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# Dichloridobis[2-(pyridin-2-yl-$\kappa N$)-1*H*-benzimidazole-$\kappa N^3$]nickel(II) monohydrate. Corrigendum

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In the paper by MacNeil *et al.* [*IUCrData*, (2020), **5**, x200040], the address of the second author is incorrect.

In the paper by MacNeil *et al.* (2020), the address of the second author, Aloice O. Ogweno, should be 'Department of Pure and Applied Sciences, Technical University of Mombasa, Mombasa, Kenya', as given above.

## References

MacNeil, C. S., Ogweno, A.O., Ojwach, S.O. & Hayes, P.G. (2020). *IUCrData* (2020), **5**, x200040

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# Dichloridobis[2-(pyridin-2-yl-$\kappa N$)-1*H*-benzimidazole-$\kappa N^3$]nickel(II) monohydrate

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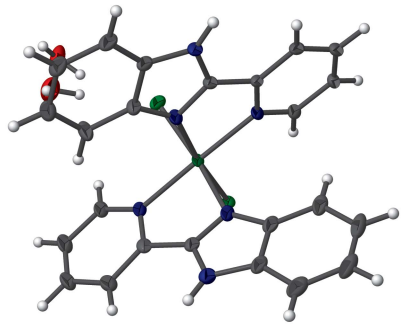
**Keywords:** crystal structure; nickel(II) complex; 2-(pyridin-2-yl)-1*H*-benzimidazole; hydrogen bonding; C—H$\cdots\pi$ interactions; transfer hydrogenation.

**CCDC reference**: 1946553

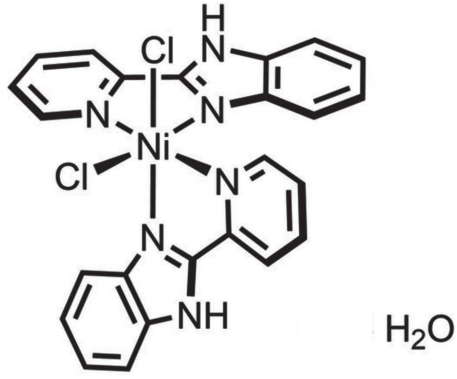
**Structural data**: full structural data are available from iucrdata.iucr.org

In the title complex, $[NiCl_2(C_{12}H_9N_3)_2]\cdot H_2O$, a divalent nickel atom is coordinated by two 2-(pyridin-2-yl)-1*H*-benzimidazole ligands in a slightly distorted octahedral environment defined by four N donors of two *N*,*N*′-chelating ligands, along with two *cis*-oriented anionic chloride donors. The title complex crystallized with a water molecule disordered over two positions. In the crystal, a combination of O—H$\cdots$Cl, O—H$\cdot\cdot$O and N—H$\cdots$Cl hydrogen bonds, together with C—H$\cdots$O, C—H$\cdots$Cl and C—H$\cdots\pi$ interactions, links the complex molecules and the water molecules to form a supramolecular three-dimensional framework. The title complex is isostructural with the cobalt(II) dichloride complex reported previously [Das *et al.* (2011). *Org. Biomol. Chem.* **9**, 7097–7107].

**3D view**



**Chemical scheme**




## Structure description

Transition-metal-catalyzed transfer hydrogenation (TH) is an effective method of reducing ketones to the corresponding secondary alcohols (Zhu *et al.*, 2014). Generally, the method is operationally simple, selective, and sources hydrogen from alcohols, thus avoiding high pressures of $H_2$ gas (Zhu *et al.*, 2014). Several transition-metal complexes have been studied in catalytic TH and have been used on laboratory and industrial scales. Complexes of precious metals (Rh, Ir, and Ru) have been the preferred catalysts for TH owing to their high activity and commercial availability (Raja *et al.*, 2012; Wang *et al.*, 2015; Li *et al.*, 2015). With growing concern surrounding the economic and environmental impact of using precious metals in chemistry, a renewed interest in Earth-abundant metal catalysis has prompted our research into TH catalysts featuring first-row transition metals, such as iron, cobalt, or nickel (Morris, 2009; Garduño & García, 2017; Abubakar

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

*Cg*1, *Cg*2, *Cg*3, *Cg*4 and *Cg*5 are the centroids of the C7–C12, N5/N6/C18/C19/C24, N1/C1–C5, N4/C13–C17 and C19–C24 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H1···Cl2 | 0.95 | 2.75 | 3.378 (2) | 124 |
| O1—H1*A*···Cl1 | 0.85 | 2.37 | 3.221 (4) | 174 |
| O2—H2*B*···Cl1 | 0.85 | 2.41 | 3.239 (4) | 165 |
| O2—H2*A*···O1$^{i}$ | 0.85 | 1.97 | 2.806 (6) | 167 |
| N3—H3···Cl2$^{ii}$ | 0.88 | 2.29 | 3.162 (2) | 171 |
| N6—H6···Cl1$^{iii}$ | 0.88 | 2.23 | 3.069 (2) | 160 |
| C2—H2···O2$^{iv}$ | 0.95 | 2.56 | 3.400 (5) | 147 |
| C20—H20···O2$^{iii}$ | 0.95 | 2.54 | 3.317 (5) | 139 |
| O1—H1*B*···*Cg*1 | 0.85 | 3.11 | 3.869 (3) | 150 |
| C3—H3*A*···*Cg*5$^{ii}$ | 0.95 | 2.97 | 3.738 (3) | 139 |
| C8—H8···*Cg*2$^{v}$ | 0.95 | 2.69 | 3.579 (3) | 155 |
| C9—H9···*Cg*5$^{v}$ | 0.95 | 2.88 | 3.542 (3) | 128 |
| C11—H11···*Cg*4 | 0.95 | 2.93 | 3.810 (3) | 155 |
| C23—H23···*Cg*3 | 0.95 | 2.94 | 3.733 (3) | 142 |

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

*et al.*, 2018; Chen *et al.*, 2010). Recognizing that nickel(II) complexes of chiral bis(phosphines) have been utilized in asymmetric TH, we turned our attention to nickel(II) complexes of the commercially available ligand 2-(pyridin-2-yl)-1*H*-benzimidazole.

The asymmetric unit of the title complex consists of a $Ni^{II}$ ion coordinated by two 2-(pyridin-2-yl)-1*H*-benzimidazole ligands bound in a $\kappa^2$-*N*,*N* arrangement, along with two *cis*-oriented anionic chloride donors (Fig. 1). The complex crystallized as a monohydrate with the water molecule disordered over two sites (Fig. 1). The metal center adopts a slightly distorted octahedral geometry. The pyridyl N-donor atoms are *trans*-disposed [N1—Ni1—N4 = 170.66 (8)°], while the chloride ligands are *cis*-disposed [Cl2—Ni1—Cl1 = 93.04 (2)°]. The disordered water molecules are linked to the complex molecule by O—H···Cl hydrogen bonds, and water H atom H2*B* is directed to the centroid of the C7–C12 ring (Fig. 1, Table 1).

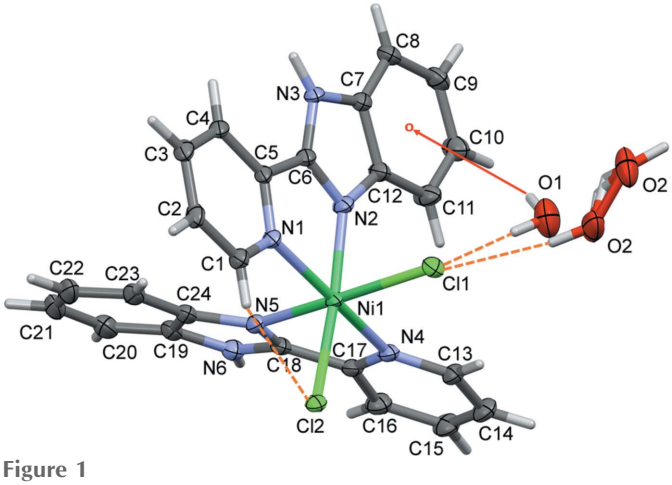



**Figure 1**
The molecular structure of the title complex, with atom labeling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as orange dashed lines and the O—H···$\pi$ interaction as a red arrow (Table 1).

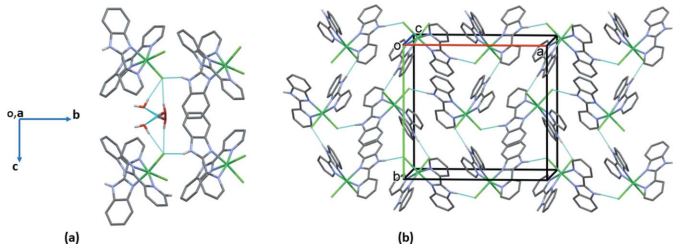



**Figure 2**
Hydrogen-bonding networks involving, (*a*) the discorded water molecule, and (*b*) the N—H···Cl hydrogen bonds. For clarity, only the H atoms involved in hydrogen bonding (dashed lines; Table 1) have been included.

In the crystal, extensive hydrogen bonding is observed involving the disordered water molecule, the ligand NH groups and the chloride ions (Fig. 2*a* and 2*b* and Table 1). The result is the formation of a supramolecular three-dimensional network (Fig. 3). There are also C—H···O and C—H···$\pi$ interactions present (Table 1) consolidating the packing.

A search of the Cambridge Structural Database (CSD, Version 5.40, May 2019; Groom *et al.*, 2016) revealed that the title compound is isostructural with the cobalt(II) complex dichloridobis-[2-(pyridin-2-yl)-1*H*-benzimidazole]cobalt(II) monohydrate (CSD refcode DACRIK; Das *et al.*, 2011). The later was reported in space group *C*2/*c* but transformation of the unit cell gives space group *I*2/*a* (ADDSYMM in *PLATON*; Spek, 2020) with almost identical cell parameters to those of the title complex – see Fig. 4.

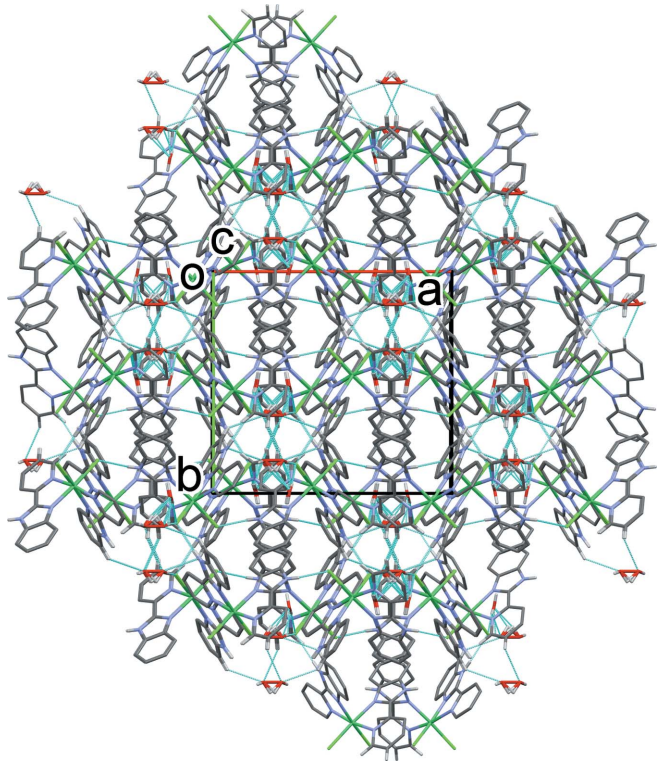



**Figure 3**
A view along the *c* axis of the crystal packing of the title complex. For clarity, only the H atoms involved in hydrogen bonding (dashed lines; Table 1) have been included.

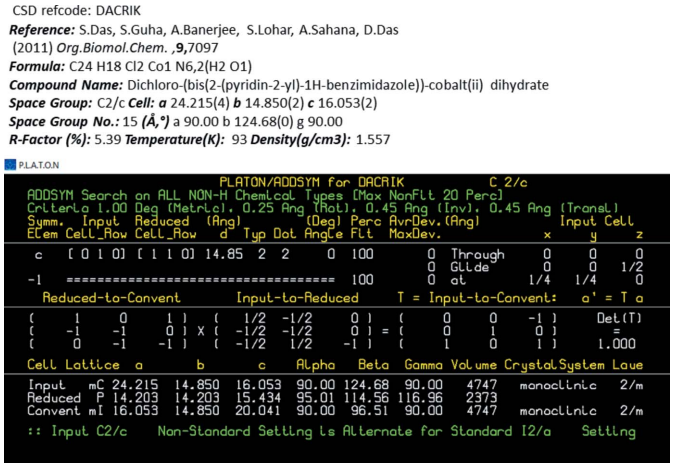



**Figure 4**
A view of the ADDSYM (*PLATON*; Spek, 2020) transformation of the cell dimensions of the isostructural compound dichloridobis[2-(pyridin-2-yl)-1*H*-benzimidazole]cobalt(II) monohydrate (CSD refcode DACRIK; Das *et al.*, 2011).

## Synthesis and crystallization

The reaction scheme for the synthesis of the title complex is given in Fig. 5. A solution of 2-(pyridin-2-yl)-1*H*-benzimidazole (0.15 g, 0.78 mmol) in ethanol (5 ml) was added dropwise to a stirring ethanolic solution of bis(triphenylphosphine)nickel(II) dichloride (0.50 g, 0.76 mmol). The mixture was stirred at room temperature for 24 h. The resulting mixture was concentrated and the product isolated by addition of diethyl ether (5 ml) giving a light-brown solid. Yield: 0.27 g (68%). Analysis calculated for $C_{24}H_{18}Cl_2N_6Ni$: C, 55.43; H, 3.49; N, 16.16%. Found: C, 55.23; H, 3.59; N, 16.25%. Light-blue plate-like crystals, suitable for X-ray diffraction analysis, were obtained by slow evaporation of a concentrated ethanol solution.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The complex crystallized as a monohydrate with the water molecule disordered over two sites (O1 and O2); occupancies fixed at 0.5 each.

## Acknowledgements

CSM is grateful to Professor Paul J. Chirik of Princeton University for hosting during the submission of the manuscript.

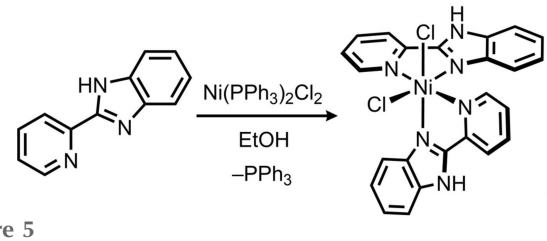



**Figure 5**
Reaction scheme for the synthesis of the title complex.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[NiCl_2(C_{12}H_9N_3)_2]\cdot H_2O$ |
| $M_r$ | 538.07 |
| Crystal system, space group | Monoclinic, *I*2/*a* |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 15.9019 (6), 14.7008 (7), 20.0039 (7) |
| $\beta$ (°) | 95.924 (4) |
| $V$ (Å$^3$) | 4651.4 (3) |
| $Z$ | 8 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.10 |
| Crystal size (mm) | 0.21 × 0.15 × 0.1 |
| | |
| Data collection | |
| Diffractometer | Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, Pilatus 200/300K |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015) |
| $T_{min}$, $T_{max}$ | 0.785, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 29773, 6268, 5296 |
| $R_{int}$ | 0.046 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.734 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.043, 0.113, 1.06 |
| No. of reflections | 6268 |
| No. of parameters | 322 |
| H-atom treatment | H-atom parameters constrained |
| | |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.16, −0.64 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010)'.

## Funding information

The authors thank the NSERC of Canada for funding. CSM is grateful to NSERC for a CGS-D fellowship. PGH thanks NSERC for a Discovery Grant and the University of Lethbridge for a Tier I Board of Governors Research Chair in Organometallic Chemistry. SOO is grateful to the University of KwaZulu-Natal and National Research Foundation–South Africa (grant No. CPRR98938) for financial support.

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# full crystallographic data

*IUCrData* (2020). **5**, x200040 [https://doi.org/10.1107/S2414314620000401]

## Dichloridobis[2-(pyridin-2-yl-$\kappa N$)-1*H*-benzimidazole-$\kappa N^3$]nickel(II) monohydrate

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### Dichloridobis[2-(pyridin-2-yl-$\kappa N$)-1*H*-benzimidazole-$\kappa N^3$]nickel(II) monohydrate

*Crystal data*

$[NiCl_2(C_{12}H_9N_3)_2]\cdot H_2O$
$M_r$ = 538.07
Monoclinic, *I*2/*a*
*a* = 15.9019 (6) Å
*b* = 14.7008 (7) Å
*c* = 20.0039 (7) Å
$\beta$ = 95.924 (4)°
*V* = 4651.4 (3) Å$^3$
*Z* = 8
*F*(000) = 2208
$D_x$ = 1.537 Mg m$^{-3}$
Mo *K*$\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 13739 reflections
$\theta$ = 3.8–30.9°
$\mu$ = 1.10 mm$^{-1}$
*T* = 100 K
Plate, clear light blue
0.21 × 0.15 × 0.1 mm

*Data collection*

Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, Pilatus 200/300K diffractometer
$\omega$ scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015)
$T_{min}$ = 0.785, $T_{max}$ = 1.000
29773 measured reflections
6268 independent reflections
5296 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.046
$\theta_{max}$ = 31.4°, $\theta_{min}$ = 3.4°
*h* = −22→21
*k* = −19→19
*l* = −29→26

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.113
*S* = 1.06
6268 reflections
322 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 11.2375P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.16 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.64 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**. The O-, N- and C-bound H atoms were included in calculated positions and treated as riding on the parent atom: O—H = 0.85 Å, N—H = 0.88 Å, C—H = 0.95 Å with $U_{iso}$(H) = 1.5$U_{eq}$(O) and 1.2$U_{eq}$(N,*C*).

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Ni1 | 0.41587 (2) | 0.53396 (2) | 0.26342 (2) | 0.01946 (9) | |
| Cl2 | 0.51535 (3) | 0.65004 (4) | 0.30400 (2) | 0.02048 (12) | |
| Cl1 | 0.34436 (3) | 0.63357 (5) | 0.17809 (3) | 0.02851 (14) | |
| N1 | 0.32601 (11) | 0.56738 (14) | 0.32888 (9) | 0.0206 (4) | |
| N4 | 0.50259 (11) | 0.47857 (14) | 0.20265 (9) | 0.0223 (4) | |
| N3 | 0.19362 (11) | 0.38608 (14) | 0.25224 (9) | 0.0214 (4) | |
| H3 | 0.1459 | 0.3800 | 0.2704 | 0.026* | |
| N5 | 0.47605 (11) | 0.43649 (14) | 0.32845 (9) | 0.0216 (4) | |
| N2 | 0.32190 (11) | 0.43767 (14) | 0.23554 (9) | 0.0230 (4) | |
| N6 | 0.54931 (12) | 0.30631 (15) | 0.33216 (10) | 0.0251 (4) | |
| H6 | 0.5796 | 0.2610 | 0.3188 | 0.030* | |
| C1 | 0.33068 (14) | 0.63587 (16) | 0.37299 (11) | 0.0220 (4) | |
| H1 | 0.3771 | 0.6767 | 0.3740 | 0.026* | |
| C6 | 0.25743 (13) | 0.44376 (16) | 0.27227 (10) | 0.0197 (4) | |
| C2 | 0.27009 (14) | 0.64957 (17) | 0.41747 (11) | 0.0239 (5) | |
| H2 | 0.2741 | 0.6996 | 0.4477 | 0.029* | |
| C13 | 0.52147 (14) | 0.50999 (18) | 0.14323 (12) | 0.0260 (5) | |
| H13 | 0.4931 | 0.5627 | 0.1250 | 0.031* | |
| C7 | 0.21767 (13) | 0.33846 (16) | 0.19770 (11) | 0.0220 (4) | |
| C5 | 0.25879 (13) | 0.51099 (16) | 0.32589 (10) | 0.0200 (4) | |
| C3 | 0.20350 (14) | 0.58805 (18) | 0.41653 (11) | 0.0251 (5) | |
| H3A | 0.1628 | 0.5939 | 0.4479 | 0.030* | |
| C4 | 0.19672 (13) | 0.51814 (17) | 0.36966 (11) | 0.0232 (5) | |
| H4 | 0.1509 | 0.4764 | 0.3676 | 0.028* | |
| C12 | 0.29871 (14) | 0.37186 (17) | 0.18758 (11) | 0.0239 (5) | |
| C17 | 0.54399 (13) | 0.40452 (16) | 0.22848 (11) | 0.0229 (4) | |
| C19 | 0.52027 (14) | 0.31581 (18) | 0.39437 (11) | 0.0266 (5) | |
| C18 | 0.52220 (13) | 0.38021 (17) | 0.29551 (11) | 0.0229 (4) | |
| C24 | 0.47421 (14) | 0.39799 (17) | 0.39175 (11) | 0.0247 (5) | |
| C8 | 0.17716 (14) | 0.27144 (18) | 0.15768 (12) | 0.0273 (5) | |
| H8 | 0.1232 | 0.2488 | 0.1658 | 0.033* | |
| C9 | 0.21903 (16) | 0.23914 (19) | 0.10533 (12) | 0.0305 (5) | |
| H9 | 0.1928 | 0.1942 | 0.0761 | 0.037* | |
| C16 | 0.60480 (15) | 0.35909 (18) | 0.19622 (12) | 0.0285 (5) | |
| H16 | 0.6329 | 0.3071 | 0.2159 | 0.034* | |
| C10 | 0.29967 (16) | 0.2715 (2) | 0.09461 (13) | 0.0335 (6) | |
| H10 | 0.3266 | 0.2477 | 0.0582 | 0.040* | |
| C14 | 0.58124 (16) | 0.46814 (19) | 0.10720 (13) | 0.0320 (6) | |
| H14 | 0.5929 | 0.4915 | 0.0648 | 0.038* | |
| C11 | 0.34100 (15) | 0.3368 (2) | 0.13516 (13) | 0.0319 (6) | |
| H11 | 0.3960 | 0.3572 | 0.1279 | 0.038* | |
| C23 | 0.43824 (16) | 0.42902 (19) | 0.44841 (11) | 0.0290 (5) | |
| H23 | 0.4070 | 0.4842 | 0.4476 | 0.035* | |
| C22 | 0.45004 (18) | 0.3760 (2) | 0.50589 (12) | 0.0345 (6) | |
| H22 | 0.4270 | 0.3959 | 0.5453 | 0.041* | |

| | | | | | |
|---|---|---|---|---|---|
| C20 | 0.53109 (16) | 0.2614 (2) | 0.45225 (13) | 0.0335 (6) | |
| H20 | 0.5614 | 0.2057 | 0.4534 | 0.040* | |
| C21 | 0.49486 (17) | 0.2940 (2) | 0.50755 (12) | 0.0362 (6) | |
| H21 | 0.5006 | 0.2596 | 0.5479 | 0.043* | |
| C15 | 0.62325 (16) | 0.3922 (2) | 0.13411 (13) | 0.0320 (5) | |
| H15 | 0.6644 | 0.3627 | 0.1105 | 0.038* | |
| O1 | 0.3180 (3) | 0.5134 (3) | 0.0429 (2) | 0.0440 (10) | 0.5 |
| H1A | 0.3268 | 0.5413 | 0.0802 | 0.066* | 0.5 |
| H1B | 0.3085 | 0.4575 | 0.0502 | 0.066* | 0.5 |
| O2 | 0.2882 (3) | 0.6487 (3) | 0.01818 (18) | 0.0429 (10) | 0.5 |
| H2A | 0.2602 | 0.6019 | 0.0042 | 0.064* | 0.5 |
| H2B | 0.3113 | 0.6391 | 0.0578 | 0.064* | 0.5 |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.01005 (13) | 0.03529 (17) | 0.01374 (13) | −0.00391 (10) | 0.00448 (10) | −0.00355 (11) |
| Cl2 | 0.0109 (2) | 0.0340 (3) | 0.0169 (2) | −0.00172 (18) | 0.00350 (17) | −0.00279 (19) |
| Cl1 | 0.0169 (2) | 0.0491 (4) | 0.0188 (2) | −0.0029 (2) | −0.00126 (19) | 0.0018 (2) |
| N1 | 0.0130 (8) | 0.0355 (10) | 0.0141 (8) | −0.0013 (7) | 0.0049 (6) | −0.0016 (7) |
| N4 | 0.0129 (8) | 0.0379 (11) | 0.0165 (8) | −0.0066 (7) | 0.0038 (7) | −0.0047 (8) |
| N3 | 0.0098 (7) | 0.0387 (11) | 0.0162 (8) | −0.0036 (7) | 0.0033 (6) | 0.0001 (8) |
| N5 | 0.0154 (8) | 0.0346 (10) | 0.0153 (8) | −0.0064 (7) | 0.0036 (7) | −0.0023 (7) |
| N2 | 0.0133 (8) | 0.0401 (11) | 0.0166 (8) | −0.0052 (8) | 0.0059 (7) | −0.0046 (8) |
| N6 | 0.0167 (8) | 0.0376 (11) | 0.0208 (9) | −0.0022 (8) | 0.0007 (7) | −0.0010 (8) |
| C1 | 0.0172 (10) | 0.0334 (12) | 0.0158 (9) | −0.0009 (8) | 0.0035 (8) | −0.0014 (8) |
| C6 | 0.0114 (9) | 0.0319 (11) | 0.0159 (9) | −0.0005 (8) | 0.0020 (7) | 0.0000 (8) |
| C2 | 0.0196 (10) | 0.0384 (13) | 0.0143 (9) | 0.0055 (9) | 0.0048 (8) | −0.0004 (9) |
| C13 | 0.0179 (10) | 0.0420 (13) | 0.0192 (10) | −0.0054 (9) | 0.0064 (8) | −0.0015 (9) |
| C7 | 0.0141 (9) | 0.0351 (12) | 0.0163 (9) | −0.0028 (8) | 0.0000 (8) | 0.0011 (9) |
| C5 | 0.0113 (9) | 0.0368 (12) | 0.0120 (8) | 0.0018 (8) | 0.0020 (7) | 0.0007 (8) |
| C3 | 0.0149 (9) | 0.0445 (14) | 0.0166 (9) | 0.0053 (9) | 0.0049 (8) | 0.0013 (9) |
| C4 | 0.0111 (9) | 0.0423 (13) | 0.0163 (9) | 0.0005 (8) | 0.0022 (8) | 0.0036 (9) |
| C12 | 0.0160 (10) | 0.0385 (13) | 0.0172 (9) | −0.0054 (9) | 0.0025 (8) | −0.0057 (9) |
| C17 | 0.0129 (9) | 0.0362 (12) | 0.0196 (10) | −0.0059 (8) | 0.0021 (8) | −0.0051 (9) |
| C19 | 0.0190 (10) | 0.0422 (13) | 0.0178 (10) | −0.0096 (9) | −0.0019 (8) | −0.0011 (9) |
| C18 | 0.0128 (9) | 0.0383 (12) | 0.0173 (9) | −0.0046 (8) | −0.0002 (8) | −0.0024 (9) |
| C24 | 0.0174 (10) | 0.0386 (13) | 0.0176 (10) | −0.0094 (9) | −0.0009 (8) | −0.0009 (9) |
| C8 | 0.0180 (10) | 0.0414 (14) | 0.0216 (10) | −0.0077 (9) | −0.0025 (9) | −0.0010 (10) |
| C9 | 0.0255 (11) | 0.0430 (14) | 0.0219 (11) | −0.0073 (10) | −0.0036 (9) | −0.0077 (10) |
| C16 | 0.0179 (10) | 0.0418 (14) | 0.0264 (11) | −0.0009 (9) | 0.0053 (9) | −0.0049 (10) |
| C10 | 0.0252 (12) | 0.0514 (16) | 0.0245 (11) | −0.0056 (11) | 0.0050 (9) | −0.0140 (11) |
| C14 | 0.0236 (12) | 0.0501 (16) | 0.0242 (11) | −0.0064 (11) | 0.0123 (10) | −0.0039 (11) |
| C11 | 0.0204 (11) | 0.0509 (15) | 0.0260 (12) | −0.0089 (10) | 0.0098 (9) | −0.0165 (11) |
| C23 | 0.0253 (11) | 0.0434 (14) | 0.0182 (10) | −0.0138 (10) | 0.0021 (9) | −0.0041 (10) |
| C22 | 0.0358 (14) | 0.0520 (16) | 0.0158 (10) | −0.0193 (12) | 0.0023 (10) | −0.0037 (10) |
| C20 | 0.0270 (12) | 0.0454 (15) | 0.0263 (12) | −0.0106 (11) | −0.0057 (10) | 0.0043 (11) |
| C21 | 0.0362 (14) | 0.0533 (17) | 0.0174 (10) | −0.0191 (12) | −0.0048 (10) | 0.0042 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C15 | 0.0201 (11) | 0.0511 (15) | 0.0268 (12) | −0.0027 (10) | 0.0114 (9) | −0.0093 (11) |
| O1 | 0.057 (3) | 0.048 (2) | 0.0260 (19) | 0.009 (2) | −0.0008 (18) | 0.0042 (17) |
| O2 | 0.052 (3) | 0.057 (3) | 0.0188 (17) | −0.022 (2) | 0.0026 (17) | −0.0022 (16) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ni1—Cl2 | 2.4101 (6) | C3—C4 | 1.388 (3) |
| Ni1—Cl1 | 2.4394 (6) | C4—H4 | 0.9500 |
| Ni1—N1 | 2.0937 (18) | C12—C11 | 1.401 (3) |
| Ni1—N4 | 2.0949 (19) | C17—C18 | 1.463 (3) |
| Ni1—N5 | 2.099 (2) | C17—C16 | 1.388 (3) |
| Ni1—N2 | 2.0918 (19) | C19—C24 | 1.411 (4) |
| N1—C1 | 1.336 (3) | C19—C20 | 1.403 (3) |
| N1—C5 | 1.349 (3) | C24—C23 | 1.398 (3) |
| N4—C13 | 1.338 (3) | C8—H8 | 0.9500 |
| N4—C17 | 1.347 (3) | C8—C9 | 1.382 (4) |
| N3—H3 | 0.8800 | C9—H9 | 0.9500 |
| N3—C6 | 1.351 (3) | C9—C10 | 1.405 (4) |
| N3—C7 | 1.383 (3) | C16—H16 | 0.9500 |
| N5—C18 | 1.326 (3) | C16—C15 | 1.393 (4) |
| N5—C24 | 1.390 (3) | C10—H10 | 0.9500 |
| N2—C6 | 1.325 (3) | C10—C11 | 1.378 (3) |
| N2—C12 | 1.385 (3) | C14—H14 | 0.9500 |
| N6—H6 | 0.8800 | C14—C15 | 1.382 (4) |
| N6—C19 | 1.378 (3) | C11—H11 | 0.9500 |
| N6—C18 | 1.356 (3) | C23—H23 | 0.9500 |
| C1—H1 | 0.9500 | C23—C22 | 1.386 (4) |
| C1—C2 | 1.392 (3) | C22—H22 | 0.9500 |
| C6—C5 | 1.457 (3) | C22—C21 | 1.398 (4) |
| C2—H2 | 0.9500 | C20—H20 | 0.9500 |
| C2—C3 | 1.391 (3) | C20—C21 | 1.385 (4) |
| C13—H13 | 0.9500 | C21—H21 | 0.9500 |
| C13—C14 | 1.394 (3) | C15—H15 | 0.9500 |
| C7—C12 | 1.413 (3) | O1—H1A | 0.8505 |
| C7—C8 | 1.386 (3) | O1—H1B | 0.8503 |
| C5—C4 | 1.389 (3) | O2—H2A | 0.8507 |
| C3—H3A | 0.9500 | O2—H2B | 0.8498 |
| | | | |
| Cl2—Ni1—Cl1 | 93.04 (2) | C5—C4—H4 | 120.9 |
| N1—Ni1—Cl2 | 95.15 (5) | C3—C4—C5 | 118.1 (2) |
| N1—Ni1—Cl1 | 89.87 (5) | C3—C4—H4 | 120.9 |
| N1—Ni1—N4 | 170.66 (8) | N2—C12—C7 | 108.96 (19) |
| N1—Ni1—N5 | 93.99 (7) | N2—C12—C11 | 131.4 (2) |
| N4—Ni1—Cl2 | 91.27 (5) | C11—C12—C7 | 119.6 (2) |
| N4—Ni1—Cl1 | 96.57 (6) | N4—C17—C18 | 113.3 (2) |
| N4—Ni1—N5 | 78.99 (8) | N4—C17—C16 | 123.1 (2) |
| N5—Ni1—Cl2 | 91.90 (5) | C16—C17—C18 | 123.4 (2) |
| N5—Ni1—Cl1 | 173.44 (6) | N6—C19—C24 | 105.9 (2) |

| | | | |
|---|---|---|---|
| N2—Ni1—Cl2 | 174.23 (5) | N6—C19—C20 | 131.6 (3) |
| N2—Ni1—Cl1 | 87.19 (6) | C20—C19—C24 | 122.5 (2) |
| N2—Ni1—N1 | 79.09 (7) | N5—C18—N6 | 113.1 (2) |
| N2—Ni1—N4 | 94.43 (7) | N5—C18—C17 | 119.9 (2) |
| N2—Ni1—N5 | 88.32 (8) | N6—C18—C17 | 126.8 (2) |
| C1—N1—Ni1 | 126.52 (15) | N5—C24—C19 | 108.8 (2) |
| C1—N1—C5 | 118.82 (18) | N5—C24—C23 | 130.9 (2) |
| C5—N1—Ni1 | 114.63 (15) | C23—C24—C19 | 120.2 (2) |
| C13—N4—Ni1 | 127.08 (17) | C7—C8—H8 | 121.6 |
| C13—N4—C17 | 118.3 (2) | C9—C8—C7 | 116.8 (2) |
| C17—N4—Ni1 | 114.60 (15) | C9—C8—H8 | 121.6 |
| C6—N3—H3 | 126.5 | C8—C9—H9 | 119.4 |
| C6—N3—C7 | 106.94 (17) | C8—C9—C10 | 121.2 (2) |
| C7—N3—H3 | 126.5 | C10—C9—H9 | 119.4 |
| C18—N5—Ni1 | 111.00 (15) | C17—C16—H16 | 121.1 |
| C18—N5—C24 | 105.3 (2) | C17—C16—C15 | 117.9 (2) |
| C24—N5—Ni1 | 142.33 (16) | C15—C16—H16 | 121.1 |
| C6—N2—Ni1 | 112.26 (15) | C9—C10—H10 | 118.9 |
| C6—N2—C12 | 105.40 (18) | C11—C10—C9 | 122.2 (2) |
| C12—N2—Ni1 | 142.08 (15) | C11—C10—H10 | 118.9 |
| C19—N6—H6 | 126.6 | C13—C14—H14 | 120.6 |
| C18—N6—H6 | 126.6 | C15—C14—C13 | 118.9 (2) |
| C18—N6—C19 | 106.8 (2) | C15—C14—H14 | 120.6 |
| N1—C1—H1 | 118.8 | C12—C11—H11 | 121.3 |
| N1—C1—C2 | 122.4 (2) | C10—C11—C12 | 117.4 (2) |
| C2—C1—H1 | 118.8 | C10—C11—H11 | 121.3 |
| N3—C6—C5 | 126.71 (19) | C24—C23—H23 | 121.4 |
| N2—C6—N3 | 113.18 (19) | C22—C23—C24 | 117.2 (3) |
| N2—C6—C5 | 120.04 (19) | C22—C23—H23 | 121.4 |
| C1—C2—H2 | 120.9 | C23—C22—H22 | 119.0 |
| C3—C2—C1 | 118.3 (2) | C23—C22—C21 | 122.0 (2) |
| C3—C2—H2 | 120.9 | C21—C22—H22 | 119.0 |
| N4—C13—H13 | 118.8 | C19—C20—H20 | 122.1 |
| N4—C13—C14 | 122.3 (2) | C21—C20—C19 | 115.9 (3) |
| C14—C13—H13 | 118.8 | C21—C20—H20 | 122.1 |
| N3—C7—C12 | 105.53 (19) | C22—C21—H21 | 118.9 |
| N3—C7—C8 | 131.7 (2) | C20—C21—C22 | 122.1 (2) |
| C8—C7—C12 | 122.7 (2) | C20—C21—H21 | 118.9 |
| N1—C5—C6 | 113.64 (18) | C16—C15—H15 | 120.3 |
| N1—C5—C4 | 122.5 (2) | C14—C15—C16 | 119.5 (2) |
| C4—C5—C6 | 123.9 (2) | C14—C15—H15 | 120.3 |
| C2—C3—H3A | 120.1 | H1A—O1—H1B | 109.4 |
| C4—C3—C2 | 119.8 (2) | H2A—O2—H2B | 109.5 |
| C4—C3—H3A | 120.1 | | |

*Hydrogen-bond geometry (Å, º)*

*Cg*1, *Cg*2, *Cg*3, *Cg*4 and *Cg*5 are the centroids of the C7–C12, N5/N6/C18/C19/C24, N1/C1–C5, N4/C13–C17 and C19–C24 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H1···Cl2 | 0.95 | 2.75 | 3.378 (2) | 124 |
| O1—H1*A*···Cl1 | 0.85 | 2.37 | 3.221 (4) | 174 |
| O2—H2*B*···Cl1 | 0.85 | 2.41 | 3.239 (4) | 165 |
| O2—H2*A*···O1$^{i}$ | 0.85 | 1.97 | 2.806 (6) | 167 |
| N3—H3···Cl2$^{ii}$ | 0.88 | 2.29 | 3.162 (2) | 171 |
| N6—H6···Cl1$^{iii}$ | 0.88 | 2.23 | 3.069 (2) | 160 |
| C2—H2···O2$^{iv}$ | 0.95 | 2.56 | 3.400 (5) | 147 |
| C20—H20···O2$^{iii}$ | 0.95 | 2.54 | 3.317 (5) | 139 |
| O1—H1*B*···*Cg*1 | 0.85 | 3.11 | 3.869 (3) | 150 |
| C3—H3*A*···*Cg*5$^{ii}$ | 0.95 | 2.97 | 3.738 (3) | 139 |
| C8—H8···*Cg*2$^{v}$ | 0.95 | 2.69 | 3.579 (3) | 155 |
| C9—H9···*Cg*5$^{v}$ | 0.95 | 2.88 | 3.542 (3) | 128 |
| C11—H11···*Cg*4 | 0.95 | 2.93 | 3.810 (3) | 155 |
| C23—H23···*Cg*3 | 0.95 | 2.94 | 3.733 (3) | 142 |

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