Crystal structure and Hirshfeld surface analysis of dichloridotetrakis(4-methyl-1H-pyrazole-κN₂)-nickel(II) acetonitrile disolvate

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The title compound, [NiCl₂(C₄H₆N₂)₄]·2CH₃CN, is a mononuclear octahedral NiII pyrazole-based complex. Two acetonitrile molecules are linked to the Ni II complex by N—H···C₁/C₁/C₁/N hydrogen bonds. The Ni II atom is octahedrally coordinated by four N atoms of four 4-methyl-1H-pyrazole ligands, forming the equatorial plane. The axial positions are occupied by two Cl atoms. [NiCl₂(C₄H₆N₂)₄]·2CH₃CN was synthesized by the reaction of 4-methyl-1H-pyrazole with nickel(II) chloride hexahydrate in acetonitrile solution under ambient conditions and characterized by single-crystal X-ray diffraction analysis. A Hirshfeld surface analysis was performed, which suggests that the most important contributions to the surface contacts are from H···C/C···H (13.4%), H···C/C···H (13.4%) and H···Cl/Cl···H (10.1%) interactions.

1. Chemical context

Pyrazoles as ligands are widely used for the synthesis of coordination compounds because of their rich coordinative flexibility (Trofimenko, 1972; Mukherjee, 2000; Monica & Ardizzoia, 2007; Halcrow, 2009; Viciano-Chumillas et al., 2010; Klingele et al., 2009). Numerous studies of the synthesis and structure of transition-metal complexes such as Cu, Fe, Co, Ni, and Zn with pyrazole ligands indicate such compounds exhibit promising properties (Evans et al., 2004; Kirthan et al., 2020; Govor et al., 2012; Kulkarni et al., 2011; Dias et al., 2020; Naik et al., 2016; Malinkin et al., 2012). For example, CuII pyrazole-based complexes are very promising as antioxidants (Kupcewicz, Sobiesiak et al., 2013; Chkirate et al., 2019) and anti-cancer agents because of their cytotoxic activity (Kupcewicz, Ciolkowski et al., 2013; Aljuhani et al., 2021; Santini et al., 2014). Iron pyrazole-containing complexes have extraordinary electronic properties (Kulmaczewski et al., 2021; Olguín & Brooker, 2011) and catalytic activity in the hydrosilylation of organocarbonyl substrates (Lin et al., 2018). Cobalt complexes with pyrazole ligands are used as catalyst precursors for the peroxidative oxidation of cyclohexane (Silva et al., 2014) and have useful optical and photoluminescence properties (Direm et al., 2021). Zinc complexes with pyrazoles also exhibit anti-oxidative activity (Barta Holló et al., 2022) and have useful luminescent properties (Li et al., 2004; Singh et al., 2009). The study of the synthesis, structure and properties of nickel complexes with pyrazoles is also important. Nickel(II) pyrazolate complexes can be synthesized by the reaction between

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nickel(II) salts and pyrazoles in water or organic solvents (Nicholls & Warburton, 1970; Sun et al., 2002; Malecka et al., 2001; Chen et al., 2009). Nickel complexes incorporating pyrazole-based ligands are used for ethylene dimerization (Wang et al., 2015) or polymerization (Nelana et al., 2004; Moreno-Lara et al., 2015). Mononuclear nickel(II) coordination compounds with pyrazoles show anticancer activity. The cytotoxic and apoptotic effects of such compounds suggested that they could be good candidates for further pharmacological research in the field of the development of effective anticancer agents (Gogoi et al., 2019; Sobiesiak et al., 2011). There is also a report on the activation of some organonitriles by transition-metal centers, such as Ni, toward nucleophilic addition of pyrazole (Hsieh et al., 2009). Ni II complexes can activate the pyrazole-nitrile coupling reaction. As part of our continuing interest in multifunctional transition-metal complexes with pyrazole ligands, we report herein the synthesis and crystal structure of a new mononuclear octahedral nickel(II) coordination compound based on 4-methyl-1H-pyrazole.

2. Structural commentary

The title compound has a molecular crystal structure, which is built-up from neutral monomeric [NiCl2(4-MeHpz)4] units (Fig. 1) and acetonitrile as interstitial molecules in a 1:2 ratio. All the components of the structure are associated via intermolecular N···H···N and C···H···N hydrogen bonds. Intramolecular N···H···N hydrogen bonding is also observed. The NiII ion displays a distorted octahedral coordination environment formed by four pyridine-like nitrogen atoms of 4-MeHpz ligands in the equatorial positions with Ni1—N1 = 2.112 (2) Å and Ni1—N3 = 2.092 (2) Å bond distances and two Cl− anions in axial positions with an Ni1—Cl1 distance of 2.4581 (6) Å. Selected bond lengths and bond angles are given in Table 1. The orientation of the pyrazole ligands around the metal ion is different, as indicated by the plane-to-plane angles of pyrazole rings. Two pyrazole ring planes are almost perpendicular to the NiN4 equatorial plane [86.6 (1)°] whereas two other pyrazole rings are less tilted [43.9 (1)°]. The complex has an NiCl2L4 structure with a trans arrangement of the ligands and crystallographically imposed centrosymmetry.

| Bond Lengths (Å) | Bond Angles (°) |
|------------------|-----------------|
| Ni1—N3           | 2.091 (2)       |
| Ni1—N1           | 2.112 (2)       |
| N3—Ni1—N3        | 180.0           |
| N3—Ni1—Cl1       | 90.57 (6)       |
| N3—Ni1—N1        | 180.0           |
| N3—Ni1—Cl1       | 90.09 (6)       |

Symmetry code: (i) −x + 1, −y + 1, −z + 2.

The title compound has a molecular crystal structure, which is built-up from neutral monomeric [NiCl2(4-MeHpz)4] units (Fig. 1) and acetonitrile as interstitial molecules in a 1:2 ratio. All the components of the structure are associated via intermolecular N···H···N and C···H···N hydrogen bonds. Intramolecular N···H···N hydrogen bonding is also observed. The NiII ion displays a distorted octahedral coordination environment formed by four pyridine-like nitrogen atoms of 4-MeHpz ligands in the equatorial positions with Ni1—N1 = 2.112 (2) Å and Ni1—N3 = 2.092 (2) Å bond distances and two Cl− anions in axial positions with an Ni1—Cl1 distance of 2.4581 (6) Å. Selected bond lengths and bond angles are given in Table 1. The orientation of the pyrazole ligands around the metal ion is different, as indicated by the plane-to-plane angles of pyrazole rings. Two pyrazole ring planes are almost perpendicular to the NiN4 equatorial plane [86.6 (1)°] whereas two other pyrazole rings are less tilted [43.9 (1)°]. The complex has an NiCl2L4 structure with a trans arrangement of the ligands and crystallographically imposed centrosymmetry.

3. Supramolecular features

The crystal structure is built up from the parallel packing of discrete supramolecular chains running along the a-axis direction with an Ni···Ni separation of 6.9625 (4) Å. A perspective view of a chain is depicted in Fig. 2. Within the chain, the complex molecules interact through N—H···Cl···N interactions.
hydrogen bonds, while the association with the interstitial acetonitrile molecules occurs via N—H···N hydrogen bonds. The geometric parameters of the hydrogen bonds are given in Table 2.

### 4. Hirshfeld surface analysis

The Hirshfeld surface analysis was performed and the associated two-dimensional fingerprint plots were generated using Crystal Explorer 17.5 software (Spackman et al., 2021), with a standard resolution of the three-dimensional $d_{	ext{norm}}$ surfaces plotted over a fixed color scale of 0.3714 (red) to 2.0459 (blue) a.u. There are six red spots on the $d_{	ext{norm}}$ surface (Fig. 3). The dark-red spots arise from interatomic contacts less than the sum of the corresponding van der Waals radii and represent negative $d_{	ext{norm}}$ values on the surface, while the other weaker intermolecular interactions appear as light-red spots. The Hirshfeld surfaces mapped over $d_{	ext{norm}}$ are shown for the H···H, H···N/N···H, H···C/C···H, and H···Cl/Cl···H contacts. The Hirshfeld surface representations with the function $d_{	ext{norm}}$, which were plotted onto the surface for interactions mentioned above, the overall two-dimensional fingerprint plot, and the decomposed two-dimensional fingerprint plots for the several interactions are given in Fig. 4. The most significant contributions to the overall crystal packing are from H···H (62.1%), H···N/N···H (13.7%), H···C/C···H (13.4%), and H···Cl/Cl···H (10.1%). There is also a small contribution from weak Cl···C/C···Cl (0.2%) and C···C (0.4%) intermolecular contacts. These contacts are not visible as red spots on the Hirshfeld surface. The H···H contacts are located in the middle region of the two-dimensional fingerprint plot, while H···Cl/Cl···H contacts form sharp wings on the sides of the corresponding two-dimensional plot.

### 5. Database survey

A search of the Cambridge Structural Database (CSD version 5.43, November 2021; Groom et al., 2016) for the Ni(C$_3$H$_7$N$_2$)$_4$ moiety (C$_3$H$_7$N$_2$ is the skeleton of pyrazole ring which is coordinated in a monodentate way) gave 60 hits while the fragment Ni(C$_3$H$_7$N$_2$)$_4$X$_2$, where $X$ is any halogen, gave 20 hits (complexes with Cl and Br were found). Most similar to the title compound are the mononuclear nickel(II) pyrazole-based complexes AZEREC (Nelana et al., 2004) and BOGFIN (Tao et al., 2008). These complexes also crystallized in the triclinic $P\overline{1}$ space group and have similar crystal packings. Other pyrazole-containing complexes are BRTPNI (Mighell et al., 1969), MUWFER (Serpas et al., 2016), NIPYRA (Reimann et al., 1967), NIPYRA01 (Helmholt et al., 1987), SAGBAH (Akbar et al., 2020) and SANSUW (Michaud et al., 2005), which crystallized in the monoclinic crystal system and.

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**Table 2**

Hydrogen-bond geometry (Å, °).

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N2—H2···N5** | 0.86 | 2.60 | 3.217 (4) | 130 |
| N2—H2···Cl1 | 0.86 | 2.50 | 3.088 (3) | 127 |
| N4—H4···Cl1** | 0.86 | 2.45 | 3.217 (2) | 149 |
| C5—H5···N5** | 0.93 | 2.74 | 3.5785 (2) | 150 |

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

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**Figure 3**

Two projections of Hirshfeld surfaces mapped over $d_{	ext{norm}}$ showing the intermolecular interactions within the molecule. The N4—H4···Cl1 and N2—H2···N5 contacts are shown as pink and yellow dashed lines, respectively.

**Figure 4**

(a) The Hirshfeld surface representations with the function $d_{	ext{norm}}$ plotted onto the surface for selected interactions and (b) two-dimensional fingerprint plots for the title compound, showing the contributions of different types of interactions.
6. Synthesis and crystallization

The title compound was obtained by the reaction of 4-MeHpz (1.7 mmol, 0.14g) with NiCl₂·6H₂O (0.84mmol, 0.2 g) in acetonitrile (10 ml). The mixture of solid starting materials was stirred for 8 h at room temperature and the resultant green–blue solution was then filtered. Light-blue crystals of [NiCl₂(C₄H₆N₂)₄]·2CH₃CN were obtained upon slow evaporation of the solvent over two weeks. CHN elemental analysis: calculated for NiCl₂(C₄H₆N₂)₄: C 41.95, H 5.28, N 24.46%; found: C 41.79, H 5.07, N 24.78%. The IR spectra of the starting 4-methyl-1H-pyrazole and clear, light-blue crystals of the title coordination compound are given in the supporting information for this article. The synthesis can be described by the following reaction: NiCl₂·6H₂O + 4C₄H₆N₂ + 2CH₃CN = [NiCl₂(C₄H₆N₂)₄]·2CH₃CN + 6H₂O.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were placed in calculated positions [C—N = 0.86 Å, C—H = 0.93 Å (0.96 Å for C-methyl)] and refined as riding with $U_{	ext{iso}}(H) = 1.2U_{	ext{eq}}$(CN) or 1.5$U_{	ext{eq}}$(C-methyl). Reflections with ($\Delta F^2$/esd) > 10 were omitted from the refinement.

### Table 3

| Crystal data | Chemical formula | $M_r$ | Temperature (K) | $a$, $b$, $c$ (Å) | $\alpha$, $\beta$, $\gamma$ (°) | $V$ (Å³) | Z | Radiation type | $\mu$ (mm⁻¹) | Crystal size (mm) |
|--------------|------------------|------|-----------------|------------------|------------------|----------|----|----------------|-------------|------------------|
| [NiCl₂(C₄H₆N₂)₄]·2CH₃CN | 540.15 | Triclinic, $P\overline{1}$ | 293 | 6.9625 (4), 9.8482 (8), 11.0920 (12) | 74.417 (8), 81.495 (6), 71.191 (6) | 691.92 (10) | 1 | Mo $K\alpha$ | 0.92 | 0.2 × 0.15 × 0.03 |

### Data collection

| Crystal system, space group | $T_{	ext{min}}$, $T_{	ext{max}}$ | No. of measured reflections | $R_{	ext{int}}$ | No. of parameters | $\Delta F_{	ext{max}}$, $\Delta F_{	ext{min}}$ (e Å⁻³) |
|-----------------------------|------------------|------------------|-------------|-------------|------------------|
| $\beta$, $\gamma$, $\nu$ (°) | 0.691 | (sin $\theta$/λ)$_{\text{max}}$ (Å⁻¹) | 0.031 | 154 | 0.57, −0.45 |

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Crystal structure and Hirshfeld surface analysis of dichloridotetrakis(4-methyl-1H-pyrazole-κN²)nickel(II) acetonitrile disolvate

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Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2021); cell refinement: CrysAlis PRO (Rigaku OD, 2021); data reduction: CrysAlis PRO (Rigaku OD, 2021); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

Dichloridotetrakis(4-methyl-1H-pyrazole-κN²)nickel(II) acetonitrile disolvate

Crystal data

\[\text{[NiCl}_2\text{(C}_4\text{H}_6\text{N}_2)_4\text{]}\cdot 2\text{C}_2\text{H}_3\text{N}\]

\(M_r = 540.15\)

Triclinic, \(P\overline{1}\)

\(a = 6.9625 (4) \, \text{Å}\)

\(b = 9.8482 (8) \, \text{Å}\)

\(c = 11.0920 (12) \, \text{Å}\)

\(\alpha = 74.417 (8)^\circ\)

\(\beta = 81.495 (6)^\circ\)

\(\gamma = 71.191 (6)^\circ\)

\(V = 691.92 (10) \, \text{Å}^3\)

Data collection

Xcalibur, Eos

diffraclometer

Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1593 pixels mm\(^{-1}\)

\(\omega\) scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2021)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.047\)

\(wR(F^2) = 0.130\)

\(S = 1.03\)

3161 reflections

154 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
where $w = 1/[σ(F_o^2) + (0.0597P)^2 + 0.1286P]$

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

$(\Delta/σ)^{\text{max}} < 0.001$

**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

|      | x     | y     | z     | Uiso* Ueq |
|------|-------|-------|-------|-----------|
| Ni1  | 0.500000 | 0.500000 | 1.000000 | 0.03038 (17) |
| C3   | 0.7595 (4) | 0.6698 (3) | 0.7894 (3) | 0.0418 (7) |
| H3   | 0.885178 | 0.600521 | 0.807503 | 0.050* |
| N2   | 0.4458 (4) | 0.7836 (3) | 0.7985 (2) | 0.0433 (6) |
| H2   | 0.318650 | 0.807118 | 0.822630 | 0.052* |
| N3   | 0.4456 (3) | 0.4131 (2) | 0.8602 (2) | 0.0357 (5) |
| C5   | 0.2833 (5) | 0.3210 (4) | 0.7604 (3) | 0.0509 (8) |
| H5   | 0.184629 | 0.285430 | 0.742681 | 0.061* |
| C2   | 0.7297 (5) | 0.7927 (4) | 0.6882 (3) | 0.0451 (7) |
| C7   | 0.5519 (4) | 0.3886 (3) | 0.7546 (3) | 0.0423 (7) |
| H7   | 0.676277 | 0.406895 | 0.728729 | 0.051* |
| C6   | 0.4560 (5) | 0.3325 (3) | 0.6874 (3) | 0.0464 (7) |
| C1   | 0.5283 (5) | 0.8623 (4) | 0.6981 (3) | 0.0522 (8) |
| H1   | 0.458925 | 0.949441 | 0.644659 | 0.063* |
| C8   | 0.5300 (7) | 0.2883 (5) | 0.5643 (4) | 0.0789 (12) |
| H8A  | 0.602413 | 0.184814 | 0.580475 | 0.118* |
| H8B  | 0.618933 | 0.343879 | 0.517855 | 0.118* |
| H8C  | 0.415733 | 0.308009 | 0.516557 | 0.118* |
| N1   | 0.5870 (3) | 0.6636 (2) | 0.8565 (2) | 0.0354 (5) |
| C11  | 0.14603 (9) | 0.65951 (7) | 0.99696 (7) | 0.0397 (2) |
| N4   | 0.2819 (3) | 0.3701 (3) | 0.8618 (3) | 0.0433 (6) |
| H4   | 0.186829 | 0.373560 | 0.921075 | 0.052* |
| C4   | 0.8908 (6) | 0.8343 (5) | 0.5915 (4) | 0.0752 (12) |
| H4A  | 1.021370 | 0.791110 | 0.626254 | 0.113* |
| H4B  | 0.861116 | 0.939785 | 0.568022 | 0.113* |
| H4C  | 0.892391 | 0.798492 | 0.518891 | 0.113* |
| C9   | 0.9065 (6) | 0.0384 (4) | 0.8290 (4) | 0.0599 (9) |
| N5   | 1.0344 (5) | 0.0551 (4) | 0.7595 (4) | 0.0803 (11) |
| C10  | 0.7409 (5) | 0.0148 (4) | 0.9202 (4) | 0.0674 (11) |
| H10A | 0.620906 | 0.035123 | 0.877485 | 0.101* |
| H10B | 0.714797 | 0.079430 | 0.975807 | 0.101* |
| H10C | 0.777646 | −0.085902 | 0.967767 | 0.101* |
### Atomic displacement parameters (Å²)

|       | $U_{11}$     | $U_{22}$     | $U_{33}$     | $U_{12}$     | $U_{13}$     | $U_{23}$   |
|-------|--------------|--------------|--------------|--------------|--------------|------------|
| Ni1   | 0.0233 (2)   | 0.0330 (3)   | 0.0342 (3)   | −0.01078 (19)| 0.00342 (19)| −0.0069 (2)|
| C3    | 0.0322 (14)  | 0.0492 (18)  | 0.0462 (18)  | −0.0196 (13) | 0.0066 (13) | −0.0110 (15)|
| N2    | 0.0338 (12)  | 0.0407 (15)  | 0.0471 (15)  | −0.0084 (11) | 0.0012 (11) | −0.0019 (12)|
| N3    | 0.0285 (11)  | 0.0391 (13)  | 0.0412 (14)  | −0.0139 (10) | 0.0028 (10) | −0.0105 (11)|
| C5    | 0.0442 (17)  | 0.057 (2)    | 0.061 (2)    | −0.0219 (15) | −0.0078 (16)| −0.0199 (17)|
| C2    | 0.0520 (18)  | 0.056 (2)    | 0.0330 (16)  | −0.0293 (16) | 0.0077 (14) | −0.0092 (14)|
| C7    | 0.0400 (15)  | 0.0505 (18)  | 0.0417 (17)  | −0.0208 (13) | 0.0078 (13) | −0.0160 (14)|
| C6    | 0.0565 (19)  | 0.0449 (19)  | 0.0390 (17)  | −0.0168 (15) | −0.0018 (14)| −0.0104 (14)|
| C1    | 0.057 (2)    | 0.052 (2)    | 0.0391 (18)  | −0.0174 (16) | −0.0001 (15)| 0.0031 (15) |
| C8    | 0.109 (3)    | 0.085 (3)    | 0.056 (3)    | −0.038 (3)   | 0.008 (2)   | −0.034 (2)  |
| N1    | 0.0320 (11)  | 0.0358 (13)  | 0.0383 (13)  | −0.0136 (10) | 0.0027 (10) | −0.0072 (11)|
| C11   | 0.0231 (3)   | 0.0415 (4)   | 0.0513 (5)   | −0.0089 (3)  | 0.0037 (3)  | −0.0101 (3) |
| N4    | 0.0299 (12)  | 0.0513 (15)  | 0.0537 (16)  | −0.0178 (11) | 0.0060 (11) | −0.0181 (13)|
| C4    | 0.079 (3)    | 0.092 (3)    | 0.056 (2)    | −0.047 (2)   | 0.023 (2)   | −0.007 (2)  |
| C9    | 0.057 (2)    | 0.052 (2)    | 0.067 (3)    | −0.0080 (17) | −0.011 (2)  | −0.0142 (19)|
| N5    | 0.066 (2)    | 0.081 (3)    | 0.091 (3)    | −0.0224 (18) | 0.009 (2)   | −0.022 (2)  |
| C10   | 0.059 (2)    | 0.065 (3)    | 0.071 (3)    | −0.0125 (19) | −0.002 (2)  | −0.014 (2)  |

### Geometric parameters (Å, °)

|       | C2—C4       | C7—H7       | C6—C7       | N4—H4       | N2—C1—C2   | C6—C7—H7   | Ni1—Ni3   | Ni1—Ni3i   | Ni1—N1   | Ni1—Ni1i | Ni1—Cl1i   | C8—H8A | C3—H3 | C3—C2 | C3—N1 | N2—H2 | N2—C1 | N2—N1 | N3—C7 | N3—N4 | N3—N4 | C5—H5 | C5—C6 | C5—N4 | C2—C1 | N3—Ni1—Ni3i | N3—Ni3—Ni1 | N3—Ni3—Ni1i | N3—Ni3—Ni1 | N3—Ni1—Cl1i |
|-------|--------------|--------------|--------------|--------------|-------------|-------------|-----------|------------|---------|----------|--------------|---------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|---------|----------------|----------------|----------------|----------------|----------------|
| Ni1—N3 | 2.091 (2)    |              |              |              |             |              |           |            |         |          |              | 0.9300  | 0.9300| 1.394 (4) | 1.326 (3) | 0.8600 | 1.344 (4) | 1.345 (3) | 1.327 (4) | 1.334 (3) | 1.334 (3) | 0.9300 | 1.365 (4) | 1.337 (4) | 1.350 (5) | 180.0 | 104.0 (3) | 128.1 (3) | 127.9 (3) | 108.0 (3) | 126.0 |
| Ni1—N3i| 2.092 (2)    |              |              |              |             |              |           |            |         |          |              | 0.9300  |      |       |       |       |       |       |       |       |       |       |       |       |        |                  |                    |                  |                  |                  |
| Ni1—N1 | 2.112 (2)    |              |              |              |             |              |           |            |         |          |              | 1.383 (4) | 1.394 (4) | 1.326 (3) | 0.8600 | 1.344 (4) | 1.345 (3) | 1.327 (4) | 1.334 (3) | 1.334 (3) | 0.9300 | 1.365 (4) | 1.337 (4) | 1.350 (5) | 180.0 | 104.0 (3) | 128.1 (3) | 127.9 (3) | 108.0 (3) | 126.0 |
| Ni1—N1i| 2.112 (2)    |              |              |              |             |              |           |            |         |          |              | 1.383 (4) |      |       |       |       |       |       |       |       |       |       |       |       |        |                  |                    |                  |                  |                  |                  |
| Ni1—Cl1i| 2.4581 (6)  |              |              |              |             |              |           |            |         |          |              | 0.9300  | 1.394 (4) | 1.326 (3) | 0.8600 | 1.344 (4) | 1.345 (3) | 1.327 (4) | 1.334 (3) | 1.334 (3) | 0.9300 | 1.365 (4) | 1.337 (4) | 1.350 (5) | 180.0 | 104.0 (3) | 128.1 (3) | 127.9 (3) | 108.0 (3) | 126.0 |
supporting information

N3—Ni1—Cl1 90.57 (6) C2—C1—H1 126.0
N3—Ni1—Cl1 89.43 (6) C6—C8—H8A 109.5
N3—Ni1—Cl1 90.57 (6) C6—C8—H8B 109.5
N1—Ni1—Ni1 180.0 C6—C8—H8C 109.5
N1—Ni1—Cl1 89.91 (6) H8A—C8—H8B 109.5
N1—Ni1—Cl1 90.09 (6) H8A—C8—H8C 109.5
N1—Ni1—Cl1 89.91 (6) H8B—C8—H8C 109.5
N1—Ni1—Cl1 90.09 (6) C3—N1—Ni1 134.1 (2)
Cl1—Ni1—Cl1 180.0 C3—N1—N2 104.4 (2)
C2—C3—H3 124.1 N2—N1—Ni1 120.53 (17)
N1—C3—H3 124.1 N3—N4—C5 111.9 (3)
N1—C3—C2 111.8 (3) N3—N4—H4 124.0
C1—N2—H2 124.3 C5—N4—H4 124.0
C1—N2—N1 111.4 (2) C5—N4—H4 124.0
N1—N2—H2 124.3 C2—C4—H4A 109.5
C7—N3—Ni1 131.41 (19) C2—C4—H4B 109.5
C7—N3—N4 104.5 (2) H4A—C4—H4B 109.5
C6—C5—H5 126.2 H4A—C4—H4C 109.5
C6—C5—H5 126.2 N5—C9—C10 179.3 (5)
C3—C2—C4 126.4 (3) C9—C10—H10A 109.5
C1—C2—C3 104.3 (3) C9—C10—H10B 109.5
C1—C2—C4 129.3 (3) C9—C10—H10C 109.5
N3—C7—H7 124.0 H10A—C10—H10B 109.5
N3—C7—C6 112.1 (3) H10A—C10—H10C 109.5
N1—N3—C7—C6 −178.4 (2) C1—N2—N1—Ni1 −170.4 (2)
N1—N3—N4—C5 179.1 (2) C1—N2—N1—C3 0.0 (3)
C3—C2—C1—N2 −0.5 (4) N1—C3—C2—C1 0.5 (4)
N3—C7—C6—C5 −1.2 (4) N1—C3—C2—C4 −179.4 (3)
N3—C7—C6—C8 −178.9 (3) N1—N2—C1—C2 0.3 (4)
C2—C3—N1—Ni1 168.1 (2) N4—N3—C7—C6 1.0 (3)
C2—C3—N1—N2 −0.3 (3) N4—C5—C6—C7 0.8 (4)
C7—N3—N4—C5 −0.5 (3) N4—C5—C6—C8 178.5 (3)
C6—C5—N4—N3 −0.3 (4) C4—C2—C1—N2 179.4 (3)

Symmetry code: (i) −x+1, −y+1, −z+2.

Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H  | H···A | D···A   | D—H···A |
|-------------|------|------|--------|---------|
| N2—H2···N5ii | 0.86 | 2.60 | 3.217 (4) | 130 |
| C10···H10C—···Cl1 | 0.96 | 2.94 | 3.697 (3) | 137 |
| N2—H2···Cl1 | 0.86 | 2.50 | 3.088 (3) | 127 |
| N4—H4···Cl1ii | 0.86 | 2.45 | 3.217 (2) | 149 |

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|             | d (Å) | r (Å) | D (Å)  | β (°) |
|-------------|-------|-------|--------|-------|
| C10-H10B···Cl1 | 0.96  | 3.12  | 3.8958 (3) | 139   |
| C5-H5···N5iv  | 0.93  | 2.74  | 3.5785 (2) | 150   |

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