Crystal structure and Hirshfeld surface analysis of (nitrato-κ^2O,O')(1,4,7,10-tetraazacyclododecane-κ^4N)nickel(II) nitrate

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The crystal structure of the title compound, [Ni($C_8H_{20}N_4$)(NO_3)]NO_3, at room temperature, has monoclinic ($P2_1/n$) symmetry. The structure displays intermolecular hydrogen bonding. The nickel displays a distorted bipyramidal geometry with the symmetric bidentate bonded nitrate occupying an equatorial site. The 1,4,7,10-tetraazacyclododecane (cyclen) backbone has the [4,8] configuration, with three nitrogen-bound H atoms directed above the plane of the nitrogen atoms towards the offset nickel atom with the fourth nitrogen-bound hydrogen directed below from the plane of the nitrogen atoms. The nitrate anion O atoms are seen to hydrogen bond to the H atoms bound to the N atoms of the ligand.

1. Chemical context

The scientific community has long been acquainted with 1,4,7,10-tetraazacyclododecane (cyclen) transition-metal complexes to nitrate with nitrate as a counter-ion. Nevertheless, it is important to emphasize that the structure of the coordinated complex of nickel(cyclen) and nitrate, with nitrate as the counter-ion, has not been previously documented. The absence of such a publication can be attributed to the difficulties encountered in crystallizing the [Ni(cyclen)NO_3]NO_3 complex. This manuscript provides a comprehensive overview of the synthesis, crystallization, and structural analysis of [Ni(cyclen)NO_3]NO_3. It is noteworthy to mention that this manuscript represents the culmination of a crystallographic workshop conducted by students and faculty of Prairie View A&M and Texas A&M Universities.
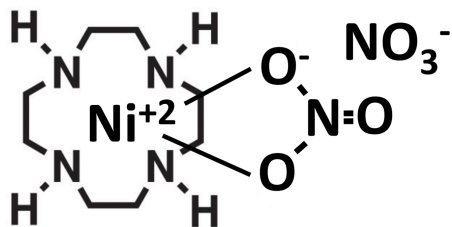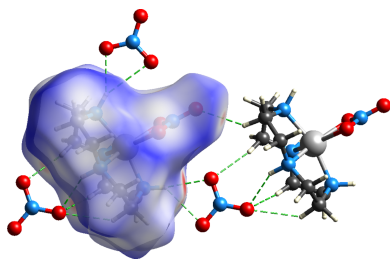
2. Structural commentary

Fig. 1 illustrates the structure of the title compound, which crystallizes in the $P2_1/n$ space group and also displays a cyclen backbone that exhibits the [4,8] configuration (four bonds between the corner atoms C3 and C7 and eight bonds between
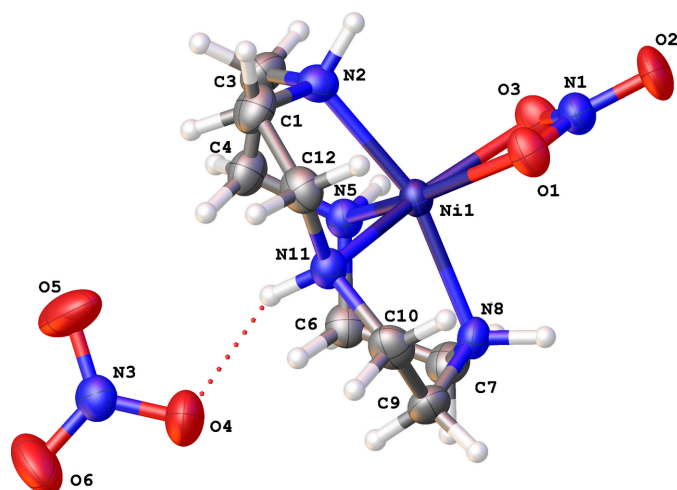
Figure 1
Displacement plot (50% probability ellipsoids) of [Ni(cyclen)NO₃]NO₃.

C7 back to C3; Meyer *et al.*, 1998). Three of the four hydrogen atoms bound to nitrogens (N2, N5, N8) of the cyclen ring are positioned above the plane of the nitrogen atoms and on the same side as the displaced nickel atom, and the hydrogen bound to the remaining nitrogen (N11) is below the plane of the nitrogen atoms. The nickel atom can be characterized as having a distorted trigonal–bipyramidal structure, with N2 and N8 (cyclen) occupying the axial positions, and N5 (cyclen), N11 (cyclen), and the bidentate nitrate occupying the equatorial sites. There are two nitrates present, one nitrate is the counter-ion and the second nitrate is bonded to the nickel in a bidentate B01 configuration (Morozov *et al.*, 2008). The cause of distortion to the expected [3,3,3,3] conformation (as seen in Cu^{II} structures) is unknown but can possibly be attributed to the Jahn–Teller effect expected in the Cu^{II} species *versus* Ni^{II}, which is greater for Cu^{II} than for Ni^{II} (Reinen *et al.*, 1988).

There exists a 'twisting' around the trigonal plane (of the trigonal–bipyramidal structure) of nitrate oxygens to the nitrogen N11 – H (on N11) to N5 – H (on N5). In the Cu^{II} cyclen nitrate study by Gasser *et al.* (2007), they showed that there was repulsion between the hydrogen of the nitrogen between the two most distorted angles, which caused a longer Cu—O bond on that side of the complex *versus* the Cu—O bond closer to the more symmetric N—Cu—N angles. This distortion, potentially caused by the nitrate, is also seen in the nickel macrocycle reported here, to the point of causing a shift in the coordination sphere geometry of the nickel.

Additionally, the nitrate group bond in [Ni(cyclen)NO₃]-NO₃, has a distorted bidentate bond to the nickel atom [Ni1···O1 = 2.151 (3) Å, Ni1··· O3 2.113 (3) Å] with a potentially large area of interaction with nickel's coordination space. The nitrate ligand is bound by two separate bonds (bidentate) and occupies more than a single bond space, with its resonance causing an increase of ligand energy close to the metal. This contributes to the 'twisting' of the structure that was also seen in the similar structure of nickel cyclen acetate (Verma *et al.*, 2022). Most notably, copper and nickel structures of the same form, experience distortions to their cyclen

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$O4^i	0.98	2.22	3.091 (5)	147
N5—H5$\cdots$O3^{ii}	0.98	2.32	3.130 (4)	139
N8—H8$\cdots$O5^{iii}	0.98	2.28	3.253 (5)	172
N8—H8$\cdots$O6^{iii}	0.98	2.50	3.273 (5)	135
N11—H11$\cdots$O4	0.98	2.14	3.030 (5)	151

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

conformations when nitrate is present. For copper, there is a distortion to the [3,3,3,3] symmetry and for nickel, there is a 'twisting' causing a [4,8] conformation.

3. Supramolecular features

The anion, NO₃⁻, forms a hydrogen bond with the hydrogen bound to N2 of the cyclen ring and the hydrogen bound to N11 of an adjacent [Ni(cyclen)NO₃]⁺ complex, effectively bridging the two cationic complexes through the same nitrate oxygen atom (O4) (see Fig. 2, Table 1). The remaining oxygens atoms of the anion (O5, O6) form hydrogen bonds to the hydrogen bound to N8 of an adjacent cation. Hydrogen bonds to the NO₃⁻ anion are: N11···O4 = 3.030 (5) Å, N2···O4($-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$) = 3.091 (5) Å, N8···O5($x + 1, y, z$) = 3.253 (5) Å, N8 ··· O6($x + 1, y, z$) = 3.273 (5) Å and to the bound nitrate the distances are: N5···O3($-x + 1, -y + 1, -z + 1$) = 3.130 (4) Å, see Fig. 2.
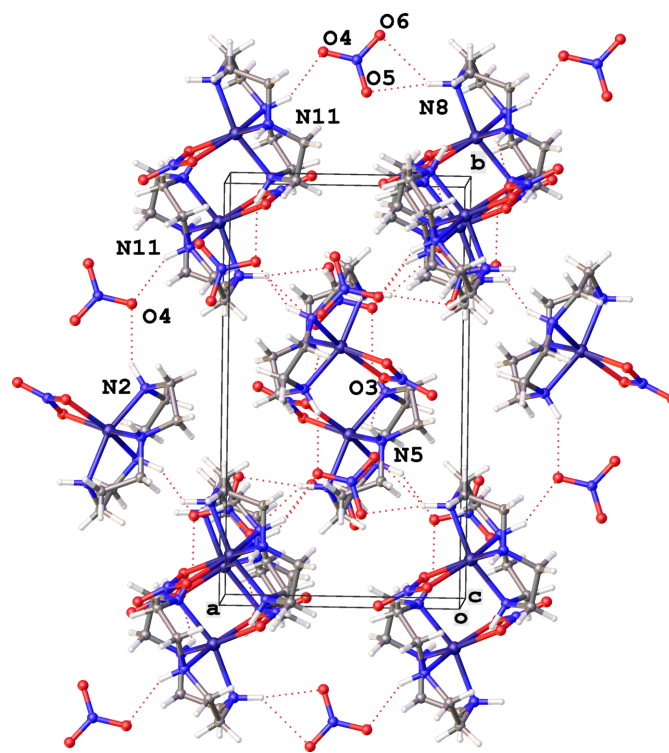

Figure 2
A packing plot (with unit-cell box, viewed down the *c* axis, where the *a* axis is horizontal and the *b* axis is vertical) highlighting the hydrogen bonds to NO₃⁻ in [Ni(cyclen)NO₃]NO₃. Dashed lines indicate hydrogen bonds (Table 1).
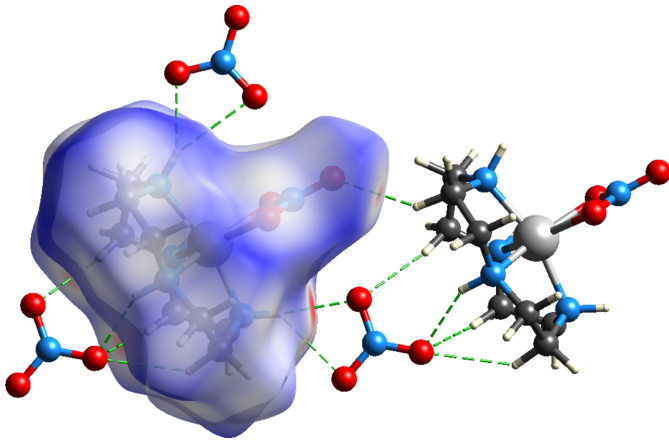
Figure 3
Hirshfeld surface plot of [Ni(cyclen)NO$_3$]NO$_3$. Dashed lines indicate hydrogen bonds and close contacts.

Fig. 3 shows the Hirshfeld surface (Spackman *et al.*, 2021) and indicates short contacts for hydrogens bound to nitrogen and nitrate oxygens of the unbound nitrate (anion) and a slightly longer contact between the carbon hydrogens and the terminal oxygen of the bound nitrate, while the bound oxygen atom of the bound nitrate forms a long hydrogen bond to the nitrogen atom of a nearby cation. The fingerprint plot (Fig. 4) indicates that the [Ni(cyclen)NO$_3$]$^+$ hydrogens to nitrate anion oxygen contacts make about 33.3% (N—H$_{inside}$···O$_{outside}$) of all close contacts, while the fingerprint plot (Fig. 5) indicates that the [Ni(cyclen)NO$_3$]$^+$ oxygens to [Ni(cyclen)NO$_3$]$^+$ hydrogens (adjacent molecules) make about 15.6% [O$_{insi-}$

Figure 5
Fingerprint plot of the close contacts between [Ni(cyclen)NO$_3$]$^+$ cation O atoms to adjacent [Ni(cycle)NO$_3$] H atoms [O(in)···H(out)], which equals 15.6% of the surface area.

de···H—N$_{outside}$ and O$_{inside}$···H—C$_{outside}$] of the close contacts.

4. Database survey

A search of the Cambridge Structural Database (CSD, updated to June 2024, Groom *et al.*, 2016) found the [Ni(cyclen)acetate]Br complex (CSD refcode: KALQUN; Verma *et al.*, 2022), which displays a similar trigonal–bipyramidal nickel complexed to a cyclen in a [4,8] configuration with a bidentate acetate bound in one of the axial positions of the trigonal bipyramid. This configuration is relatively common for nickel cyclen complexes as opposed to the similar size copper cyclen complexes, which have the [3,3,3,3] 'square' configuration (Verma *et al.*, 2022). However, Gasser *et al.* (2007) reported a distortion to some copper cyclen complex geometries including one with a monodentate nitrate (CSD refcode: TZCDCU; Clay *et al.*, 1979) and one with an additional ligand (ferrocene methyl) that caused the nitrate to appear bidentate (CSD refcode: UDINOL; Gasser *et al.* 2007). They suspect that the second bond of the nitrate to the copper was electrostatic due to the steric interference of the ligand on the cyclen. The zinc cyclen nitrate compound, as described by Vargova *et al.* (2007) (CSD refcode: MIKBOY), displays the nitrate ligand in a monodentate coordination, while the tetramethylcyclen nickel nitrate structure, as reported by Yenuganti *et al.* (2020) (CSD refcode: XACDEO), showcases a symmetrical bidentate B01 nitrate ligand. Furthermore, both structures share the cyclen backbone in the [3,3,3,3] 'square' structure, which is also seen in the uncomplexed (free) cyclen ligand (CSD refcode:VUCGEF; Reibenspies, 1992)
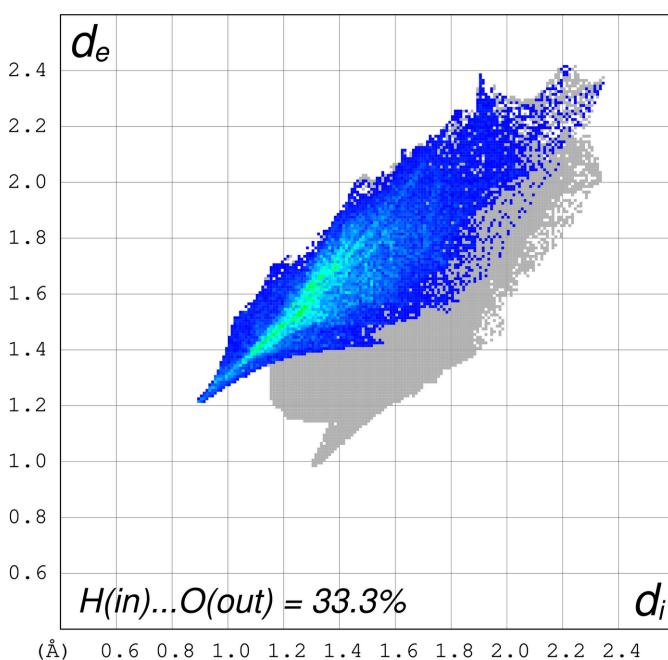

Figure 4
Fingerprint plot of the close contacts between [Ni(cyclen)NO$_3$]$^+$ cation H atoms to the adjacent nitrate anion O atoms [H(in)···O(out)], which equals 33.3% of the surface area.

Table 2
Experimental details.

Crystal data
Chemical formula	$[Ni(C_8H_{20}N_4)(NO_3)]NO_3$
M_r	355.01
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, b, c (Å)	8.7321 (5), 15.2444 (9), 10.8545 (6)
β (°)	94.973 (5)
V (Å^3)	1439.47 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.39
Crystal size (mm)	$0.4 \times 0.3 \times 0.02$

Data collection
Diffractometer	XtaLAB Mini II
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2024)
T_{min}, T_{max}	0.899, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12195, 12195, 9604
R_{int}	0.038

Refinement
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.104, 1.09
No. of reflections	12195
No. of parameters	191
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.28

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXT* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b) and *OLEX2* (Dolomanov et al., 2009).

5. Synthesis and crystallization

0.2 g of cyclen were added to a solution of Ni(NO$_3$)$_2$·6H$_2$O (0.3 g dissolved in 1 ml of distilled water), resulting in the formation of a deep-blue solution, which was then transferred to a 5 ml uncapped vial, which was placed inside a 10 ml vial. The 10 ml vial was filled with 3 ml of absolute ethanol (outside of the 5 ml vial). The 10 ml vial was capped and after 24 h, the ethanol had diffused into the aqueous solution, but no crystals were observed. To address this, the cap of the vapor diffusion apparatus (10 ml vial) was removed, allowing the aqueous/ethanol solution to evaporate. After an additional 24 h, light-blue crystals were discovered above the concentrated blue solution and collected from the 5 ml vial. It is important to note that normal evaporation of the aqueous solution will yield a blue oil without any crystallization.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. During the final stages of refinement a twin was detected from analysis of the structure factor file (FCF), which contains the calculated and observed structure factors (Dolomanov et al., 2009). The refinement of the twin (1 0 0.139 0 − 1 0 0 0 − 1, BASF of 0.177, twofold about the *a* axis) resulted in an improved structure and a decrease in the residual values. Publication documents were generated with the program *publCIF* (Westrip, 2010).

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Computing details

(Nitrato-κ^2O,O')(1,4,7,10-tetraazacyclododecane-κ^4N)nickel(II) nitrate

Crystal data

[Ni(C$_8$H$_{20}$N$_4$)(NO$_3$)]NO$_3$	$F(000) = 744$
$M_r = 355.01$	$D_x = 1.638$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.7321$ (5) Å	Cell parameters from 4001 reflections
$b = 15.2444$ (9) Å	$\theta = 2.3–29.9°$
$c = 10.8545$ (6) Å	$\mu = 1.39$ mm^{-1}
$\beta = 94.973$ (5)°	$T = 293$ K
$V = 1439.47$ (14) Å^3	Plate, blue
$Z = 4$	$0.4 \times 0.3 \times 0.02$ mm

Data collection

XtaLAB Mini II diffractometer	12195 independent reflections
Detector resolution: 10.0000 pixels mm^{-1}	9604 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.038$
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2024)	$\theta_{max} = 26.4°$, $\theta_{min} = 2.3°$
	$h = -10 \rightarrow 8$
$T_{min} = 0.899$, $T_{max} = 1.000$	$k = -19 \rightarrow 19$
12195 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.8788P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	
$S = 1.09$	
12195 reflections	$(\Delta/\sigma)_{max} < 0.001$
191 parameters	$\Delta\rho_{max} = 0.39$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.28$ e Å^{-3}
Primary atom site location: dual	

Special details

Experimental. Single crystals of $C_8H_{20}N_6NiO_6$ [Ni(cyclen)NO₃]NO₃ were obtained by vapor diffusion followed by evaporation. A suitable crystal was selected and mounted on a RIGAKU XtaLAB Mini II diffractometer. The crystal was kept at 293 (2) K during data collection (*CrysAlis PRO* : Rigaku Oxford Diffraction, 2024). Employing *Olex2* (Dolomanov *et al.*, 2009), the structure was solved with the *SHELXT* (Sheldrick, 2015a) structure solution program and refined with the *SHELXL* (Sheldrick, 2015b) refinement package using full-matrix least-squares minimization.

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.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.47429 (5)	0.40178 (3)	0.71868 (4)	0.02627 (16)
O1	0.6641 (3)	0.44290 (18)	0.8450 (2)	0.0402 (7)
O2	0.8551 (3)	0.5139 (2)	0.7739 (3)	0.0626 (10)
O3	0.6572 (3)	0.47217 (18)	0.6500 (2)	0.0414 (8)
N1	0.7303 (4)	0.4775 (2)	0.7575 (3)	0.0395 (9)
N2	0.3234 (4)	0.5046 (2)	0.7480 (3)	0.0323 (8)
H2	0.381537	0.558870	0.764991	0.039*
N5	0.3440 (3)	0.38312 (19)	0.5547 (3)	0.0292 (8)
H5	0.392730	0.413234	0.488510	0.035*
N8	0.5615 (3)	0.2762 (2)	0.6909 (3)	0.0313 (8)
H8	0.674094	0.277112	0.700910	0.038*
N11	0.3508 (3)	0.3385 (2)	0.8461 (3)	0.0298 (8)
H11	0.255201	0.314213	0.805949	0.036*
C1	0.2362 (5)	0.4818 (3)	0.8563 (4)	0.0418 (11)
H1A	0.133206	0.462931	0.827328	0.050*
H1B	0.227560	0.533312	0.907739	0.050*
C3	0.2243 (5)	0.5135 (3)	0.6305 (4)	0.0396 (11)
H3A	0.274368	0.551436	0.574398	0.048*
H3B	0.127546	0.540508	0.646862	0.048*
C4	0.1937 (4)	0.4249 (3)	0.5703 (4)	0.0362 (10)
H4A	0.134359	0.388525	0.621993	0.043*
H4B	0.135815	0.431978	0.490575	0.043*
C6	0.3441 (4)	0.2873 (3)	0.5311 (3)	0.0344 (10)
H6A	0.310735	0.275553	0.445087	0.041*
H6B	0.274129	0.258079	0.582361	0.041*
C7	0.5067 (5)	0.2534 (3)	0.5614 (4)	0.0386 (11)
H7A	0.508492	0.190241	0.550862	0.046*
H7B	0.574574	0.279217	0.505188	0.046*
C9	0.5013 (5)	0.2164 (3)	0.7832 (4)	0.0379 (11)
H9A	0.579747	0.173954	0.810634	0.045*
H9B	0.413183	0.184602	0.745263	0.045*
C10	0.4544 (5)	0.2678 (3)	0.8934 (4)	0.0399 (11)
H10A	0.402253	0.229681	0.947894	0.048*

H10B	0.544393	0.292262	0.939630	0.048*
C12	0.3177 (5)	0.4090 (3)	0.9320 (3)	0.0382 (10)
H12A	0.412467	0.430823	0.974336	0.046*
H12B	0.252712	0.387293	0.993362	0.046*
O4	0.1146 (4)	0.2042 (2)	0.7487 (3)	0.0663 (10)
O5	−0.0669 (4)	0.2984 (2)	0.7302 (4)	0.0846 (13)
O6	−0.1194 (4)	0.1630 (2)	0.7286 (4)	0.0803 (12)
N3	−0.0252 (4)	0.2221 (3)	0.7343 (3)	0.0398 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0229 (3)	0.0294 (3)	0.0263 (3)	−0.0023 (3)	0.0015 (2)	0.0014 (3)
O1	0.0360 (17)	0.050 (2)	0.0343 (16)	−0.0097 (15)	0.0008 (13)	0.0018 (14)
O2	0.0263 (17)	0.059 (2)	0.101 (3)	−0.0173 (17)	0.0009 (18)	0.000 (2)
O3	0.0414 (17)	0.048 (2)	0.0355 (16)	−0.0093 (16)	0.0057 (14)	0.0057 (15)
N1	0.029 (2)	0.036 (2)	0.053 (2)	−0.0034 (18)	0.0035 (18)	−0.0012 (19)
N2	0.0348 (19)	0.0290 (19)	0.0328 (18)	−0.0017 (17)	0.0005 (15)	−0.0021 (16)
N5	0.0276 (18)	0.033 (2)	0.0273 (17)	−0.0006 (16)	0.0020 (14)	0.0025 (15)
N8	0.0221 (17)	0.036 (2)	0.0353 (19)	0.0023 (16)	0.0023 (15)	0.0006 (16)
N11	0.0271 (18)	0.034 (2)	0.0284 (18)	0.0007 (16)	0.0028 (14)	0.0029 (16)
C1	0.038 (3)	0.050 (3)	0.037 (2)	0.009 (2)	0.007 (2)	−0.008 (2)
C3	0.041 (3)	0.037 (3)	0.040 (2)	0.010 (2)	−0.001 (2)	0.004 (2)
C4	0.031 (2)	0.045 (3)	0.032 (2)	0.006 (2)	−0.0025 (18)	−0.002 (2)
C6	0.035 (2)	0.041 (3)	0.028 (2)	−0.001 (2)	0.0012 (18)	−0.006 (2)
C7	0.041 (3)	0.038 (3)	0.038 (2)	0.004 (2)	0.007 (2)	−0.006 (2)
C9	0.037 (3)	0.031 (2)	0.045 (2)	0.006 (2)	0.001 (2)	0.006 (2)
C10	0.044 (3)	0.040 (3)	0.036 (2)	−0.003 (2)	0.003 (2)	0.011 (2)
C12	0.039 (2)	0.045 (3)	0.031 (2)	−0.004 (2)	0.0088 (19)	0.000 (2)
O4	0.0309 (18)	0.064 (2)	0.105 (3)	0.0029 (18)	0.0066 (19)	0.005 (2)
O5	0.087 (3)	0.045 (2)	0.128 (4)	0.025 (2)	0.045 (3)	0.020 (2)
O6	0.054 (2)	0.075 (3)	0.113 (3)	−0.029 (2)	0.012 (2)	−0.026 (2)
N3	0.037 (2)	0.044 (3)	0.039 (2)	−0.001 (2)	0.0092 (18)	0.000 (2)

Geometric parameters (Å, º)

Ni1—O1	2.151 (3)	C1—H1B	0.9700
Ni1—O3	2.113 (3)	C1—C12	1.521 (5)
Ni1—N2	2.090 (3)	C3—H3A	0.9700
Ni1—N5	2.048 (3)	C3—H3B	0.9700
Ni1—N8	2.092 (3)	C3—C4	1.515 (5)
Ni1—N11	2.065 (3)	C4—H4A	0.9700
O1—N1	1.269 (4)	C4—H4B	0.9700
O2—N1	1.221 (4)	C6—H6A	0.9700
O3—N1	1.283 (4)	C6—H6B	0.9700
N2—H2	0.9800	C6—C7	1.520 (5)
N2—C1	1.496 (5)	C7—H7A	0.9700
N2—C3	1.484 (4)	C7—H7B	0.9700

N5—H5	0.9800	C9—H9A	0.9700
N5—C4	1.481 (4)	C9—H9B	0.9700
N5—C6	1.483 (4)	C9—C10	1.516 (5)
N8—H8	0.9800	C10—H10A	0.9700
N8—C7	1.487 (4)	C10—H10B	0.9700
N8—C9	1.484 (4)	C12—H12A	0.9700
N11—H11	0.9800	C12—H12B	0.9700
N11—C10	1.471 (4)	O4—N3	1.248 (4)
N11—C12	1.467 (4)	O5—N3	1.218 (4)
C1—H1A	0.9700	O6—N3	1.218 (4)
O3—Ni1—O1	60.82 (10)	C12—C1—H1A	109.6
N2—Ni1—O1	98.38 (11)	C12—C1—H1B	109.6
N2—Ni1—O3	100.29 (12)	N2—C3—H3A	109.5
N2—Ni1—N8	161.91 (12)	N2—C3—H3B	109.5
N5—Ni1—O1	159.07 (12)	N2—C3—C4	110.9 (3)
N5—Ni1—O3	98.27 (11)	H3A—C3—H3B	108.1
N5—Ni1—N2	85.77 (12)	C4—C3—H3A	109.5
N5—Ni1—N8	85.96 (12)	C4—C3—H3B	109.5
N5—Ni1—N11	103.55 (12)	N5—C4—C3	107.9 (3)
N8—Ni1—O1	95.08 (11)	N5—C4—H4A	110.1
N8—Ni1—O3	96.80 (11)	N5—C4—H4B	110.1
N11—Ni1—O1	97.33 (12)	C3—C4—H4A	110.1
N11—Ni1—O3	158.13 (11)	C3—C4—H4B	110.1
N11—Ni1—N2	82.85 (12)	H4A—C4—H4B	108.4
N11—Ni1—N8	83.49 (12)	N5—C6—H6A	110.1
N1—O1—Ni1	91.2 (2)	N5—C6—H6B	110.1
N1—O3—Ni1	92.5 (2)	N5—C6—C7	108.2 (3)
O1—N1—O3	115.5 (3)	H6A—C6—H6B	108.4
O2—N1—O1	122.6 (4)	C7—C6—H6A	110.1
O2—N1—O3	121.9 (4)	C7—C6—H6B	110.1
Ni1—N2—H2	109.8	N8—C7—C6	110.1 (3)
C1—N2—Ni1	108.4 (2)	N8—C7—H7A	109.6
C1—N2—H2	109.8	N8—C7—H7B	109.6
C3—N2—Ni1	105.5 (2)	C6—C7—H7A	109.6
C3—N2—H2	109.8	C6—C7—H7B	109.6
C3—N2—C1	113.5 (3)	H7A—C7—H7B	108.2
Ni1—N5—H5	109.1	N8—C9—H9A	109.5
C4—N5—Ni1	105.7 (2)	N8—C9—H9B	109.5
C4—N5—H5	109.1	N8—C9—C10	110.5 (3)
C4—N5—C6	117.2 (3)	H9A—C9—H9B	108.1
C6—N5—Ni1	106.2 (2)	C10—C9—H9A	109.5
C6—N5—H5	109.1	C10—C9—H9B	109.5
Ni1—N8—H8	110.2	N11—C10—C9	107.7 (3)
C7—N8—Ni1	105.0 (2)	N11—C10—H10A	110.2
C7—N8—H8	110.2	N11—C10—H10B	110.2
C9—N8—Ni1	108.1 (2)	C9—C10—H10A	110.2
C9—N8—H8	110.2	C9—C10—H10B	110.2

C9—N8—C7	113.0 (3)	H10A—C10—H10B	108.5
Ni1—N11—H11	110.6	N11—C12—C1	107.5 (3)
C10—N11—Ni1	103.6 (2)	N11—C12—H12A	110.2
C10—N11—H11	110.6	N11—C12—H12B	110.2
C12—N11—Ni1	103.1 (2)	C1—C12—H12A	110.2
C12—N11—H11	110.6	C1—C12—H12B	110.2
C12—N11—C10	117.6 (3)	H12A—C12—H12B	108.5
N2—C1—H1A	109.6	O5—N3—O4	120.0 (4)
N2—C1—H1B	109.6	O5—N3—O6	120.4 (4)
N2—C1—C12	110.3 (3)	O6—N3—O4	119.6 (4)
H1A—C1—H1B	108.1		
Ni1—O1—N1—O2	−179.3 (3)	N2—C1—C12—N11	−50.0 (4)
Ni1—O1—N1—O3	1.0 (3)	N2—C3—C4—N5	−55.3 (4)
Ni1—O3—N1—O1	−1.0 (3)	N5—C6—C7—N8	56.3 (4)
Ni1—O3—N1—O2	179.3 (3)	N8—C9—C10—N11	52.0 (4)
Ni1—N2—C1—C12	17.8 (4)	C1—N2—C3—C4	−83.8 (4)
Ni1—N2—C3—C4	34.8 (4)	C3—N2—C1—C12	134.6 (3)
Ni1—N5—C4—C3	45.1 (3)	C4—N5—C6—C7	−160.9 (3)
Ni1—N5—C6—C7	−43.1 (3)	C6—N5—C4—C3	163.1 (3)
Ni1—N8—C7—C6	−38.1 (4)	C7—N8—C9—C10	−138.3 (3)
Ni1—N8—C9—C10	−22.5 (4)	C9—N8—C7—C6	79.5 (4)
Ni1—N11—C10—C9	−53.5 (3)	C10—N11—C12—C1	168.9 (3)
Ni1—N11—C12—C1	55.7 (3)	C12—N11—C10—C9	−166.4 (3)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2⋯O4[i]	0.98	2.22	3.091 (5)	147
N5—H5⋯O3[ii]	0.98	2.32	3.130 (4)	139
N8—H8⋯O5[iii]	0.98	2.28	3.253 (5)	172
N8—H8⋯O6[iii]	0.98	2.50	3.273 (5)	135
N11—H11⋯O4	0.98	2.14	3.030 (5)	151

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