Mirror-plane disorder in a nickel chloride Schiff base complex: a suitable case study for crystallographic instruction

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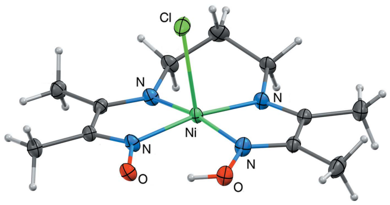
The nickel chloride complex of the Schiff base N^2,$N^{2'}$-propanediylbis(2,3-butanedione-2-imine-3-oxime), namely, chlorido(3,9-dimethylundeca-3,8-diene-2,10-dione 10-oxime 2-oximato-$\kappa^4 N,N',N'',N'''$)nickel(II), [NiCl($C_{11}H_{19}N_4O_2$)], at 100 K crystallizes in the orthorhombic space group *Cmce*. The structure exhibits mirror disorder of the main molecule that is not present in the bromide analogue. The relatively small number of unique reflections in the data set and the disorder imposed by the crystallographic mirror plane present a challenging educational case study.



1. Introduction

The Ni complexes with the Schiff base N^2,$N^{2'}$-propanediylbis(2,3-butanedione-2-imine-3-oxime) (H*L*) (Korvenranta & Saarinen, 1979; Uyeda & Peters, 2013; Saarinen *et al.*, 1979; Wang *et al.*, 1990; Summers *et al.*, 1996; Jacques *et al.*, 2009) have been studied for applications such as a model for nickel tetrapyrrole cofactor F430 (Uyeda & Peters, 2013) and as potential electrocatalysts for hydrogen evolution reaction (HER) (Jacques *et al.*, 2009). We have been investigating this Schiff base ligand as its metal complexes, which proves to be a good model system to investigate HER performance through different active site metal ions (*e.g.* Ni *versus* Co) and their secondary coordination spheres (Wang & Johnson, 2019; Wang, 2021). Coincidentally, the title compound, denoted NiCl*L*, crystallizes with a crystallographic mirror imposed perpendicular to the approximate molecular mirror. The small unit-cell volume, centrosymmetry, and high orthorhombic cell symmetry co-operatively results in a relatively small unique reflection set of 1558 that affords faster calculations during classroom demonstrations and is thus practical for instruction in X-ray crystallography. It can be challenging to find crystallographic data sets suitable for educational case studies. Although suitable structures can be occasionally discovered in the Cambridge Structural Database (Groom *et al.*, 2016), and the instruction and reflection files might be extracted from the CIF (Hall *et al.*, 1991) with utilities such as *ShredCIF* (Sheldrick, 2015*b*) or *PLATON* (Spek, 2020), there are no clear data-mining methods to specifically search based on a specific crystallographic problem or data reflection file size. Hence, for example, the structures contained in *OLEX2* (Dolomanov *et al.*, 2009) and those collated by the Molecular Structure Laboratory at UW–Madison (Guzei, 2021) are greatly appreciated.

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2. Experimental

2.1. Synthesis and crystallization

The title compound, NiCl*L* [where *L* is the monoanionic form of N^2,$N^{2'}$-propanediylbis(2,3-butanedione-2-imine-3-oxime)] (Fig. 1), was prepared according to a literature synthesis (Uhlig & Friedrich, 1966) modified by using 1,3-bis(diacetyl monoxime imine)propane (240 mg, 1 mmol) with $NiCl_2$ (130 mg, 1 mmol) in ethanol/water at room temperature for 2 h. The reaction solvent was removed under vacuum, which yielded a brown powder (yield 253 mg). The powder was recrystallized from CH_2Cl_2 as brown crystals, which were dried under vacuum (yield 130 mg, 46.68%). ^1H NMR (500 MHz, CD_2Cl_2): δ 3.46 (*t*, *J* = 5.1 Hz, 4H), 2.30–2.26 (*m*, 2H), 2.08 (*s*, 6H), 2.07 (*s*, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 169.0, 152.0, 48.9, 29.1, 16.6, 12.7. HR–MS (ESI): calculated for $[C_{11}H_{19}ClN_4NiO_2 - Cl]^+$: 297.08615; found: 297.08549. The ^1H NMR, ^{13}C NMR and HR–MS (ESI) spectra are available in the supporting information.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Equal atomic displacement parameter constraints were applied to each O/C pair affected by the mirror plane. H atoms were placed in calculated positions, with U_{iso}(H) values equal to 1.2–1.5U_{eq} of the attached atom.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[NiCl(C_{11}H_{19}N_4O_2)]$
M_r	333.46
Crystal system, space group	Orthorhombic, *Cmce* (*Cmca*)
Temperature (K)	100
a, *b*, *c* (Å)	14.3402 (14), 14.2577 (12), 13.1777 (13)
V (Å^3)	2694.3 (4)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	1.64
Crystal size (mm)	0.10 × 0.08 × 0.03
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.623, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	56076, 1558, 1256
R_{int}	0.104
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.643
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.080, 1.09
No. of reflections	1558
No. of parameters	115
No. of restraints	12
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.61, −0.46

Computer programs: *APEX3* (Bruker, 2019), *SAINT* (Bruker, 2019), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *Mercury* (Macrae *et al.*, 2020).

3. Results and discussion

The literature NiBr*L* structure (Korvenranta & Saarinen, 1979) was determined at room temperature in the range 283–303 K, while the current report was determined at 100 K. Since the C=C double-bond distances, $C{=}C_{rt(ave)}$ = 1.469 Å *versus* $C{=}C_{100K(ave)}$ = 1.466 (5) Å, are indistinguishable within error, it would appear that thermal librational effects, in this case, are not significant. Similar to the bromide analogue, the Ni atom in NiCl*L* is five-coordinate with a square-pyramidal geometry. The symmetry-unique Ni—N distances are 1.882 (2) and 1.887 (2) Å, which compare favorably with the bromide compound [1.879 (9)–1.913 (10) Å]. It is not surprising that the Ni—Cl distance [2.5014 (11) Å] is shorter than the Ni—Br distance [2.662 (13) Å] because of the smaller

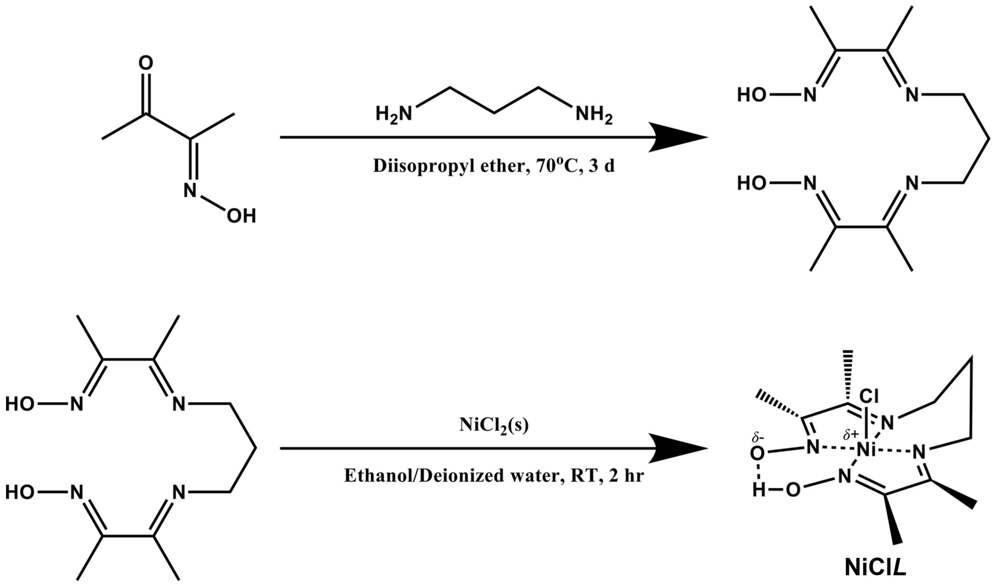

Figure 1
The synthesis of NiCl*L*.

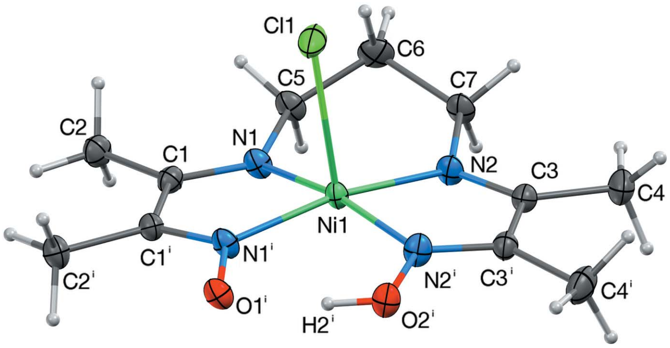

Figure 2
The molecular diagram and atom-labeling scheme of NiCl*L*. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius. [Symmetry code: (i) $-x + 1, y, z$.]

chloride ion radius. However, it is remarkable that reducing the axial dimension of the square pyramid by 0.16 Å has a significant effect on the packing, leading to a change in space group. NiCl*L* (Fig. 2) crystallizes in the orthorhombic space group *Cmce* (renamed from *Cmca* with updated diamond glide notation; Wolff *et al.*, 1992) (No. 64), with $Z' = 0.5$, and the molecule rests on a mirror plane perpendicular and bisecting the N_4 macrocyclic basal plane and the C═C double bonds. In comparison, the bromide case is in the space group $P2_1/n$, with $Z = 4$ and $Z' = 1$, without a similar mirror plane. It is tempting to extend a similar argument to the thiocyanide (Summers *et al.*, 1996) and perchlorate (Jacques *et al.*, 2009) compounds, also packed without mirror disorder, having Ni—S and Ni—O distances of 2.655 and 2.826 Å, respectively, but, of course, the thiocyanide ligand and perchlorate ion are not colinear with respect to the Ni—S and Ni—O vectors, hence the molecular shapes are not comparable. Attempts to correlate the pyrimidal coordination metrics to the incidence of crystallographic symmetry were unsuccessful suggesting that a more complicated set of factors could be involved.

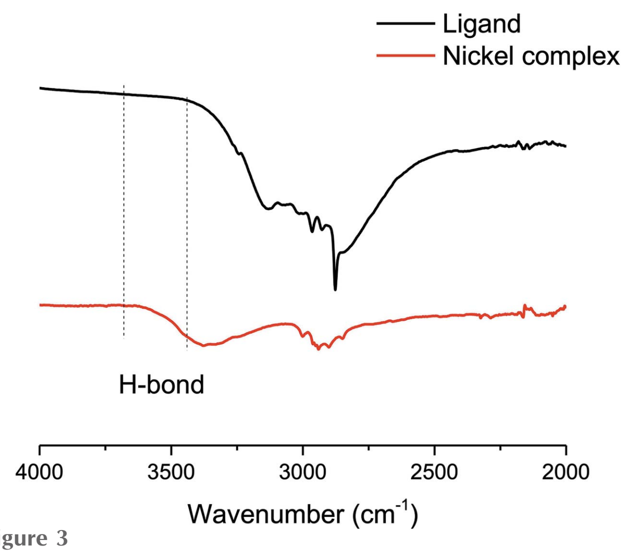

Figure 3
Comparative IR spectrum in the O—H region for the free ligand (upper, black trace) and NiCl*L* (lower, red trace).

The crystallographic mirror introduces electron-density ambiguity between the O atoms and the –$CH_2CH_2CH_2$– unit. Upon splitting the ambiguous electron-density peaks adjacent to the two symmetry-unique N atoms and refining at half-occupancy, the atoms proximal to N have distances of 1.332 (10) and 1.363 (11) Å, which compare favorably with the N—O distances in the bromide (1.324 and 1.354 Å). Similarly, the atoms distal to N have distances of 1.487 (15) and 1.464 (17) Å, which compare well to the N—C(sp^3) distances in the bromide (1.468 and 1.469 Å). As a secondary check for the correct C *versus* O atom assignments, the C—C distances to the middle C atom will show the correctly identified C atoms (in this case, C5 and C7) to have normal C—C single-bond distances [1.47 (2) and 1.51 (2) Å], with a C5—C6—C7 angle of 114.6 (12)°, which is close to the ideal tetrahedral angle of 109°. An incorrect assignment will lead to an apparent C—C distance greater than 1.6 Å with an angle of 95°. Although the penultimate difference map shows a peak midway between atoms O1 and O2, because of the overall noise level, we opted to more realistically arbitrarily assign a proton to O2 with the nominally longer N—O, albeit statistically ambiguous, distance in a calculated position instead. This localized model is consistent with the solid-state IR spectrum. Compared to the free ligand, a broad absorption in the range 3300–3600 cm^{-1} observed from the Ni complex (Fig. 3) suggests that a hydrogen bond exists between the protonated and unprotonated oxime groups. This assignment is further supported by observing two different stretching peaks (red trace) (Fig. 4) for N—O, *i.e.* 1350 and 1380 cm^{-1} (Dede *et al.*, 2018). A fully delocalized model wherein the proton is equally shared between the two oximes making them chemically equivalent should have only one IR active parallel stretch. The antiparallel stretching mode would not change the net dipole moment and is thus IR silent.

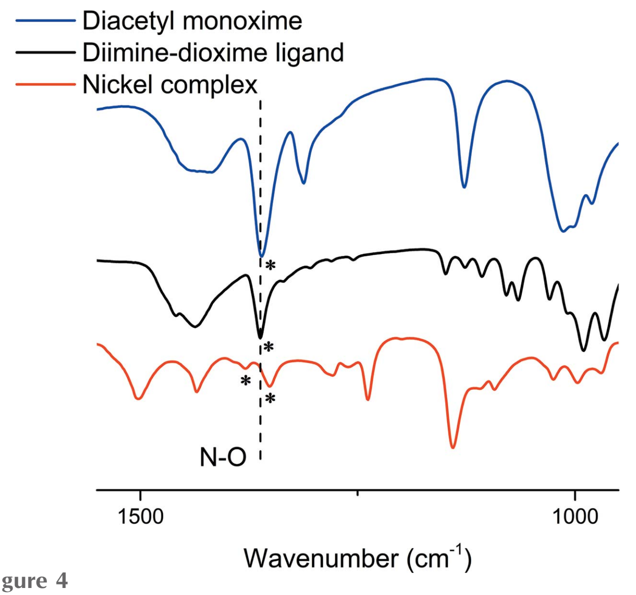

Figure 4
Comparative IR spectrum in the C—O region for the diacetyl monoxime (upper, blue trace), the free ligand (middle, black trace), and NiBr*L* (lower, red trace).

In conclusion, we were able to obtain a good-quality low-temperature structure of NiCl*L* which is consistent, but with different symmetry, with the previously reported bromide. While the electronic structure of the title compound could have significant implications for HER, we also find the structure to be a suitable crystallographic case study. The structure displays a classical, yet challenging, textbook case of disorder arising from a higher crystallographic symmetry imposed on lower true molecular symmetry.

Funding information

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References

Bruker (2016). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2019). *APEX3* and *SAINT*. Bruker Nano Inc., Madison, Wisconsin, USA.

Dede, B., Özen, N. & Görgülü, G. (2018). *J. Mol. Struct.* **1163**, 357–367.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Guzei, I. A. (2021). *(UW-Madison) Crystallographic Problems*, http://xray.chem.wisc.edu/crystallographic-problems/.

Hall, S. R., Allen, F. H. & Brown, I. D. (1991). *Acta Cryst.* A**47**, 655–685.

Jacques, P.-A., Artero, V., Pécaut, J. & Fontecave, M. (2009). *Proc. Natl Acad. Sci. USA*, **106**, 20627–20632.

Korvenranta, J. & Saarinen, H. (1979). *Finn. Chem. Lett.* **7–8**, 219–222.

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.

Saarinen, H., Korvenranta, J. & Nasakkala, E. (1979). *Cryst. Struct. Commun.* **8**, 359–362.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.

Summers, M., Rheingold, A. L. & Allen, M. B. (1996). Private communication (refcode: ZOHTOF). CCDC, Cambridge, England.

Uhlig, E. & Friedrich, M. Z. (1966). *Z. Anorg. Allg. Chem.* **343**, 299–307.

Uyeda, C. & Peters, J. C. (2013). *Chem. Sci.* **4**, 157–163.

Wang, V. C.-C. (2021). *ACS Catal.* **11**, 8292–8303.

Wang, V. C.-C. & Johnson, B. A. (2019). *ACS Catal.* **9**, 7109–7123.

Wang, Y.-M., Chung, C.-S., Cheng, C.-Y. & Wang, S.-L. (1990). *Acta Cryst.* C**46**, 1429–1432.

Wolff, P. M. de, Billiet, Y., Donnay, J. D. H., Fischer, W., Galiulin, R. B., Glazer, A. M., Hahn, T., Senechal, M., Shoemaker, D. P., Wondratschek, H., Wilson, A. J. C. & Abrahams, S. C. (1992). *Acta Cryst.* A**48**, 727–732.

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Supporting Information

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Computing details

Data collection: *APEX3* (Bruker, 2019); cell refinement: *SAINT* (Bruker, 2019); data reduction: *SAINT* (Bruker, 2019); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *Mercury* (Macrae *et al.*, 2020).

Chlorido(3,9-dimethylundeca-3,8-diene-2,10-dione 10-oxime 2-oximato-κ^4N,N',N'',N''')nickel(II)

Crystal data

$[\mathrm{NiCl(C_{11}H_{19}N_4O_2)}]$
$M_r = 333.46$
Orthorhombic, *Cmce*
$a = 14.3402\ (14)$ Å
$b = 14.2577\ (12)$ Å
$c = 13.1777\ (13)$ Å
$V = 2694.3\ (4)$ Å^3
$Z = 8$
$F(000) = 1392$

$D_x = 1.644$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7235 reflections
$\theta = 2.5$–$27.2°$
$\mu = 1.64$ mm^{-1}
$T = 100$ K
Plate, brown
0.10 × 0.08 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{\min} = 0.623$, $T_{\max} = 0.746$
56076 measured reflections

1558 independent reflections
1256 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.104$
$\theta_{\max} = 27.2°$, $\theta_{\min} = 2.5°$
$h = -18 \rightarrow 18$
$k = -18 \rightarrow 18$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.080$
$S = 1.09$
1558 reflections
115 parameters
12 restraints
Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.021P)^2 + 11.8731P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.61$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ 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.

Refinement. 1. Fixed Uiso At 1.2 times of: All C(H,H) groups At 1.5 times of: All C(H,H,H) groups, All O(H) groups 2. Uiso/Uaniso restraints and constraints N1 ~ O1 ~ C5: within 2A with sigma of 0.002 and sigma for terminal atoms of 0.004 within 2A N2 ~ O2 ~ C7: within 2A with sigma of 0.002 and sigma for terminal atoms of 0.004 within 2A 3. Others Fixed Sof: O1(0.5) O2(0.5) H2(0.5) C5(0.5) H5A(0.5) H5B(0.5) C6(0.5) H6A(0.5) H6B(0.5) C7(0.5) H7A(0.5) H7B(0.5) 4.a Secondary CH2 refined with riding coordinates: C5(H5A,H5B), C6(H6A,H6B), C7(H7A,H7B) 4.b Idealised Me refined as rotating group: C2(H2A,H2B,H2C), C4(H4A,H4B,H4C) 4.c Idealised tetrahedral OH refined as rotating group: O2(H2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.500000	0.62249 (3)	0.63581 (3)	0.01318 (14)	
Cl1	0.500000	0.62131 (7)	0.82563 (7)	0.0291 (2)	
N1	0.41391 (14)	0.52300 (14)	0.62930 (17)	0.0158 (4)	
N2	0.41383 (15)	0.72035 (15)	0.61322 (17)	0.0173 (5)	
C1	0.44918 (17)	0.43926 (17)	0.63273 (19)	0.0155 (5)	
C2	0.39092 (18)	0.35273 (17)	0.6383 (2)	0.0200 (6)	
H2A	0.431498	0.297431	0.639172	0.030*	
H2B	0.349725	0.349825	0.579038	0.030*	
H2C	0.353252	0.354084	0.700333	0.030*	
C3	0.44866 (18)	0.80203 (18)	0.59531 (19)	0.0166 (5)	
C4	0.3943 (2)	0.88915 (19)	0.5744 (2)	0.0279 (7)	
H4A	0.415144	0.939212	0.620013	0.042*	
H4B	0.327801	0.876996	0.585622	0.042*	
H4C	0.404144	0.908442	0.503838	0.042*	
O1	0.3218 (7)	0.5321 (10)	0.6216 (11)	0.0166 (18)	0.5
O2	0.3204 (8)	0.7038 (9)	0.6068 (9)	0.019 (2)	0.5
H2	0.310498	0.645796	0.610017	0.029*	0.5
C5	0.3120 (11)	0.5400 (18)	0.6394 (19)	0.028 (4)	0.5
H5A	0.283806	0.539140	0.570793	0.033*	0.5
H5B	0.284291	0.487639	0.678419	0.033*	0.5
C6	0.2869 (4)	0.6285 (4)	0.6891 (4)	0.0232 (11)	0.5
H6A	0.317844	0.631006	0.756180	0.028*	0.5
H6B	0.218703	0.629051	0.700928	0.028*	0.5
C7	0.3130 (12)	0.7157 (15)	0.6300 (15)	0.021 (3)	0.5
H7A	0.280482	0.715311	0.563689	0.026*	0.5
H7B	0.292500	0.772015	0.667838	0.026*	0.5

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0099 (2)	0.0108 (2)	0.0189 (2)	0.000	0.000	−0.00033 (19)
Cl1	0.0557 (7)	0.0154 (5)	0.0162 (4)	0.000	0.000	0.0001 (4)
N1	0.0098 (10)	0.0149 (10)	0.0226 (11)	−0.0010 (8)	−0.0003 (9)	−0.0024 (8)

N2	0.0102 (10)	0.0172 (11)	0.0246 (12)	0.0016 (8)	0.0023 (8)	0.0025 (9)
C1	0.0157 (13)	0.0145 (12)	0.0162 (12)	−0.0019 (10)	−0.0005 (11)	0.0005 (10)
C2	0.0192 (13)	0.0166 (13)	0.0243 (13)	−0.0031 (10)	0.0013 (11)	−0.0009 (10)
C3	0.0191 (14)	0.0134 (12)	0.0173 (12)	0.0000 (10)	0.0010 (11)	0.0008 (10)
C4	0.0386 (17)	0.0175 (15)	0.0276 (15)	0.0072 (13)	0.0024 (13)	0.0042 (11)
O1	0.011 (3)	0.009 (3)	0.030 (5)	0.001 (2)	−0.001 (2)	0.000 (3)
O2	0.011 (3)	0.011 (4)	0.036 (5)	0.003 (2)	0.002 (3)	0.006 (4)
C5	0.007 (3)	0.034 (7)	0.042 (9)	0.000 (3)	−0.003 (4)	−0.010 (5)
C6	0.011 (2)	0.030 (3)	0.028 (3)	0.000 (2)	0.006 (2)	0.002 (3)
C7	0.008 (3)	0.021 (5)	0.036 (7)	0.002 (3)	0.002 (4)	−0.008 (4)

Geometric parameters (Å, º)

Ni1—N1	1.882 (2)	C2—H2C	0.9800
Ni1—N1$^{\mathrm{i}}$	1.882 (2)	C3—C3$^{\mathrm{i}}$	1.473 (5)
Ni1—N2$^{\mathrm{i}}$	1.887 (2)	C3—C4	1.492 (4)
Ni1—N2	1.887 (2)	C4—H4A	0.9800
Ni1—Cl1	2.5014 (11)	C4—H4B	0.9800
N1—C1	1.297 (3)	C4—H4C	0.9800
N1—O1	1.332 (10)	O2—H2	0.8400
N1—C5	1.487 (15)	C5—C6	1.47 (2)
N2—C3	1.289 (3)	C5—H5A	0.9900
N2—O2	1.363 (11)	C5—H5B	0.9900
N2—C7	1.464 (17)	C6—C7	1.51 (2)
C1—C1$^{\mathrm{i}}$	1.458 (5)	C6—H6A	0.9900
C1—C2	1.492 (3)	C6—H6B	0.9900
C2—H2A	0.9800	C7—H7A	0.9900
C2—H2B	0.9800	C7—H7B	0.9900
N1—Ni1—N1$^{\mathrm{i}}$	81.97 (13)	N2—C3—C3$^{\mathrm{i}}$	112.80 (15)
N1—Ni1—N2$^{\mathrm{i}}$	168.30 (10)	N2—C3—C4	125.7 (2)
N1$^{\mathrm{i}}$—Ni1—N2$^{\mathrm{i}}$	96.92 (9)	C3$^{\mathrm{i}}$—C3—C4	121.51 (15)
N1—Ni1—N2	96.92 (9)	C3—C4—H4A	109.5
N1$^{\mathrm{i}}$—Ni1—N2	168.30 (10)	C3—C4—H4B	109.5
N2$^{\mathrm{i}}$—Ni1—N2	81.79 (13)	H4A—C4—H4B	109.5
N1—Ni1—Cl1	92.32 (7)	C3—C4—H4C	109.5
N1$^{\mathrm{i}}$—Ni1—Cl1	92.32 (7)	H4A—C4—H4C	109.5
N2$^{\mathrm{i}}$—Ni1—Cl1	99.36 (7)	H4B—C4—H4C	109.5
N2—Ni1—Cl1	99.36 (7)	N2—O2—H2	109.5
C1—N1—O1	118.6 (6)	C6—C5—N1	114.9 (15)
C1—N1—C5	122.0 (10)	C6—C5—H5A	108.5
C1—N1—Ni1	115.86 (17)	N1—C5—H5A	108.5
O1—N1—Ni1	125.5 (6)	C6—C5—H5B	108.5
C5—N1—Ni1	121.2 (10)	N1—C5—H5B	108.5
C3—N2—O2	121.7 (6)	H5A—C5—H5B	107.5
C3—N2—C7	116.8 (9)	C5—C6—C7	114.6 (12)
C3—N2—Ni1	116.30 (18)	C5—C6—H6A	108.6
O2—N2—Ni1	121.7 (6)	C7—C6—H6A	108.6

C7—N2—Ni1	126.1 (9)	C5—C6—H6B	108.6
N1—C1—C1$^{\text{i}}$	112.94 (14)	C7—C6—H6B	108.6
N1—C1—C2	123.0 (2)	H6A—C6—H6B	107.6
C1$^{\text{i}}$—C1—C2	124.06 (14)	N2—C7—C6	111.0 (14)
C1—C2—H2A	109.5	N2—C7—H7A	109.4
C1—C2—H2B	109.5	C6—C7—H7A	109.4
H2A—C2—H2B	109.5	N2—C7—H7B	109.4
C1—C2—H2C	109.5	C6—C7—H7B	109.4
H2A—C2—H2C	109.5	H7A—C7—H7B	108.0
H2B—C2—H2C	109.5		

N1$^{\text{i}}$—Ni1—N1—C1	5.8 (2)	N1$^{\text{i}}$—Ni1—N2—C7	105.3 (10)
N2$^{\text{i}}$—Ni1—N1—C1	91.1 (5)	N2$^{\text{i}}$—Ni1—N2—C7	−170.2 (9)
N2—Ni1—N1—C1	174.0 (2)	Cl1—Ni1—N2—C7	−72.0 (9)
Cl1—Ni1—N1—C1	−86.25 (19)	O1—N1—C1—C1$^{\text{i}}$	175.3 (7)
N1$^{\text{i}}$—Ni1—N1—O1	−174.2 (8)	C5—N1—C1—C1$^{\text{i}}$	−173.5 (11)
N2$^{\text{i}}$—Ni1—N1—O1	−88.9 (9)	Ni1—N1—C1—C1$^{\text{i}}$	−4.7 (2)
N2—Ni1—N1—O1	−6.0 (8)	O1—N1—C1—C2	−5.9 (8)
Cl1—Ni1—N1—O1	93.7 (8)	C5—N1—C1—C2	5.2 (12)
N1$^{\text{i}}$—Ni1—N1—C5	174.7 (11)	Ni1—N1—C1—C2	174.06 (19)
N2$^{\text{i}}$—Ni1—N1—C5	−100.0 (12)	O2—N2—C3—C3$^{\text{i}}$	−173.6 (5)
N2—Ni1—N1—C5	−17.1 (12)	C7—N2—C3—C3$^{\text{i}}$	171.1 (8)
Cl1—Ni1—N1—C5	82.7 (12)	Ni1—N2—C3—C3$^{\text{i}}$	0.5 (2)
N1—Ni1—N2—C3	−168.9 (2)	O2—N2—C3—C4	5.3 (7)
N1$^{\text{i}}$—Ni1—N2—C3	−85.1 (5)	C7—N2—C3—C4	−10.0 (9)
N2$^{\text{i}}$—Ni1—N2—C3	−0.6 (2)	Ni1—N2—C3—C4	179.4 (2)
Cl1—Ni1—N2—C3	97.60 (19)	C1—N1—C5—C6	147.5 (12)
N1—Ni1—N2—O2	5.2 (6)	Ni1—N1—C5—C6	−21 (2)
N1$^{\text{i}}$—Ni1—N2—O2	89.0 (7)	N1—C5—C6—C7	66 (2)
N2$^{\text{i}}$—Ni1—N2—O2	173.4 (6)	C3—N2—C7—C6	−157.6 (7)
Cl1—Ni1—N2—O2	−88.3 (6)	Ni1—N2—C7—C6	12.0 (15)
N1—Ni1—N2—C7	21.6 (9)	C5—C6—C7—N2	−60.3 (15)

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