

# Synthesis, crystal structure, stereochemical and Hirshfeld surface analysis of *trans*-diaquabis(1-phenylpropane-1,2-diamine- $\kappa^2N,N'$ )nickel(II) dichloride dihydrate

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Received 10 September 2023

Accepted 27 September 2023

Edited by M. Weil, Vienna University of Technology, Austria

**Keywords:** synthesis; X-ray crystal structure; Ni<sup>II</sup> complex; ethylenediamine metal complex; vicinal diamine derivative; DFT; Hirshfeld surface analysis; distorted octahedral complex; *trans*-Ni complex.

**CCDC reference:** 2210342

**Supporting information:** this article has supporting information at journals.iucr.org/e

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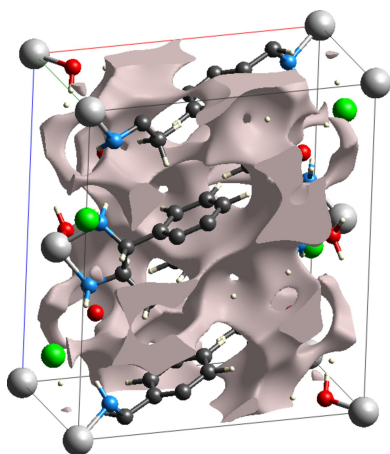
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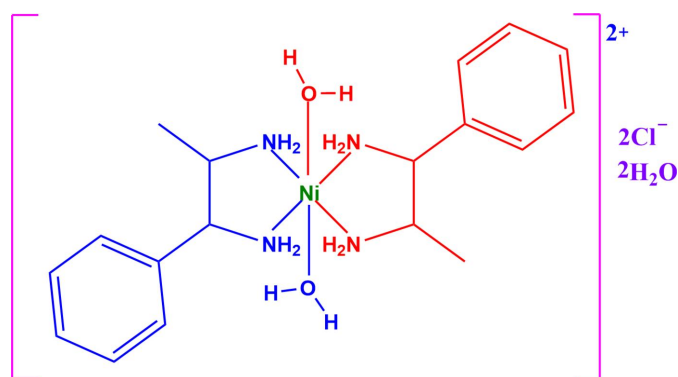
In the hydrated complex salt,  $[\text{Ni}(\text{C}_9\text{H}_{14}\text{N}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , the asymmetric unit comprises of half of the complex cation along with one chloride anion and one non-coordinating water molecule. The central nickel(II) atom is located on an inversion center and is coordinated in a *trans* octahedral fashion by four N atoms from two bidentate 1,2-diamino-1-phenylpropane ligands in the equatorial plane, and by two oxygen atoms from two water molecules occupying the axial sites. The five-membered chelate ring is in a slightly twisted envelope conformation. The crystal packing features O—H...Cl, N—H...O and N—H...Cl hydrogen bonds. Hirshfeld surface analysis revealed that the most important contributions to the crystal packing are from H...H (56.4%), O...H/H...O (16.4%) and H...Cl (13.3%) interactions. The crystal void volume was calculated to be 15.17%.

## 1. Chemical context

Unsymmetrically substituted vicinal diamines are an important class of organic compounds widely used as chelating agents. They are important structural units that have been used for decades, including in asymmetric synthesis. Besides possessing anticancer activities (Gayathri *et al.*, 2017), their metal complexes, being analogues of *cis*-platin, play crucial roles in biological processes including metal-ion-involved metabolism. In addition, such metal complexes find extensive applications in the materials field (Hussain *et al.*, 2019; Rajeshwari *et al.*, 2021). Such complexes with nickel(II) and bio-active unsymmetrically substituted vicinal diamines are interesting since nickel is found to be a major trace element, playing a crucial role as a catalytic center in many important metabolic enzymes. Exploring the molecular structure of such Ni<sup>II</sup> complexes with bio-active diamine ligands becomes inevitable in order to understand their properties and find possible applications in materials and medicinal chemistry.

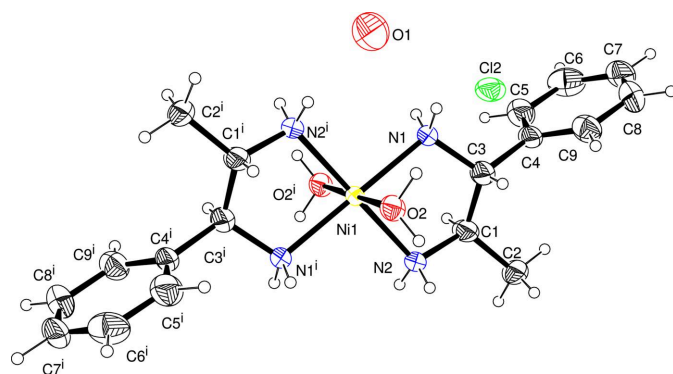
In this context, we report here on the synthesis, crystal structure and Hirshfeld surface analysis of the complex salt *trans*-diaquabis(1-phenylpropane-1,2-diamine- $\kappa^2N,N'$ )nickel(II) dichloride dihydrate,  $[\text{Ni}(\text{C}_9\text{H}_{14}\text{N}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , (I).





## 2. Structural commentary

The asymmetric unit of (I) consists of half of the cationic complex, one chloride anion and one non-coordinating water molecule. The central Ni<sup>II</sup> atom is located on an inversion center, and the other half of the cationic complex is generated by symmetry operation  $-x, -y + 1, -z + 1$ . The nickel(II) atom shows a distorted *trans*-octahedral coordination by four N atoms from two bidentate 1,2-diamino-1-phenylpropane ligands in the equatorial plane, and by two oxygen atoms from two water molecules in the axial sites (Fig. 1). The five-membered (Ni1/N1/C3/C1/N2) chelate ring is in a slightly twisted envelope conformation with puckering parameters (Cremer & Pople, 1975) of  $Q(2) = 0.346(4) \text{ \AA}$ ,  $\varphi(2) = 86.6(4)^\circ$ , closest pucker descriptor: twisted on C3–C1. The Ni1–O2 bond length is 2.158(2) Å whereas the Ni1–N bonds are shorter with 2.092(2) Å to N1 and 2.070(3) Å to N2. The differences in Ni–N bond lengths may be due to the influence of unsymmetrical substitutions at C3 and C1. The *cis*-N1–Ni1–N2 bond angle is found to be 82.45(9)° and that of *cis*-N1–Ni1–N2<sup>i</sup> is 97.55(9)°. The N1–Ni1–O2 bond angle is 91.79(9)° and that of N1<sup>i</sup>–Ni1–O2 is 88.21(9)°. The bond lengths and angles in the complex cation of (I) are comparable with those in similar structures (Sbai *et al.*, 2002; Li *et al.*, 2005; Chen *et al.*, 2006; Kim & Lee, 2002).



**Figure 1**  
View of the molecular structure of (I), showing displacement ellipsoids at the 30% probability level and spheres of arbitrary radius for the H atoms. [Symmetry code: (i)  $-x, -y + 1, -z + 1$ .]

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

<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>
O2–H2A···Cl2 <sup>i</sup>	0.85	2.29	3.134 (2)	173
O2–H2B···Cl2	0.88	2.26	3.132 (2)	170
N1–H1A···O1	0.89	2.48	3.313 (5)	157
N1–H1B···Cl2	0.89	2.69	3.464 (3)	146
N2–H2C···Cl2 <sup>i</sup>	0.84 (5)	2.68 (5)	3.460 (3)	155 (4)
N2–H2D···Cl2 <sup>ii</sup>	0.81 (5)	2.86 (5)	3.378 (3)	124 (4)

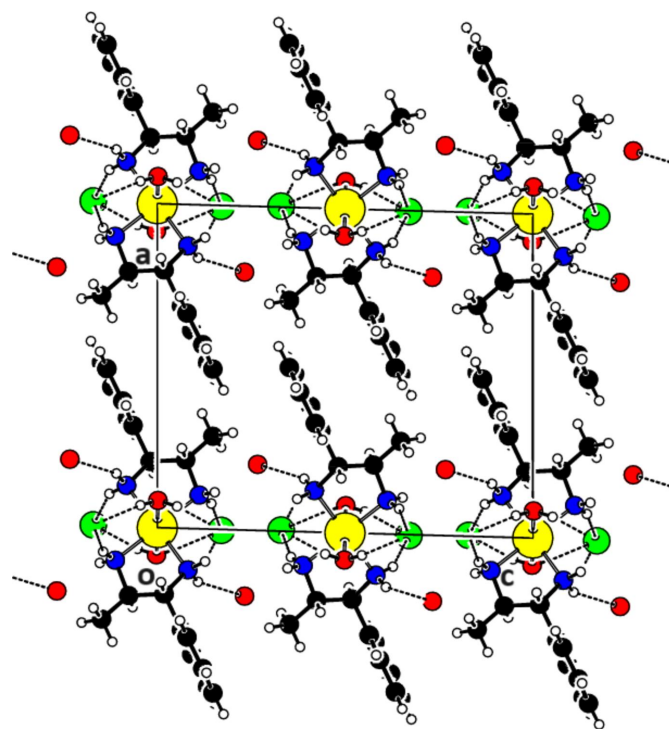
Symmetry codes: (i)  $-x, -y + 2, -z + 1$ ; (ii)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ .

## 3. Supramolecular features

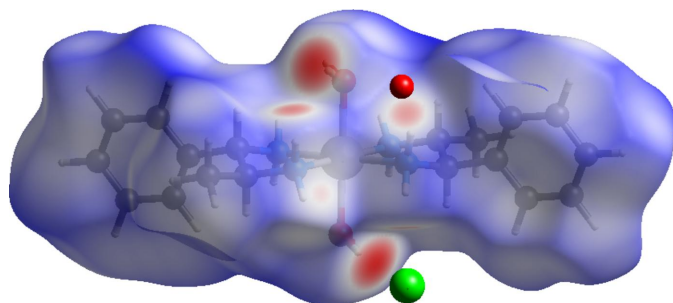
The crystal packing of (I) involves hydrogen bonding of the coordinating water molecule (O2) to the chloride anion, and of the amino groups to the non-coordinating water molecule (O1) and the chloride anion (Table 1, Fig. 2), establishing a layered arrangement parallel to (100).

## 4. Hirshfeld surface analysis

The Hirshfeld surface analysis of (I) was carried out with *CrystalExplorer* (Spackman *et al.*, 2021). Fig. 3 shows the Hirshfeld surface plotted over  $d_{\text{norm}}$  in the range  $-0.495$  to  $1.462$  a.u. where the intense red spots represent the shortest intermolecular contacts between nearest molecules, the blue spots the longest contacts and the white ones medium contacts. In this respect, interactions shorter than the van der Waals radii between O–H···Cl, N–H···Cl or N–H···O are shown as bright-red spots. The two-dimensional fingerprint



**Figure 2**  
A partial packing diagram of (I) viewed along the *b* axis showing the O–H···Cl, N–H···O and N–H···Cl hydrogen-bonding interactions as dashed lines.



**Figure 3**  
Hirshfeld surface plotted over  $d_{\text{norm}}$  for (I).

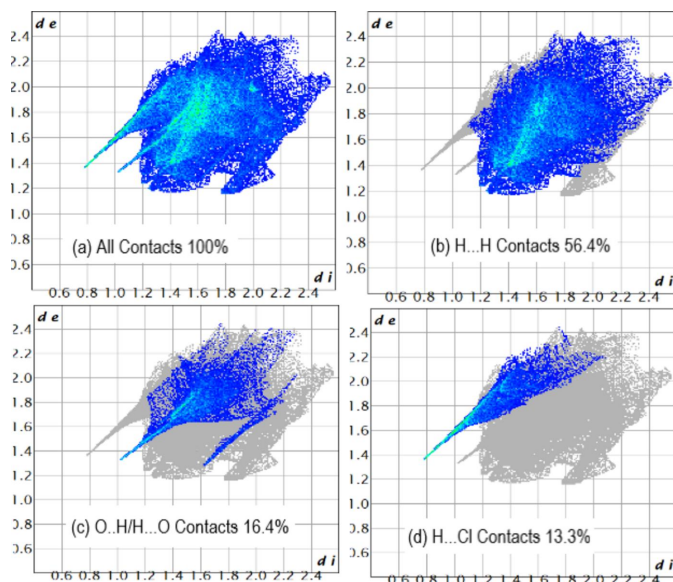
plots are plotted in Fig. 4. The most important contributions to the crystal packing are from H...H (56.4%), O...H/H...O (16.4%) and H...Cl (13.3%) interactions.

## 5. HOMO-LUMO

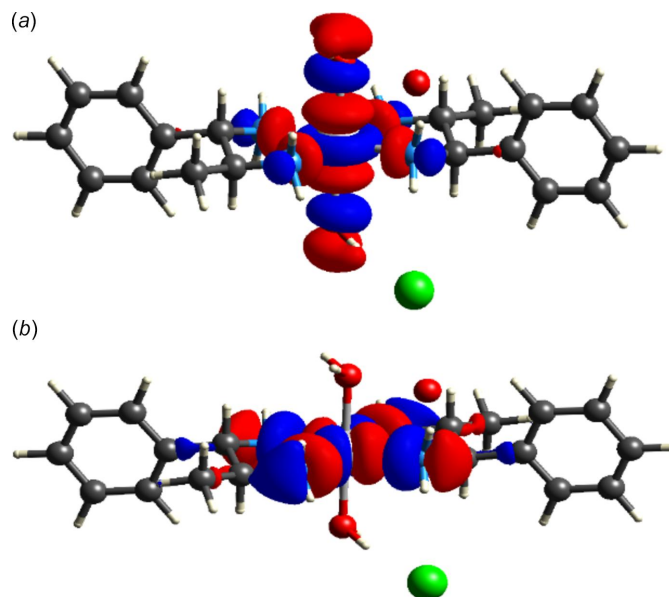
Fig. 5 represents the HOMO and LUMO of the cationic complex of (I), visualized using *TONTO* calculations in *CrystalExplorer* at the B3LYP/6-31 G(d,p) level. From the HOMO representation, it can be seen that the electrons reside mostly over the metal and water molecules, whereas in the LUMO representation, the electrons are delocalized and largely reside over the metal and amino groups.

## 6. Crystal void

In order to assess the mechanical stability of the crystal of (I), void analysis (Turner *et al.*, 2011) was performed with *CrystalExplorer*. The void volume of the crystal of (I) (Fig. 6), was calculated to be  $188.48 \text{ \AA}^3$ , *i.e.*, 15.17% of the crystal volume, which shows that the crystal is tightly packed.



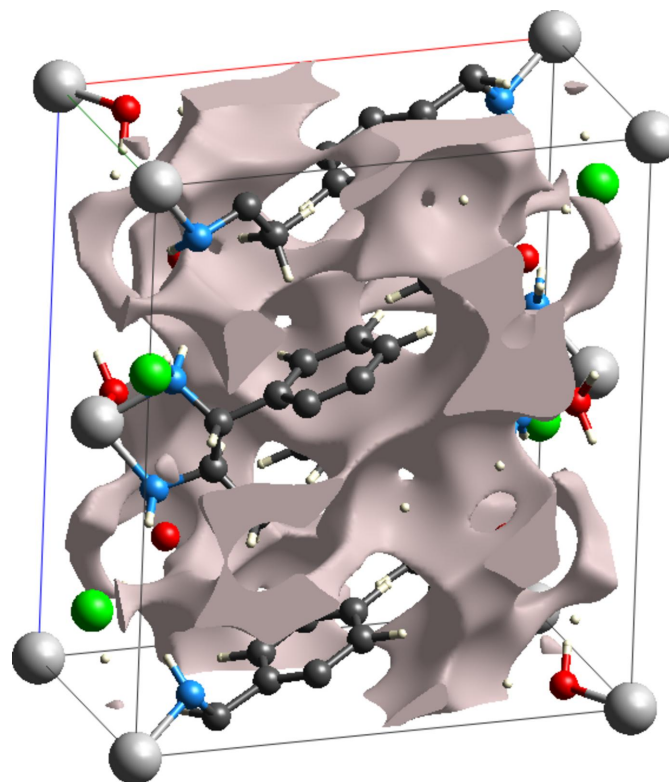
**Figure 4**  
Two-dimensional-fingerprint plots of (I).



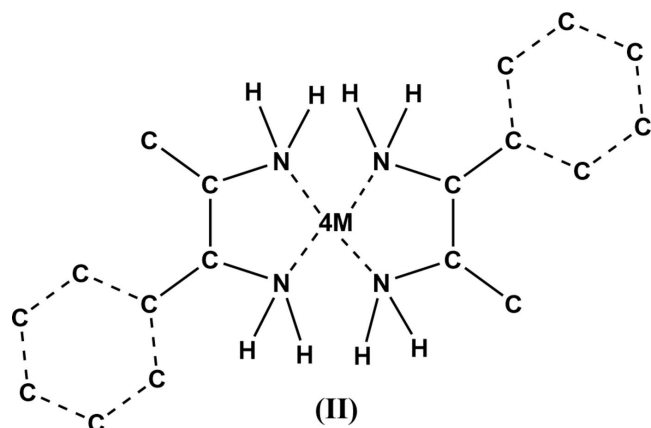
**Figure 5**  
HOMO (a) and LUMO (b) of (I).

## 7. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.44, updated June 2023; Groom *et al.*, 2016) using the molecular moiety (II) depicted in Fig. 7 for the basic skeleton of (I), with a transition-metal atom of period 4 at the center,



**Figure 6**  
Representation of the crystal voids in the crystal structure of (I).



**Figure 7**  
The molecular moiety (II) used for the CSD database search.

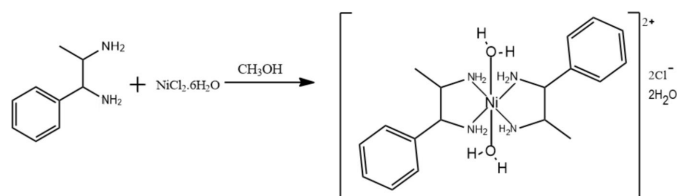
omitting aromatic H, methyl and methine H atoms, water molecules, O and Cl atoms, gave 46 hits. There are no close matches in the CSD since the title compound possesses an unsymmetrically substituted vicinal diamine ligand.

## 8. Synthesis and crystallization

The salt (I) was synthesized by addition of 1,2-diamino-1-phenylpropane (0.02 mol), prepared by the procedure reported by Noller & Baliah (1948) and Thennarasu & Perumal (2002), to a nickel dichloride hexahydrate (0.01 mol) solution in methanol (20 ml) with stirring under ice-cold conditions. The mixture was stirred in an ice bath for nearly 1 h and the pinkish-red solid formed was filtered and washed with chloroform. The schematic synthesis is shown in Fig. 8. Purification and growth of single crystals suitable for X-ray analysis was accomplished by recrystallization from methanol and slow evaporation (m.p. 497 K).

## 9. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms attached to C atoms were placed in calculated positions (with aromatic C–H = 0.93, methyl group C–H = 0.96 and methine C–H = 0.98 Å). The H atoms attached to N1 were placed at N1–H1A = 0.89 and N1–H1B = 0.89 Å. The H atoms attached to N2 were freely refined with N2–H2C = 0.84 (5) and N2–H2D = 0.81 (5) Å. O1 is the O atom of the non-coordinating water



**Figure 8**  
Synthesis scheme of (I).

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	[Ni(C <sub>9</sub> H <sub>14</sub> N <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O
<i>M<sub>r</sub></i>	502.12
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> / <i>c</i>
Temperature (K)	298
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.1130 (7), 7.3062 (4), 14.0441 (8)
$\beta$ (°)	91.589 (2)
<i>V</i> (Å <sup>3</sup> )	1242.42 (12)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.02
Crystal size (mm)	0.31 × 0.27 × 0.21
Data collection	
Diffractometer	Bruker D8 Quest XRD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.634, 0.746
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	15989, 3619, 2841
<i>R<sub>int</sub></i>	0.020
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.704
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.061, 0.140, 1.08
No. of reflections	3619
No. of parameters	144
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	1.52, -0.91

Computer programs: *APEX3* and *SAINT* (Bruker, 2017), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

molecule. The two H-atom positions around this O atom were not discernible from difference-Fourier maps and are not included in the model. The H atoms attached to O2 were placed at O2–H2A = 0.85 and O2–H2B = 0.88 Å. All H atoms (except the freely refined H2C and H2D atoms) were included as riding contributions with isotropic displacement parameters *U*<sub>iso</sub>(H) = 1.2 and 1.5*U*<sub>eq</sub>(C), 1.2*U*<sub>eq</sub>(N) and 1.5*U*<sub>eq</sub>(O).

## Acknowledgements

Authors thank DST PURSE Phase II, Department of Chemistry, Annamalai University for support of the single-crystal XRD data collection.

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## supporting information

*Acta Cryst.* (2023). E79, 967-971 [https://doi.org/10.1107/S2056989023008538]

## Synthesis, crystal structure, stereochemical and Hirshfeld surface analysis of *trans*-diaquabis(1-phenylpropane-1,2-diamine- $\kappa^2N,N'$ )nickel(II) dichloride dihydrate

**Shanmugasundaram Akila, Thankakan Vidhyasagar, Aravazhi Amalan Thiruvalluvar and Krishnan Rajeswari**

### Computing details

Data collection: *APEX3* (Bruker, 2017); cell refinement: *SAINT* (Bruker, 2017); data reduction: *SAINT* (Bruker, 2017); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### *trans*-Diaquabis(1-phenylpropane-1,2-diamine- $\kappa^2N,N'$ )nickel(II) dichloride dihydrate

#### Crystal data

[Ni(C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O  
 $M_r = 502.12$   
 Monoclinic,  $P2_1/c$   
 $a = 12.1130$  (7) Å  
 $b = 7.3062$  (4) Å  
 $c = 14.0441$  (8) Å  
 $\beta = 91.589$  (2)°  
 $V = 1242.42$  (12) Å<sup>3</sup>  
 $Z = 2$   
 $F(000) = 524$

$D_x = 1.331$  Mg m<sup>-3</sup>  
 Melting point: 497 K  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 7663 reflections  
 $\theta = 3.1\text{--}30.0^\circ$   
 $\mu = 1.02$  mm<sup>-1</sup>  
 $T = 298$  K  
 Block, pink  
 $0.31 \times 0.27 \times 0.21$  mm

#### Data collection

Bruker D8 Quest XRD  
 diffractometer  
 Detector resolution: 7.3910 pixels mm<sup>-1</sup>  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (*SADABS*; Krause *et al.*, 2015)  
 $T_{\min} = 0.634$ ,  $T_{\max} = 0.746$   
 15989 measured reflections

3619 independent reflections  
 2841 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$   
 $\theta_{\max} = 30.0^\circ$ ,  $\theta_{\min} = 3.1^\circ$   
 $h = -17 \rightarrow 16$   
 $k = -10 \rightarrow 10$   
 $l = -19 \rightarrow 17$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.061$   
 $wR(F^2) = 0.140$   
 $S = 1.08$   
 3619 reflections

144 parameters  
 0 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 2.3825P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.52 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.91 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: SHELXL-2019/3  
 (Sheldrick, 2015b),  
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.011 (2)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.000000	0.500000	0.500000	0.03444 (17)
O1	0.2039 (4)	0.2818 (7)	0.2674 (3)	0.1230 (15)
O2	-0.08403 (19)	0.7604 (3)	0.49802 (16)	0.0480 (5)
H2A	-0.067927	0.830472	0.544916	0.072*
H2B	-0.067224	0.824263	0.447313	0.072*
Cl2	0.00298 (9)	0.99682 (12)	0.32983 (6)	0.0590 (3)
N1	0.1278 (2)	0.6032 (3)	0.41843 (16)	0.0393 (5)
H1A	0.163790	0.511552	0.391321	0.047*
H1B	0.100305	0.675472	0.372616	0.047*
N2	0.1041 (2)	0.5800 (4)	0.61171 (18)	0.0402 (5)
C1	0.2120 (3)	0.6298 (7)	0.5760 (2)	0.0656 (11)
H1	0.247413	0.511203	0.565627	0.079*
C2	0.2870 (3)	0.7202 (6)	0.6481 (3)	0.0608 (10)
H2E	0.356214	0.748091	0.619709	0.091*
H2F	0.299490	0.639331	0.701219	0.091*
H2G	0.253580	0.831281	0.669762	0.091*
C3	0.2038 (3)	0.7078 (7)	0.4816 (3)	0.0670 (11)
H3	0.167920	0.826718	0.489949	0.080*
C4	0.3132 (3)	0.7513 (6)	0.4357 (2)	0.0568 (9)
C5	0.3882 (4)	0.6251 (7)	0.4081 (3)	0.0793 (13)
H5	0.374550	0.501135	0.416994	0.095*
C6	0.4867 (4)	0.6819 (9)	0.3659 (4)	0.0890 (16)
H6	0.538556	0.595730	0.347740	0.107*
C7	0.5056 (3)	0.8635 (9)	0.3517 (3)	0.0806 (15)
H7	0.570103	0.901948	0.323347	0.097*
C8	0.4309 (4)	0.9858 (7)	0.3788 (4)	0.0824 (14)
H8	0.443916	1.109789	0.368966	0.099*
C9	0.3354 (3)	0.9320 (7)	0.4208 (3)	0.0669 (10)
H9	0.284926	1.020016	0.439403	0.080*
H2C	0.079 (3)	0.667 (6)	0.644 (3)	0.068 (13)*
H2D	0.114 (4)	0.503 (6)	0.653 (3)	0.076 (14)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.0403 (3)	0.0322 (3)	0.0311 (3)	-0.0052 (2)	0.00578 (18)	0.00010 (19)
O1	0.126 (3)	0.115 (3)	0.128 (4)	0.001 (3)	0.006 (3)	0.009 (3)
O2	0.0588 (13)	0.0360 (11)	0.0495 (12)	0.0009 (10)	0.0076 (10)	0.0012 (9)
Cl2	0.0953 (7)	0.0415 (4)	0.0409 (4)	0.0030 (4)	0.0133 (4)	-0.0025 (3)
N1	0.0426 (12)	0.0424 (13)	0.0331 (11)	-0.0084 (10)	0.0038 (9)	0.0001 (10)
N2	0.0450 (13)	0.0439 (14)	0.0318 (12)	-0.0060 (11)	0.0047 (10)	0.0005 (11)
C1	0.0497 (19)	0.107 (3)	0.0399 (17)	-0.026 (2)	0.0018 (14)	0.0001 (19)
C2	0.0518 (19)	0.082 (3)	0.0479 (19)	-0.0132 (19)	-0.0065 (15)	-0.0045 (18)
C3	0.058 (2)	0.095 (3)	0.0470 (19)	-0.031 (2)	0.0043 (16)	-0.0007 (19)
C4	0.0435 (17)	0.086 (3)	0.0412 (16)	-0.0226 (18)	0.0046 (13)	-0.0004 (17)
C5	0.102 (4)	0.063 (3)	0.074 (3)	-0.008 (3)	0.015 (3)	0.002 (2)
C6	0.072 (3)	0.120 (5)	0.076 (3)	0.029 (3)	0.012 (2)	-0.008 (3)
C7	0.049 (2)	0.126 (5)	0.068 (3)	-0.027 (3)	0.0143 (18)	0.000 (3)
C8	0.084 (3)	0.079 (3)	0.085 (3)	-0.027 (3)	0.019 (3)	0.007 (3)
C9	0.057 (2)	0.080 (3)	0.065 (2)	-0.001 (2)	0.0106 (18)	0.005 (2)

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

Ni1—N2 <sup>i</sup>	2.070 (3)	C2—H2E	0.9600
Ni1—N2	2.070 (3)	C2—H2F	0.9600
Ni1—N1 <sup>i</sup>	2.092 (2)	C2—H2G	0.9600
Ni1—N1	2.092 (2)	C3—C4	1.523 (5)
Ni1—O2 <sup>i</sup>	2.158 (2)	C3—H3	0.9800
Ni1—O2	2.158 (2)	C4—C5	1.359 (6)
O2—H2A	0.8524	C4—C9	1.364 (6)
O2—H2B	0.8799	C5—C6	1.409 (7)
N1—C3	1.475 (4)	C5—H5	0.9300
N1—H1A	0.8900	C6—C7	1.362 (8)
N1—H1B	0.8900	C6—H6	0.9300
N2—C1	1.458 (4)	C7—C8	1.335 (7)
N2—H2C	0.84 (5)	C7—H7	0.9300
N2—H2D	0.81 (5)	C8—C9	1.371 (6)
C1—C3	1.444 (5)	C8—H8	0.9300
C1—C2	1.496 (5)	C9—H9	0.9300
C1—H1	0.9800		
N2 <sup>i</sup> —Ni1—N2	180.0	C3—C1—H1	103.4
N2 <sup>i</sup> —Ni1—N1 <sup>i</sup>	82.45 (9)	N2—C1—H1	103.4
N2—Ni1—N1 <sup>i</sup>	97.55 (9)	C2—C1—H1	103.4
N2 <sup>i</sup> —Ni1—N1	97.55 (9)	C1—C2—H2E	109.5
N2—Ni1—N1	82.45 (9)	C1—C2—H2F	109.5
N1 <sup>i</sup> —Ni1—N1	180.0	H2E—C2—H2F	109.5
N2 <sup>i</sup> —Ni1—O2 <sup>i</sup>	92.17 (11)	C1—C2—H2G	109.5
N2—Ni1—O2 <sup>i</sup>	87.83 (11)	H2E—C2—H2G	109.5
N1 <sup>i</sup> —Ni1—O2 <sup>i</sup>	91.79 (9)	H2F—C2—H2G	109.5



N1—Ni1—O2 <sup>i</sup>	88.21 (9)	C1—C3—N1	111.9 (3)
N2 <sup>i</sup> —Ni1—O2	87.83 (11)	C1—C3—C4	115.7 (3)
N2—Ni1—O2	92.17 (11)	N1—C3—C4	112.9 (3)
N1 <sup>i</sup> —Ni1—O2	88.21 (9)	C1—C3—H3	105.0
N1—Ni1—O2	91.79 (9)	N1—C3—H3	105.0
O2 <sup>i</sup> —Ni1—O2	180.00 (11)	C4—C3—H3	105.0
Ni1—O2—H2A	114.9	C5—C4—C9	118.5 (4)
Ni1—O2—H2B	111.0	C5—C4—C3	125.1 (4)
H2A—O2—H2B	104.7	C9—C4—C3	116.4 (4)
C3—N1—Ni1	108.45 (19)	C4—C5—C6	120.1 (5)
C3—N1—H1A	110.0	C4—C5—H5	120.0
Ni1—N1—H1A	110.0	C6—C5—H5	120.0
C3—N1—H1B	110.0	C7—C6—C5	119.8 (5)
Ni1—N1—H1B	110.0	C7—C6—H6	120.1
H1A—N1—H1B	108.4	C5—C6—H6	120.1
C1—N2—Ni1	110.06 (19)	C8—C7—C6	119.5 (4)
C1—N2—H2C	110 (3)	C8—C7—H7	120.2
Ni1—N2—H2C	114 (3)	C6—C7—H7	120.2
C1—N2—H2D	107 (3)	C7—C8—C9	121.1 (5)
Ni1—N2—H2D	115 (3)	C7—C8—H8	119.4
H2C—N2—H2D	101 (4)	C9—C8—H8	119.4
C3—C1—N2	112.0 (3)	C4—C9—C8	121.1 (4)
C3—C1—C2	118.2 (4)	C4—C9—H9	119.5
N2—C1—C2	114.3 (3)	C8—C9—H9	119.5
Ni1—N2—C1—C3	32.1 (5)	C1—C3—C4—C9	-113.5 (5)
Ni1—N2—C1—C2	169.9 (3)	N1—C3—C4—C9	115.7 (4)
N2—C1—C3—N1	-44.5 (5)	C9—C4—C5—C6	0.6 (7)
C2—C1—C3—N1	179.4 (4)	C3—C4—C5—C6	179.8 (4)
N2—C1—C3—C4	-175.8 (4)	C4—C5—C6—C7	-0.9 (8)
C2—C1—C3—C4	48.2 (6)	C5—C6—C7—C8	0.6 (8)
Ni1—N1—C3—C1	33.9 (4)	C6—C7—C8—C9	0.1 (8)
Ni1—N1—C3—C4	166.5 (3)	C5—C4—C9—C8	0.1 (7)
C1—C3—C4—C5	67.3 (6)	C3—C4—C9—C8	-179.2 (4)
N1—C3—C4—C5	-63.4 (5)	C7—C8—C9—C4	-0.4 (7)

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

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

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O2—H2A $\cdots$ Cl2 <sup>ii</sup>	0.85	2.29	3.134 (2)	173
O2—H2B $\cdots$ Cl2	0.88	2.26	3.132 (2)	170
N1—H1A $\cdots$ O1	0.89	2.48	3.313 (5)	157
N1—H1B $\cdots$ Cl2	0.89	2.69	3.464 (3)	146
N2—H2C $\cdots$ Cl2 <sup>ii</sup>	0.84 (5)	2.68 (5)	3.460 (3)	155 (4)
N2—H2D $\cdots$ Cl2 <sup>iii</sup>	0.81 (5)	2.86 (5)	3.378 (3)	124 (4)

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