et al.*, 2001; and WUJDEK, Lu *et al.*, 2002) bearing different substituents at the non-coordinated distal nitrogen atom(s) have been structurally characterized. In addition, two compounds with other structures have been described. One represents the molecular complex in which the *trans*- $[\text{Ni}(L^A)(\text{btc})_2]^{4-}$ anion compensates the charge of the two *trans*- $[\text{Ni}(L^A)(\text{H}_2\text{O})_2]^{2+}$ cations ($L^A = 3,10$ -dibutyl-1,3,5,8,10,12-hexaazacyclotetradecane) (SUXXEQ, Shin *et al.*, 2016), and the other is the hydrated (3.5 water molecules of crystallization) one-dimensional coordination polymer

formed by the $[\text{Ni}(L^B)]^{2+}$ cation and the μ_2 Hbtc^{2-} linker ($L^B = 1,3,6,9,11,14$ -hexaazatricyclo[12.2.1.1^{6,9}]octadecane) (SEFLOG, Tao *et al.*, 2012). The structure of the latter is similar to the structure of **I** – it is a neutral one-dimensional coordination polymer with parallel alignment of the chains formed due to the carboxylate displaying the *rm-syn/syn* mode of the bridging function. Correspondingly, the $\text{Ni}\cdots\text{Ni}$ distance in this compound (11.313 Å) is close to that observed in **I**, though the chains, in contrast to **I**, are linear.

5. Synthesis and crystallization

All chemicals and solvents used in this work were purchased from Sigma–Aldrich and used without further purification. The complex $[\text{Ni}(L)](\text{ClO}_4)_2$ was prepared from ethanol solution as described in the literature (Bosnich *et al.*, 1965).

The complex $[\text{Ni}(L)(\text{Hbtc})\cdot 8\text{H}_2\text{O}]$, (**I**), was prepared as follows. $[\text{Ni}(L)](\text{ClO}_4)_2$ (153 mg, 0.33 mmol) and H_3btc (50 mg, 0.24 mmol) were dissolved in 10 ml of a DMF/ H_2O mixture (4:1 by volume) and the solution was heated at 358 K for 30 h. A small amount of pink needle-like crystals in the form of concretions was formed in a week. These were filtered off, washed with small amounts of methanol and diethyl ether, and dried in air. Yield: 15 mg (10% based on acid). Analysis calculated for $\text{C}_{19}\text{H}_{44}\text{N}_4\text{NiO}_{14}$: C 37.36, H 7.27, N 9.18%. Found: C 37.52, H 7.31, N 9.15%. Single crystals of **I** suitable for X-ray diffraction analysis were selected from the sample formed after refrigerating the mother liquor for several days.

Apparently, the complex $[\text{Ni}(L)(\text{Hbtc})\cdot \text{H}_2\text{O}]$, (**II**), is more thermodynamically stable than **I** and it was prepared according to similar procedure, except that initially precipitated crystals were left to remain under the mother liquor at ambient temperature. Over *ca* one week, the needle-like crystals of **I** dissolved; instead, a precipitate in the form of rhomb-shaped plates was formed and single crystals of **II** suitable for X-ray diffraction analysis were selected from this reaction mixture. Alternatively, larger amounts of **II** can be obtained using an analogous procedure but using higher concentrations of the reagents. $[\text{Ni}(L)](\text{ClO}_4)_2$ (200 mg, 0.44 mmol) and H_3btc (65 mg, 0.31 mmol) were dissolved in 10 ml of a DMF/ H_2O mixture (4:1 by volume) and the solution was heated at 358 K for 24 h. After cooling of the reaction mixture, the product began to crystallize in several hours in the form of pink plate-like concretions. It was filtered off, washed with small amounts of methanol and diethyl ether, and dried in air. Yield: 38 mg (25% based on acid). Analysis calculated for $\text{C}_{19}\text{H}_{30}\text{N}_4\text{NiO}_7$: C 47.09, H 6.24, N 11.57%. Found: C 47.15, H 6.31, N 11.65%.

Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled with care.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The H atoms in **I** and **II** were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances of 0.93 Å

Table 4
Experimental details.

	I	II
Crystal data		
Chemical formula	[Ni(C ₉ H ₄ O ₆)(C ₁₀ H ₂₄ N ₄)]·8H ₂ O	[Ni(C ₉ H ₄ O ₆)(C ₁₀ H ₂₄ N ₄)]·H ₂ O
<i>M_r</i>	467.16	485.18
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	293	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.3650 (6), 22.0401 (8), 14.3567 (7)	9.3852 (3), 15.1459 (4), 15.7561 (5)
β (°)	91.457 (5)	98.604 (3)
<i>V</i> (Å ³)	2962.3 (3)	2214.49 (12)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.69	0.92
Crystal size (mm)	0.40 × 0.20 × 0.10	0.20 × 0.20 × 0.07
Data collection		
Diffractometer	Rigaku Xcalibur Eos	Rigaku Xcalibur Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2021)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2021)
<i>T</i> _{min} , <i>T</i> _{max}	0.751, 1.000	0.988, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	21516, 6875, 3858	14088, 4534, 2876
<i>R</i> _{int}	0.058	0.042
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.688	0.625
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.059, 0.125, 1.08	0.045, 0.108, 1.03
No. of reflections	6875	4534
No. of parameters	272	287
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.31, -0.32	0.32, -0.43

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXS* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *Mercury* (Macrae et al., 2020) and *publCIF* (Westrip, 2010).

(ring H atoms), 0.97 Å (methylene H atoms), N—H distances of 0.98 Å, O—H distances of 0.82 Å (protonated carboxylate group) and 0.85 Å (water molecules) with *U*_{iso}(H) values of 1.2*U*_{eq} or 1.5*U*_{eq} times those of the corresponding parent atoms. SQUEEZE calculations indicate the presence of eight water molecules of crystallization per asymmetric unit of **I**.

References

- Bosnich, B., Tobe, M. L. & Webb, G. A. (1965). *Inorg. Chem.* **4**, 1109–1112.
- Choi, H. J., Lee, T. S. & Suh, M. P. (1999). *Angew. Chem. Int. Ed.* **38**, 1405–1408.
- Choi, H. J., Lee, T. S. & Suh, M. P. (2001). *J. Inclusion Phenom. Macrocyclic Chem.* **41**, 155–162.
- Choi, H. J. & Suh, M. P. (1998). *J. Am. Chem. Soc.* **120**, 10622–10628.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Lampeka, Ya. D. & Tsymbal, L. V. (2004). *Theor. Exp. Chem.* **40**, 345–371.
- Lampeka, Ya. D., Tsymbal, L. V., Barna, A. V., Shuǐga, Y. L., Shova, S. & Arion, V. B. (2012). *Dalton Trans.* **41**, 4118–4125.
- Lu, T.-B., Xiang, H., Luck, R. L., Jiang, L., Mao, Z.-W. & Ji, L.-N. (2002). *New J. Chem.* **26**, 969–971.
- Lu, T.-B., Xiang, H., Luck, R. L., Mao, Z.-W., Wang, D., Chen, C. & Ji, L.-N. (2001). *CrystEngComm*, **3**, 168–169.
- 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.
- Meng, X.-R., Zhong, D.-C., Jiang, L., Li, H.-Y. & Lu, T.-B. (2011). *Cryst. Growth Des.* **11**, 2020–2025.
- Parsons, S., Jagaln, V. B., Harrison, A., Parkin, A. & Johnstone, R. (2006). *Private Communication*.
- Rao, C. N. R., Natarajan, S. & Vaidhyanathan, R. (2004). *Angew. Chem. Int. Ed.* **43**, 1466–1496.
- Rigaku OD (2021). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
- Ryoo, J. J., Shin, J. W., Dho, H.-S. & Min, K. S. (2010). *Inorg. Chem.* **49**, 7232–7234.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Shin, J. W., Kim, D.-W. & Moon, D. (2016). *Polyhedron*, **105**, 62–70.
- Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.
- Stackhouse, C. A. & Ma, S. (2018). *Polyhedron*, **145**, 154–165.
- Suh, M. P. & Moon, H. R. (2007). *Advances in Inorganic Chemistry*, Vol. 59, edited by R. van Eldik & K. Bowman-James, pp. 39–79. San Diego: Academic Press.
- Suh, M. P., Park, H. J., Prasad, T. K. & Lim, D.-W. (2012). *Chem. Rev.* **112**, 782–835.
- Tadokoro, M., Suda, T., Shouji, T., Ohno, K., Honda, K., Takeuchi, A., Yoshizawa, M., Isoda, K., Kamebuchi, H. & Matsui, H. (2015). *Bull. Chem. Soc. Jpn.* **88**, 1707–1715.
- Tao, B., Cheng, F., Jiang, X. & Xia, H. (2012). *J. Mol. Struct.* **1028**, 176–180.
- Tsymbal, L. V., Andriichuk, I. L., Shova, S., Trzybiński, D., Woźniak, K., Arion, V. B. & Lampeka, Ya. D. (2021). *Cryst. Growth Des.* **21**, 2355–2370.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

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Syntheses and structural characterizations of the first coordination polymers assembled from the Ni(cyclam)²⁺ cation and the benzene-1,3,5-tricarboxylate linker

Sergey P. Gavrish, Sergiu Shova and Yaroslaw D. Lampeka

Computing details

For both structures, data collection: *CrysAlis PRO* (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* (Rigaku OD, 2021); data reduction: *CrysAlis PRO* (Rigaku OD, 2021); program(s) used to solve structure: *SHELXS* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

catena-Poly[[[(1,4,8,11-tetraazacyclotetradecane-κ⁴N¹,N⁴,N⁸,N¹¹)nickel(II)]-μ₂-5-carboxybenzene-1,3-dicarboxylato-κ²O¹:O³] octahydrate] (I)

Crystal data

[Ni(C₉H₄O₆)(C₁₀H₂₄N₄)]·8H₂O

M_r = 467.16

Monoclinic, *P*2₁/*n*

a = 9.3650 (6) Å

b = 22.0401 (8) Å

c = 14.3567 (7) Å

β = 91.457 (5)°

V = 2962.3 (3) Å³

Z = 4

F(000) = 984

D_x = 1.047 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 3816 reflections

θ = 1.9–23.7°

μ = 0.69 mm⁻¹

T = 293 K

Prism, clear light pink

0.40 × 0.20 × 0.10 mm

Data collection

Rigaku Xcalibur Eos

diffractometer

Radiation source: fine-focus sealed X-ray tube,

Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1593 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Rigaku OD, 2021)

T_{min} = 0.751, *T_{max}* = 1.000

21516 measured reflections

6875 independent reflections

3858 reflections with *I* > 2σ(*I*)

R_{int} = 0.058

θ_{max} = 29.3°, θ_{min} = 2.6°

h = -11→11

k = -27→27

l = -18→17

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.059

wR(*F*²) = 0.125

S = 1.08

6875 reflections

272 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.69720 (4)	0.55885 (2)	0.75502 (3)	0.03961 (15)
O1	0.6534 (2)	0.46933 (8)	0.79800 (14)	0.0538 (6)
O2	0.5619 (3)	0.41875 (8)	0.67715 (16)	0.0719 (8)
O3	0.7624 (2)	0.15022 (8)	0.78673 (14)	0.0485 (6)
O4	0.6373 (3)	0.19208 (9)	0.67255 (18)	0.1011 (11)
O5	0.9540 (3)	0.27371 (10)	1.04356 (19)	0.0971 (11)
H5	1.026567	0.284652	1.072019	0.146*
O6	0.8741 (3)	0.36664 (10)	1.06441 (17)	0.0918 (10)
N1	0.8659 (3)	0.52742 (12)	0.6799 (3)	0.0696 (9)
H1	0.855311	0.483290	0.675135	0.084*
N2	0.5551 (3)	0.55160 (11)	0.6431 (2)	0.0596 (9)
H2	0.528340	0.508716	0.638191	0.072*
N3	0.5242 (4)	0.58978 (12)	0.8261 (2)	0.0730 (10)
H3	0.528845	0.634199	0.825184	0.088*
N4	0.8406 (4)	0.56357 (11)	0.8647 (2)	0.0710 (10)
H4	0.876485	0.605323	0.866867	0.085*
C1	0.8744 (6)	0.55061 (19)	0.5861 (4)	0.1075 (18)
H1A	0.957482	0.533515	0.556787	0.129*
H1B	0.886094	0.594320	0.588217	0.129*
C2	0.7421 (7)	0.5352 (2)	0.5283 (3)	0.114 (2)
H2A	0.762054	0.542420	0.463294	0.137*
H2B	0.722629	0.492262	0.535306	0.137*
C3	0.6120 (6)	0.56943 (17)	0.5518 (3)	0.0911 (17)
H3A	0.539192	0.562589	0.503691	0.109*
H3B	0.633845	0.612446	0.552779	0.109*
C4	0.4290 (5)	0.58417 (17)	0.6676 (4)	0.0880 (15)
H4A	0.348784	0.571120	0.628441	0.106*
H4B	0.443004	0.627298	0.657987	0.106*
C5	0.3984 (5)	0.57217 (18)	0.7675 (4)	0.0958 (16)
H5A	0.315607	0.595338	0.785710	0.115*
H5B	0.377847	0.529444	0.776235	0.115*
C6	0.5197 (6)	0.5718 (2)	0.9226 (4)	0.1113 (19)
H6A	0.502707	0.528444	0.925611	0.134*
H6B	0.439987	0.592000	0.951231	0.134*
C7	0.6542 (8)	0.5863 (2)	0.9777 (3)	0.129 (2)
H7A	0.677056	0.628688	0.967197	0.154*

H7B	0.634114	0.581925	1.043262	0.154*
C8	0.7827 (7)	0.55005 (17)	0.9583 (3)	0.111 (2)
H8A	0.758997	0.507277	0.961644	0.133*
H8B	0.855740	0.558380	1.005650	0.133*
C9	0.9589 (5)	0.52540 (18)	0.8405 (4)	0.107 (2)
H9A	0.933373	0.482969	0.846677	0.129*
H9B	1.040926	0.533639	0.881155	0.129*
C10	0.9923 (5)	0.53932 (19)	0.7435 (5)	0.110 (2)
H10A	1.072151	0.514566	0.724517	0.132*
H10B	1.020103	0.581576	0.738609	0.132*
C11	0.6747 (3)	0.36318 (11)	0.8010 (2)	0.0399 (8)
C12	0.6602 (3)	0.30772 (11)	0.7576 (2)	0.0420 (8)
H12	0.612201	0.305534	0.700194	0.050*
C13	0.7152 (3)	0.25504 (11)	0.7973 (2)	0.0401 (8)
C14	0.7864 (3)	0.25897 (12)	0.8827 (2)	0.0486 (9)
H14	0.825804	0.224222	0.909616	0.058*
C15	0.7995 (3)	0.31362 (12)	0.9283 (2)	0.0463 (8)
C16	0.7405 (3)	0.36579 (12)	0.8868 (2)	0.0424 (8)
H16	0.746168	0.402657	0.918165	0.051*
C17	0.6238 (4)	0.42117 (12)	0.7530 (2)	0.0450 (8)
C18	0.7045 (4)	0.19457 (12)	0.7481 (2)	0.0506 (9)
C19	0.8792 (4)	0.32119 (14)	1.0186 (2)	0.0618 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0576 (3)	0.0201 (2)	0.0402 (3)	0.00044 (18)	-0.0169 (2)	-0.00049 (15)
O1	0.0879 (18)	0.0212 (11)	0.0512 (14)	-0.0037 (11)	-0.0180 (12)	0.0000 (9)
O2	0.116 (2)	0.0268 (12)	0.0699 (18)	0.0005 (12)	-0.0539 (16)	0.0005 (10)
O3	0.0769 (16)	0.0214 (11)	0.0455 (13)	0.0068 (10)	-0.0287 (12)	-0.0031 (9)
O4	0.176 (3)	0.0313 (13)	0.091 (2)	0.0219 (15)	-0.100 (2)	-0.0163 (11)
O5	0.156 (3)	0.0365 (14)	0.094 (2)	0.0040 (15)	-0.091 (2)	-0.0084 (13)
O6	0.150 (3)	0.0500 (15)	0.0726 (19)	0.0118 (15)	-0.0564 (18)	-0.0265 (13)
N1	0.069 (2)	0.0365 (17)	0.103 (3)	-0.0020 (15)	0.012 (2)	-0.0088 (16)
N2	0.083 (2)	0.0269 (15)	0.067 (2)	-0.0068 (14)	-0.0393 (18)	0.0016 (13)
N3	0.097 (3)	0.0377 (17)	0.085 (3)	0.0057 (16)	0.018 (2)	-0.0059 (16)
N4	0.112 (3)	0.0204 (14)	0.077 (2)	-0.0101 (15)	-0.059 (2)	0.0079 (13)
C1	0.156 (5)	0.066 (3)	0.103 (4)	-0.017 (3)	0.057 (4)	-0.010 (3)
C2	0.227 (7)	0.065 (3)	0.052 (3)	-0.029 (4)	0.018 (4)	-0.009 (2)
C3	0.163 (5)	0.056 (3)	0.052 (3)	-0.026 (3)	-0.052 (3)	0.004 (2)
C4	0.079 (3)	0.056 (3)	0.127 (4)	-0.002 (2)	-0.051 (3)	0.008 (3)
C5	0.066 (3)	0.061 (3)	0.160 (5)	0.003 (2)	-0.002 (4)	-0.011 (3)
C6	0.180 (6)	0.077 (3)	0.080 (4)	-0.008 (3)	0.056 (4)	-0.007 (3)
C7	0.284 (8)	0.060 (3)	0.041 (3)	-0.014 (4)	0.004 (4)	-0.007 (2)
C8	0.232 (7)	0.041 (2)	0.055 (3)	-0.019 (3)	-0.062 (4)	0.012 (2)
C9	0.095 (4)	0.050 (3)	0.172 (6)	-0.007 (2)	-0.086 (4)	0.015 (3)
C10	0.055 (3)	0.049 (3)	0.223 (7)	-0.003 (2)	-0.022 (4)	-0.012 (3)
C11	0.055 (2)	0.0183 (16)	0.046 (2)	-0.0037 (13)	-0.0130 (16)	0.0015 (12)

C12	0.057 (2)	0.0269 (17)	0.041 (2)	0.0024 (13)	-0.0192 (16)	-0.0036 (12)
C13	0.057 (2)	0.0214 (16)	0.0409 (19)	-0.0007 (13)	-0.0190 (16)	-0.0010 (12)
C14	0.069 (2)	0.0227 (16)	0.053 (2)	-0.0013 (14)	-0.0261 (18)	0.0011 (13)
C15	0.063 (2)	0.0270 (17)	0.048 (2)	-0.0046 (14)	-0.0208 (17)	0.0009 (13)
C16	0.062 (2)	0.0214 (16)	0.043 (2)	-0.0050 (14)	-0.0119 (17)	-0.0053 (12)
C17	0.057 (2)	0.0216 (16)	0.055 (2)	-0.0046 (14)	-0.0146 (18)	0.0023 (14)
C18	0.080 (3)	0.0225 (17)	0.047 (2)	0.0004 (16)	-0.0342 (19)	-0.0003 (13)
C19	0.100 (3)	0.034 (2)	0.049 (2)	-0.0126 (19)	-0.035 (2)	0.0023 (15)

Geometric parameters (Å, °)

Ni1—O1	2.1106 (18)	C3—H3B	0.9700
Ni1—O3 ⁱ	2.1377 (18)	C4—H4A	0.9700
Ni1—N1	2.056 (3)	C4—H4B	0.9700
Ni1—N2	2.066 (2)	C4—C5	1.494 (6)
Ni1—N3	2.053 (3)	C5—H5A	0.9700
Ni1—N4	2.046 (3)	C5—H5B	0.9700
O1—C17	1.270 (3)	C6—H6A	0.9700
O2—C17	1.221 (3)	C6—H6B	0.9700
O3—C18	1.241 (3)	C6—C7	1.505 (7)
O4—C18	1.241 (3)	C7—H7A	0.9700
O5—H5	0.8200	C7—H7B	0.9700
O5—C19	1.305 (4)	C7—C8	1.477 (7)
O6—C19	1.200 (3)	C8—H8A	0.9700
N1—H1	0.9800	C8—H8B	0.9700
N1—C1	1.445 (5)	C9—H9A	0.9700
N1—C10	1.499 (5)	C9—H9B	0.9700
N2—H2	0.9800	C9—C10	1.467 (6)
N2—C3	1.481 (5)	C10—H10A	0.9700
N2—C4	1.434 (5)	C10—H10B	0.9700
N3—H3	0.9800	C11—C12	1.377 (3)
N3—C5	1.481 (5)	C11—C16	1.364 (4)
N3—C6	1.443 (5)	C11—C17	1.523 (4)
N4—H4	0.9800	C12—H12	0.9300
N4—C8	1.492 (5)	C12—C13	1.387 (3)
N4—C9	1.441 (6)	C13—C14	1.383 (4)
C1—H1A	0.9700	C13—C18	1.511 (4)
C1—H1B	0.9700	C14—H14	0.9300
C1—C2	1.512 (7)	C14—C15	1.375 (4)
C2—H2A	0.9700	C15—C16	1.403 (4)
C2—H2B	0.9700	C15—C19	1.488 (4)
C2—C3	1.479 (6)	C16—H16	0.9300
C3—H3A	0.9700		
O1—Ni1—O3 ⁱ	178.71 (9)	C5—C4—H4B	109.9
N1—Ni1—O1	89.78 (10)	N3—C5—C4	109.3 (4)
N1—Ni1—O3 ⁱ	91.51 (10)	N3—C5—H5A	109.8
N1—Ni1—N2	93.13 (14)	N3—C5—H5B	109.8

N2—Ni1—O1	91.66 (9)	C4—C5—H5A	109.8
N2—Ni1—O3 ⁱ	88.28 (8)	C4—C5—H5B	109.8
N3—Ni1—O1	90.19 (10)	H5A—C5—H5B	108.3
N3—Ni1—O3 ⁱ	88.52 (10)	N3—C6—H6A	108.8
N3—Ni1—N1	178.04 (14)	N3—C6—H6B	108.8
N3—Ni1—N2	84.92 (14)	N3—C6—C7	113.7 (4)
N4—Ni1—O1	87.21 (9)	H6A—C6—H6B	107.7
N4—Ni1—O3 ⁱ	92.89 (8)	C7—C6—H6A	108.8
N4—Ni1—N1	85.55 (15)	C7—C6—H6B	108.8
N4—Ni1—N2	178.25 (12)	C6—C7—H7A	107.9
N4—Ni1—N3	96.41 (15)	C6—C7—H7B	107.9
C17—O1—Ni1	132.4 (2)	H7A—C7—H7B	107.2
C18—O3—Ni1 ⁱⁱ	134.01 (19)	C8—C7—C6	117.4 (4)
C19—O5—H5	109.5	C8—C7—H7A	107.9
Ni1—N1—H1	107.1	C8—C7—H7B	107.9
C1—N1—Ni1	115.5 (3)	N4—C8—H8A	109.2
C1—N1—H1	107.1	N4—C8—H8B	109.2
C1—N1—C10	116.4 (4)	C7—C8—N4	112.2 (3)
C10—N1—Ni1	103.2 (3)	C7—C8—H8A	109.2
C10—N1—H1	107.1	C7—C8—H8B	109.2
Ni1—N2—H2	106.8	H8A—C8—H8B	107.9
C3—N2—Ni1	115.4 (2)	N4—C9—H9A	110.3
C3—N2—H2	106.8	N4—C9—H9B	110.3
C4—N2—Ni1	106.8 (2)	N4—C9—C10	106.9 (4)
C4—N2—H2	106.8	H9A—C9—H9B	108.6
C4—N2—C3	113.7 (3)	C10—C9—H9A	110.3
Ni1—N3—H3	106.8	C10—C9—H9B	110.3
C5—N3—Ni1	104.9 (3)	N1—C10—H10A	109.5
C5—N3—H3	106.8	N1—C10—H10B	109.5
C6—N3—Ni1	115.4 (3)	C9—C10—N1	110.9 (4)
C6—N3—H3	106.8	C9—C10—H10A	109.5
C6—N3—C5	115.5 (4)	C9—C10—H10B	109.5
Ni1—N4—H4	106.9	H10A—C10—H10B	108.0
C8—N4—Ni1	115.9 (3)	C12—C11—C17	120.9 (3)
C8—N4—H4	106.9	C16—C11—C12	118.9 (2)
C9—N4—Ni1	106.2 (2)	C16—C11—C17	120.2 (2)
C9—N4—H4	106.9	C11—C12—H12	119.1
C9—N4—C8	113.6 (3)	C11—C12—C13	121.7 (3)
N1—C1—H1A	109.3	C13—C12—H12	119.1
N1—C1—H1B	109.3	C12—C13—C18	121.8 (2)
N1—C1—C2	111.6 (4)	C14—C13—C12	118.5 (2)
H1A—C1—H1B	108.0	C14—C13—C18	119.6 (2)
C2—C1—H1A	109.3	C13—C14—H14	119.6
C2—C1—H1B	109.3	C15—C14—C13	120.8 (3)
C1—C2—H2A	108.4	C15—C14—H14	119.6
C1—C2—H2B	108.4	C14—C15—C16	119.1 (3)
H2A—C2—H2B	107.5	C14—C15—C19	123.4 (3)
C3—C2—C1	115.4 (4)	C16—C15—C19	117.5 (2)

C3—C2—H2A	108.4	C11—C16—C15	120.9 (2)
C3—C2—H2B	108.4	C11—C16—H16	119.5
N2—C3—H3A	109.1	C15—C16—H16	119.5
N2—C3—H3B	109.1	O1—C17—C11	114.2 (3)
C2—C3—N2	112.5 (3)	O2—C17—O1	125.6 (3)
C2—C3—H3A	109.1	O2—C17—C11	120.2 (2)
C2—C3—H3B	109.1	O3—C18—C13	117.6 (2)
H3A—C3—H3B	107.8	O4—C18—O3	124.2 (3)
N2—C4—H4A	109.9	O4—C18—C13	118.3 (2)
N2—C4—H4B	109.9	O5—C19—C15	113.8 (3)
N2—C4—C5	109.0 (3)	O6—C19—O5	123.2 (3)
H4A—C4—H4B	108.3	O6—C19—C15	123.0 (3)
C5—C4—H4A	109.9		
Ni1—O1—C17—O2	-29.8 (5)	C10—N1—C1—C2	179.3 (4)
Ni1—O1—C17—C11	149.4 (2)	C11—C12—C13—C14	-0.1 (5)
Ni1 ⁱⁱ —O3—C18—O4	9.4 (6)	C11—C12—C13—C18	-177.5 (3)
Ni1 ⁱⁱ —O3—C18—C13	-171.6 (2)	C12—C11—C16—C15	3.5 (5)
Ni1—N1—C1—C2	-59.5 (4)	C12—C11—C17—O1	-175.0 (3)
Ni1—N1—C10—C9	40.3 (4)	C12—C11—C17—O2	4.1 (5)
Ni1—N2—C3—C2	56.1 (4)	C12—C13—C14—C15	1.5 (5)
Ni1—N2—C4—C5	-40.1 (4)	C12—C13—C18—O3	176.8 (3)
Ni1—N3—C5—C4	-42.2 (4)	C12—C13—C18—O4	-4.2 (5)
Ni1—N3—C6—C7	52.7 (5)	C13—C14—C15—C16	-0.4 (5)
Ni1—N4—C8—C7	-51.9 (4)	C13—C14—C15—C19	-177.7 (3)
Ni1—N4—C9—C10	45.1 (4)	C14—C13—C18—O3	-0.7 (5)
N1—C1—C2—C3	72.3 (5)	C14—C13—C18—O4	178.4 (3)
N2—C4—C5—N3	57.0 (4)	C14—C15—C16—C11	-2.1 (5)
N3—C6—C7—C8	-71.3 (6)	C14—C15—C19—O5	10.1 (5)
N4—C9—C10—N1	-59.4 (4)	C14—C15—C19—O6	-169.3 (4)
C1—N1—C10—C9	167.9 (4)	C16—C11—C12—C13	-2.4 (5)
C1—C2—C3—N2	-70.2 (5)	C16—C11—C17—O1	2.6 (5)
C3—N2—C4—C5	-168.5 (3)	C16—C11—C17—O2	-178.2 (3)
C4—N2—C3—C2	179.9 (3)	C16—C15—C19—O5	-167.3 (3)
C5—N3—C6—C7	175.5 (4)	C16—C15—C19—O6	13.4 (6)
C6—N3—C5—C4	-170.4 (3)	C17—C11—C12—C13	175.2 (3)
C6—C7—C8—N4	69.6 (6)	C17—C11—C16—C15	-174.2 (3)
C8—N4—C9—C10	173.6 (3)	C18—C13—C14—C15	179.0 (3)
C9—N4—C8—C7	-175.2 (4)	C19—C15—C16—C11	175.3 (3)

Symmetry codes: (i) $-x+3/2, y+1/2, -z+3/2$; (ii) $-x+3/2, y-1/2, -z+3/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5 \cdots O4 ⁱⁱⁱ	0.82	1.83	2.604 (3)	157
N2—H2 \cdots O2	0.98	2.08	2.969 (3)	150

N4—H4···O4 ⁱ	0.98	2.00	2.891 (3)	151
N4—H4···O6 ^{iv}	0.98	2.59	3.226 (4)	123

Symmetry codes: (i) $-x+3/2, y+1/2, -z+3/2$; (iii) $x+1/2, -y+1/2, z+1/2$; (iv) $-x+2, -y+1, -z+2$.

catena-Poly[[[(1,4,8,11-tetraazacyclotetradecane- κ^4 N¹,N⁴,N⁸,N¹¹)nickel(II)]- μ_2 -5-carboxybenzene-1,3-dicarboxylato- κ^2 O¹:O³] monohydrate] (II)

Crystal data

[Ni(C₉H₄O₆)(C₁₀H₂₄N₄)]·H₂O

$M_r = 485.18$

Monoclinic, $P2_1/n$

$a = 9.3852$ (3) Å

$b = 15.1459$ (4) Å

$c = 15.7561$ (5) Å

$\beta = 98.604$ (3)°

$V = 2214.49$ (12) Å³

$Z = 4$

$F(000) = 1024$

$D_x = 1.455$ Mg m⁻³

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

Cell parameters from 3646 reflections

$\theta = 2.4$ – 25.9 °

$\mu = 0.92$ mm⁻¹

$T = 293$ K

Prism, clear light pink

$0.20 \times 0.20 \times 0.07$ mm

Data collection

Rigaku Xcalibur Eos

diffractometer

Radiation source: fine-focus sealed X-ray tube,

Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1593 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2021)

$T_{\min} = 0.988$, $T_{\max} = 1.000$

14088 measured reflections

4534 independent reflections

2876 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\max} = 26.4$ °, $\theta_{\min} = 1.9$ °

$h = -9$ → 11

$k = -16$ → 18

$l = -19$ → 19

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.108$

$S = 1.03$

4534 reflections

287 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 0.0138P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.32$ e Å⁻³

$\Delta\rho_{\min} = -0.43$ e Å⁻³

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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.500000	0.000000	0.500000	0.02584 (15)
Ni2	0.000000	0.500000	0.500000	0.02872 (16)
O1	0.4273 (2)	0.05862 (11)	0.60827 (13)	0.0353 (5)
O3	0.0632 (2)	0.39590 (12)	0.58677 (14)	0.0414 (6)
O4	-0.1125 (2)	0.36910 (12)	0.66423 (15)	0.0447 (6)

O2	0.4878 (2)	0.20071 (13)	0.60647 (14)	0.0467 (6)
O6	-0.1510 (3)	0.05141 (13)	0.75736 (16)	0.0520 (6)
O5	0.0511 (2)	-0.02739 (14)	0.77650 (18)	0.0554 (7)
H5	-0.000820	-0.064204	0.794730	0.083*
N2	0.7014 (3)	-0.01412 (16)	0.57185 (18)	0.0457 (7)
H2	0.701145	0.020446	0.624409	0.055*
N4	0.1739 (3)	0.46959 (16)	0.44077 (17)	0.0430 (7)
H4	0.167340	0.507198	0.389722	0.052*
N3	0.1428 (3)	0.57669 (15)	0.58082 (17)	0.0471 (7)
H3	0.171423	0.541563	0.632809	0.057*
N1	0.4558 (3)	-0.12013 (14)	0.55014 (17)	0.0449 (7)
H1	0.465282	-0.164283	0.505861	0.054*
C15	0.0616 (3)	0.11465 (16)	0.71803 (17)	0.0285 (7)
C14	-0.0002 (3)	0.19775 (16)	0.70186 (17)	0.0298 (7)
H14	-0.090488	0.209866	0.716643	0.036*
C16	0.1962 (3)	0.09647 (17)	0.69488 (17)	0.0303 (7)
H16	0.236652	0.040675	0.704847	0.036*
C11	0.2702 (3)	0.16131 (16)	0.65700 (17)	0.0277 (7)
C13	0.0737 (3)	0.26238 (16)	0.66354 (17)	0.0276 (7)
C12	0.2094 (3)	0.24429 (16)	0.64298 (17)	0.0294 (7)
H12	0.260129	0.288490	0.619479	0.035*
C18	0.0012 (3)	0.34979 (17)	0.63708 (19)	0.0315 (7)
C17	0.4080 (3)	0.13921 (18)	0.62309 (18)	0.0320 (7)
C19	-0.0245 (4)	0.04389 (19)	0.75310 (19)	0.0342 (7)
C10	0.2721 (4)	0.5851 (2)	0.5387 (2)	0.0638 (12)
H10A	0.354096	0.601851	0.580611	0.077*
H10B	0.257072	0.630564	0.494968	0.077*
C9	0.3017 (4)	0.4978 (2)	0.4984 (3)	0.0638 (12)
H9A	0.382015	0.504040	0.466614	0.077*
H9B	0.327024	0.453820	0.542783	0.077*
C3	0.8229 (4)	0.0180 (3)	0.5312 (3)	0.0659 (12)
H3A	0.832111	-0.018523	0.481770	0.079*
H3B	0.911249	0.012526	0.571549	0.079*
C4	0.7132 (4)	-0.1070 (2)	0.5974 (2)	0.0665 (12)
H4A	0.789513	-0.114001	0.645772	0.080*
H4B	0.737125	-0.142464	0.550269	0.080*
C8	0.1819 (4)	0.3768 (2)	0.4105 (2)	0.0617 (12)
H8A	0.194636	0.337322	0.459597	0.074*
H8B	0.264607	0.370223	0.380824	0.074*
C2	0.1962 (4)	-0.1130 (3)	0.4971 (3)	0.0791 (14)
H2A	0.218068	-0.147555	0.448833	0.095*
H2B	0.105101	-0.134149	0.511227	0.095*
C1	0.3115 (5)	-0.1306 (2)	0.5727 (3)	0.0694 (13)
H1A	0.299479	-0.090074	0.618793	0.083*
H1B	0.300638	-0.190172	0.593296	0.083*
C6	0.0876 (5)	0.6599 (2)	0.6088 (2)	0.0658 (12)
H6A	0.066868	0.699100	0.559851	0.079*
H6B	0.161339	0.687604	0.650001	0.079*

C7	-0.0465 (5)	0.6485 (2)	0.6492 (2)	0.0715 (13)
H7A	-0.064849	0.703405	0.677396	0.086*
H7B	-0.028017	0.603571	0.693318	0.086*
C5	0.5729 (5)	-0.1376 (2)	0.6218 (2)	0.0699 (13)
H5A	0.577720	-0.200247	0.634537	0.084*
H5B	0.553957	-0.106461	0.672815	0.084*
O1W	-0.1024 (3)	-0.15256 (17)	0.8190 (3)	0.0910 (11)
H1WA	-0.064587	-0.195140	0.849607	0.137*
H1WB	-0.191789	-0.155991	0.822448	0.137*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0253 (3)	0.0224 (3)	0.0308 (3)	0.0006 (2)	0.0073 (2)	-0.0004 (2)
Ni2	0.0254 (3)	0.0257 (3)	0.0350 (3)	0.0011 (2)	0.0041 (3)	0.0068 (2)
O1	0.0420 (13)	0.0267 (11)	0.0410 (13)	0.0045 (9)	0.0185 (11)	-0.0043 (9)
O3	0.0428 (14)	0.0343 (11)	0.0494 (14)	0.0083 (10)	0.0142 (11)	0.0191 (10)
O4	0.0421 (14)	0.0413 (12)	0.0554 (15)	0.0157 (10)	0.0229 (12)	0.0162 (10)
O2	0.0449 (15)	0.0371 (12)	0.0647 (16)	-0.0149 (10)	0.0293 (13)	-0.0184 (11)
O6	0.0456 (16)	0.0403 (13)	0.0755 (18)	0.0032 (11)	0.0268 (14)	0.0123 (11)
O5	0.0472 (15)	0.0363 (12)	0.0852 (19)	0.0030 (11)	0.0187 (14)	0.0283 (12)
N2	0.0368 (18)	0.0553 (17)	0.0431 (18)	0.0092 (13)	0.0003 (14)	-0.0133 (13)
N4	0.0342 (17)	0.0477 (15)	0.0477 (18)	0.0095 (13)	0.0082 (14)	0.0201 (13)
N3	0.058 (2)	0.0397 (15)	0.0406 (17)	-0.0138 (13)	-0.0039 (15)	0.0103 (12)
N1	0.069 (2)	0.0270 (13)	0.0444 (18)	-0.0054 (13)	0.0263 (16)	-0.0009 (12)
C15	0.0353 (18)	0.0260 (15)	0.0243 (16)	-0.0008 (13)	0.0046 (14)	0.0023 (11)
C14	0.0329 (18)	0.0288 (15)	0.0294 (17)	0.0026 (12)	0.0105 (14)	0.0021 (12)
C16	0.0395 (19)	0.0246 (15)	0.0271 (16)	0.0040 (13)	0.0056 (14)	-0.0011 (12)
C11	0.0305 (18)	0.0275 (15)	0.0253 (16)	0.0009 (12)	0.0053 (14)	-0.0026 (12)
C13	0.0338 (18)	0.0276 (15)	0.0218 (15)	0.0031 (12)	0.0052 (13)	0.0009 (11)
C12	0.0345 (18)	0.0247 (15)	0.0299 (17)	-0.0015 (12)	0.0077 (14)	0.0024 (12)
C18	0.035 (2)	0.0265 (16)	0.0315 (17)	0.0047 (13)	-0.0001 (15)	0.0008 (12)
C17	0.0337 (19)	0.0302 (17)	0.0315 (17)	0.0001 (14)	0.0025 (15)	-0.0028 (13)
C19	0.041 (2)	0.0280 (17)	0.0348 (18)	0.0018 (14)	0.0103 (16)	0.0022 (12)
C10	0.043 (2)	0.082 (3)	0.060 (3)	-0.031 (2)	-0.015 (2)	0.027 (2)
C9	0.031 (2)	0.085 (3)	0.075 (3)	0.0057 (19)	0.006 (2)	0.032 (2)
C3	0.026 (2)	0.100 (3)	0.073 (3)	-0.003 (2)	0.009 (2)	-0.036 (2)
C4	0.078 (3)	0.069 (3)	0.046 (2)	0.035 (2)	-0.013 (2)	-0.0007 (19)
C8	0.087 (3)	0.047 (2)	0.062 (3)	0.034 (2)	0.046 (3)	0.0191 (18)
C2	0.049 (3)	0.084 (3)	0.113 (4)	-0.037 (2)	0.041 (3)	-0.041 (3)
C1	0.092 (4)	0.047 (2)	0.081 (3)	-0.029 (2)	0.055 (3)	-0.010 (2)
C6	0.107 (4)	0.043 (2)	0.045 (2)	-0.023 (2)	0.002 (2)	0.0031 (17)
C7	0.128 (4)	0.042 (2)	0.047 (2)	0.010 (2)	0.022 (3)	-0.0051 (17)
C5	0.121 (4)	0.045 (2)	0.043 (2)	0.017 (2)	0.012 (3)	0.0146 (17)
O1W	0.0553 (18)	0.0570 (17)	0.170 (3)	0.0166 (14)	0.047 (2)	0.0672 (18)

Geometric parameters (Å, °)

Ni1—O1	2.1242 (19)	C16—H16	0.9300
Ni1—O1 ⁱ	2.1242 (19)	C16—C11	1.388 (4)
Ni1—N2	2.064 (3)	C11—C12	1.384 (3)
Ni1—N2 ⁱ	2.064 (3)	C11—C17	1.509 (4)
Ni1—N1 ⁱ	2.051 (2)	C13—C12	1.388 (4)
Ni1—N1	2.051 (2)	C13—C18	1.518 (4)
Ni2—O3 ⁱⁱ	2.1129 (18)	C12—H12	0.9300
Ni2—O3	2.1129 (18)	C10—H10A	0.9700
Ni2—N4 ⁱⁱ	2.050 (3)	C10—H10B	0.9700
Ni2—N4	2.050 (3)	C10—C9	1.510 (5)
Ni2—N3	2.063 (2)	C9—H9A	0.9700
Ni2—N3 ⁱⁱ	2.063 (2)	C9—H9B	0.9700
O1—C17	1.261 (3)	C3—H3A	0.9700
O3—C18	1.262 (3)	C3—H3B	0.9700
O4—C18	1.243 (3)	C3—C2 ⁱ	1.508 (5)
O2—C17	1.247 (3)	C4—H4A	0.9700
O6—C19	1.205 (3)	C4—H4B	0.9700
O5—H5	0.8200	C4—C5	1.500 (5)
O5—C19	1.314 (4)	C8—H8A	0.9700
N2—H2	0.9800	C8—H8B	0.9700
N2—C3	1.472 (4)	C8—C7 ⁱⁱ	1.512 (5)
N2—C4	1.463 (4)	C2—H2A	0.9700
N4—H4	0.9800	C2—H2B	0.9700
N4—C9	1.455 (4)	C2—C1	1.508 (5)
N4—C8	1.490 (4)	C1—H1A	0.9700
N3—H3	0.9800	C1—H1B	0.9700
N3—C10	1.473 (4)	C6—H6A	0.9700
N3—C6	1.457 (4)	C6—H6B	0.9700
N1—H1	0.9800	C6—C7	1.503 (5)
N1—C1	1.459 (4)	C7—H7A	0.9700
N1—C5	1.477 (4)	C7—H7B	0.9700
C15—C14	1.393 (4)	C5—H5A	0.9700
C15—C16	1.394 (4)	C5—H5B	0.9700
C15—C19	1.497 (4)	O1W—H1WA	0.8501
C14—H14	0.9300	O1W—H1WB	0.8501
C14—C13	1.389 (4)		
O1 ⁱ —Ni1—O1	180.0	C11—C12—H12	119.6
N2—Ni1—O1	88.88 (9)	C13—C12—H12	119.6
N2 ⁱ —Ni1—O1	91.12 (9)	O3—C18—C13	115.2 (3)
N2—Ni1—O1 ⁱ	91.11 (9)	O4—C18—O3	125.9 (3)
N2 ⁱ —Ni1—O1 ⁱ	88.88 (9)	O4—C18—C13	118.9 (3)
N2—Ni1—N2 ⁱ	180.0	O1—C17—C11	115.8 (2)
N1 ⁱ —Ni1—O1 ⁱ	87.34 (8)	O2—C17—O1	125.2 (3)
N1—Ni1—O1	87.34 (8)	O2—C17—C11	118.8 (2)
N1—Ni1—O1 ⁱ	92.66 (8)	O6—C19—O5	123.8 (3)

N1 ⁱ —Ni1—O1	92.65 (8)	O6—C19—C15	122.9 (3)
N1—Ni1—N2	85.31 (11)	O5—C19—C15	113.2 (3)
N1 ⁱ —Ni1—N2 ⁱ	85.31 (11)	N3—C10—H10A	109.8
N1—Ni1—N2 ⁱ	94.69 (11)	N3—C10—H10B	109.8
N1 ⁱ —Ni1—N2	94.69 (11)	N3—C10—C9	109.3 (3)
N1—Ni1—N1 ⁱ	180.00 (16)	H10A—C10—H10B	108.3
O3—Ni2—O3 ⁱⁱ	180.0	C9—C10—H10A	109.8
N4—Ni2—O3 ⁱⁱ	92.22 (9)	C9—C10—H10B	109.8
N4—Ni2—O3	87.78 (9)	N4—C9—C10	109.5 (3)
N4 ⁱⁱ —Ni2—O3	92.22 (9)	N4—C9—H9A	109.8
N4 ⁱⁱ —Ni2—O3 ⁱⁱ	87.78 (9)	N4—C9—H9B	109.8
N4 ⁱⁱ —Ni2—N4	180.0	C10—C9—H9A	109.8
N4 ⁱⁱ —Ni2—N3	94.62 (11)	C10—C9—H9B	109.8
N4—Ni2—N3	85.38 (11)	H9A—C9—H9B	108.2
N4—Ni2—N3 ⁱⁱ	94.62 (11)	N2—C3—H3A	109.2
N4 ⁱⁱ —Ni2—N3 ⁱⁱ	85.38 (11)	N2—C3—H3B	109.2
N3—Ni2—O3 ⁱⁱ	94.18 (9)	N2—C3—C2 ⁱ	112.2 (3)
N3 ⁱⁱ —Ni2—O3 ⁱⁱ	85.83 (9)	H3A—C3—H3B	107.9
N3—Ni2—O3	85.82 (9)	C2 ⁱ —C3—H3A	109.2
N3 ⁱⁱ —Ni2—O3	94.18 (9)	C2 ⁱ —C3—H3B	109.2
N3—Ni2—N3 ⁱⁱ	180.0	N2—C4—H4A	109.8
C17—O1—Ni1	128.73 (18)	N2—C4—H4B	109.8
C18—O3—Ni2	135.10 (19)	N2—C4—C5	109.5 (3)
C19—O5—H5	109.5	H4A—C4—H4B	108.2
Ni1—N2—H2	106.9	C5—C4—H4A	109.8
C3—N2—Ni1	115.6 (2)	C5—C4—H4B	109.8
C3—N2—H2	106.9	N4—C8—H8A	109.4
C4—N2—Ni1	106.0 (2)	N4—C8—H8B	109.4
C4—N2—H2	106.9	N4—C8—C7 ⁱⁱ	111.1 (3)
C4—N2—C3	114.0 (3)	H8A—C8—H8B	108.0
Ni2—N4—H4	106.6	C7 ⁱⁱ —C8—H8A	109.4
C9—N4—Ni2	106.7 (2)	C7 ⁱⁱ —C8—H8B	109.4
C9—N4—H4	106.6	C3 ⁱ —C2—H2A	108.2
C9—N4—C8	113.6 (3)	C3 ⁱ —C2—H2B	108.2
C8—N4—Ni2	116.0 (2)	C3 ⁱ —C2—C1	116.2 (3)
C8—N4—H4	106.6	H2A—C2—H2B	107.4
Ni2—N3—H3	106.4	C1—C2—H2A	108.2
C10—N3—Ni2	105.9 (2)	C1—C2—H2B	108.2
C10—N3—H3	106.4	N1—C1—C2	111.8 (3)
C6—N3—Ni2	116.5 (2)	N1—C1—H1A	109.3
C6—N3—H3	106.4	N1—C1—H1B	109.3
C6—N3—C10	114.6 (3)	C2—C1—H1A	109.3
Ni1—N1—H1	106.6	C2—C1—H1B	109.3
C1—N1—Ni1	116.0 (2)	H1A—C1—H1B	107.9
C1—N1—H1	106.6	N3—C6—H6A	109.0
C1—N1—C5	113.9 (3)	N3—C6—H6B	109.0
C5—N1—Ni1	106.4 (2)	N3—C6—C7	112.8 (3)
C5—N1—H1	106.6	H6A—C6—H6B	107.8

C14—C15—C16	120.0 (2)	C7—C6—H6A	109.0
C14—C15—C19	118.8 (3)	C7—C6—H6B	109.0
C16—C15—C19	121.0 (2)	C8 ⁱⁱ —C7—H7A	108.2
C15—C14—H14	120.2	C8 ⁱⁱ —C7—H7B	108.2
C13—C14—C15	119.7 (3)	C6—C7—C8 ⁱⁱ	116.4 (3)
C13—C14—H14	120.2	C6—C7—H7A	108.2
C15—C16—H16	119.9	C6—C7—H7B	108.2
C11—C16—C15	120.3 (2)	H7A—C7—H7B	107.3
C11—C16—H16	119.9	N1—C5—C4	109.3 (3)
C16—C11—C17	120.4 (2)	N1—C5—H5A	109.8
C12—C11—C16	119.4 (3)	N1—C5—H5B	109.8
C12—C11—C17	120.0 (2)	C4—C5—H5A	109.8
C14—C13—C18	120.1 (3)	C4—C5—H5B	109.8
C12—C13—C14	119.8 (2)	H5A—C5—H5B	108.3
C12—C13—C18	119.8 (2)	H1WA—O1W—H1WB	104.5
C11—C12—C13	120.9 (3)		
Ni1—O1—C17—O2	-39.4 (4)	C14—C13—C18—O4	13.4 (4)
Ni1—O1—C17—C11	135.4 (2)	C16—C15—C14—C13	-0.7 (4)
Ni1—N2—C3—C2 ⁱ	54.6 (4)	C16—C15—C19—O6	-164.3 (3)
Ni1—N2—C4—C5	-40.7 (3)	C16—C15—C19—O5	14.1 (4)
Ni1—N1—C1—C2	56.5 (4)	C16—C11—C12—C13	-2.3 (4)
Ni1—N1—C5—C4	-39.1 (3)	C16—C11—C17—O1	20.0 (4)
Ni2—O3—C18—O4	-19.0 (5)	C16—C11—C17—O2	-164.8 (3)
Ni2—O3—C18—C13	159.41 (19)	C12—C11—C17—O1	-153.7 (3)
Ni2—N4—C9—C10	-39.8 (3)	C12—C11—C17—O2	21.5 (4)
Ni2—N4—C8—C7 ⁱⁱ	55.9 (3)	C12—C13—C18—O3	9.5 (4)
Ni2—N3—C10—C9	-39.6 (3)	C12—C13—C18—O4	-171.9 (3)
Ni2—N3—C6—C7	54.0 (4)	C18—C13—C12—C11	-172.1 (2)
N2—C4—C5—N1	55.0 (4)	C17—C11—C12—C13	171.5 (3)
N3—C10—C9—N4	54.9 (4)	C19—C15—C14—C13	-175.3 (3)
N3—C6—C7—C8 ⁱⁱ	-70.5 (4)	C19—C15—C16—C11	175.6 (3)
C15—C14—C13—C12	-1.1 (4)	C10—N3—C6—C7	178.4 (3)
C15—C14—C13—C18	173.6 (2)	C9—N4—C8—C7 ⁱⁱ	-179.8 (3)
C15—C16—C11—C12	0.4 (4)	C3—N2—C4—C5	-169.0 (3)
C15—C16—C11—C17	-173.3 (3)	C3 ⁱ —C2—C1—N1	-71.5 (4)
C14—C15—C16—C11	1.1 (4)	C4—N2—C3—C2 ⁱ	177.9 (3)
C14—C15—C19—O6	10.2 (5)	C8—N4—C9—C10	-169.0 (3)
C14—C15—C19—O5	-171.4 (3)	C1—N1—C5—C4	-168.3 (3)
C14—C13—C12—C11	2.6 (4)	C6—N3—C10—C9	-169.5 (3)
C14—C13—C18—O3	-165.2 (3)	C5—N1—C1—C2	-179.4 (3)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5 \cdots O1W	0.82	1.72	2.531 (3)	170

N2—H2···O6 ⁱⁱⁱ	0.98	2.38	3.199 (4)	141
N4—H4···O4 ⁱⁱ	0.98	2.09	2.959 (3)	147
N1—H1···O2 ⁱ	0.98	1.97	2.872 (3)	153
O1 <i>W</i> —H1 <i>WA</i> ···O2 ^{iv}	0.85	1.83	2.664 (3)	168
O1 <i>W</i> —H1 <i>WB</i> ···O4 ^v	0.85	1.92	2.747 (3)	165

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $x+1, y, z$; (iv) $-x+1/2, y-1/2, -z+3/2$; (v) $-x-1/2, y-1/2, -z+3/2$.