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Bis[3-chloro-6-(3,5-dimethyl-1H-pyrazol-1-yl)picolinato]nickel(II) tetrahydrate

Kai Zhao,^{a,b} Xian-Hong Yin,^{a*} Yu Feng,^a Jie Zhu^b and Cui-Wu Lin^b

^aCollege of Chemistry and Ecological Engineering, Guangxi University for Nationalities, Nanning 530006, People's Republic of China, and ^bCollege of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, People's Republic of China

Correspondence e-mail: yxhphd@163.com

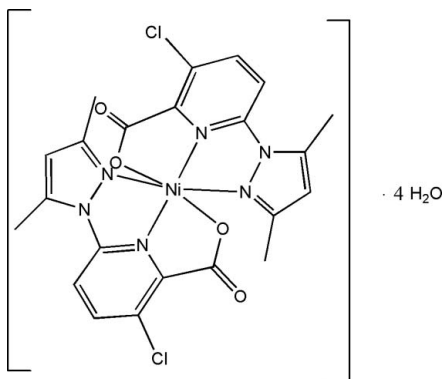
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.040; wR factor = 0.107; data-to-parameter ratio = 13.0.

In the title complex, $[\text{Ni}(\text{C}_{11}\text{H}_9\text{ClN}_3\text{O}_2)_2] \cdot 4\text{H}_2\text{O}$, the Ni atom is coordinated by four N atoms and two O atoms derived from two tridentate 3-chloro-6-(3,5-dimethyl-1H-pyrazol-1-yl)picolinato ligands. The *cis*- N_4O_2 donor set defines a distorted octahedral geometry. In the crystal structure, the complex and water molecules are linked by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds.

Related literature

For related literature, see: Yin *et al.* (2007); Zhao *et al.* (2007).



Experimental

Crystal data

$[\text{Ni}(\text{C}_{11}\text{H}_9\text{ClN}_3\text{O}_2)_2] \cdot 4\text{H}_2\text{O}$

$M_r = 632.10$

Triclinic, $P\bar{1}$

$a = 9.5907$ (10) Å

$b = 11.2776$ (17) Å

$c = 14.2659$ (19) Å

$\alpha = 92.593$ (2)°

$\beta = 105.206$ (3)°

$\gamma = 113.820$ (3)°

$V = 1342.0$ (3) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 0.98$ mm⁻¹

$T = 298$ (2) K

$0.52 \times 0.49 \times 0.37$ mm

Data collection

Siemens SMART CCD area-

detector diffractometer

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\text{min}} = 0.630$, $T_{\text{max}} = 0.713$

6957 measured reflections

4644 independent reflections

3549 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.107$

$S = 1.01$

4644 reflections

356 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.40$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.41$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------|-------------|-----------|-------------|
| Ni1—N4 | 1.998 (2) | Ni1—O3 | 2.079 (2) |
| Ni1—N1 | 2.000 (2) | Ni1—N3 | 2.096 (3) |
| Ni1—O1 | 2.069 (2) | Ni1—N6 | 2.112 (3) |
| N4—Ni1—N1 | 178.42 (10) | O1—Ni1—N3 | 155.49 (9) |
| N4—Ni1—O1 | 101.86 (9) | O3—Ni1—N3 | 92.01 (10) |
| N1—Ni1—O1 | 78.75 (9) | N4—Ni1—N6 | 76.94 (10) |
| N4—Ni1—O3 | 78.49 (9) | N1—Ni1—N6 | 104.50 (10) |
| N1—Ni1—O3 | 100.08 (9) | O1—Ni1—N6 | 93.55 (10) |
| O1—Ni1—O3 | 90.29 (10) | O3—Ni1—N6 | 155.40 (9) |
| N4—Ni1—N3 | 102.51 (10) | N3—Ni1—N6 | 94.43 (10) |
| N1—Ni1—N3 | 76.82 (9) | | |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|--|--------------|---------------------|--------------|-----------------------|
| O5—H5A ⁱ ⋯O4 | 0.85 | 1.96 | 2.800 (4) | 170 |
| O5—H5B ⁱ ⋯O6 ⁱ | 0.85 | 1.95 | 2.790 (4) | 170 |
| O6—H6A ⁱ ⋯O2 ⁱⁱ | 0.85 | 2.21 | 3.063 (5) | 176 |
| O6—H6B ⁱ ⋯O7 ⁱⁱⁱ | 0.85 | 1.84 | 2.693 (4) | 176 |
| O7—H7D ⁱ ⋯O4 ^{iv} | 0.85 | 2.13 | 2.942 (4) | 161 |
| O7—H7E ⁱ ⋯O2 ^v | 0.85 | 1.94 | 2.758 (4) | 160 |
| O8—H8A ⁱ ⋯O5 ^{vi} | 0.85 | 1.95 | 2.802 (5) | 179 |
| O8—H8B ⁱ ⋯O5 ^{vii} | 0.85 | 2.09 | 2.939 (5) | 178 |

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2215).

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supplementary materials

Acta Cryst. (2008). E64, m64-m65 [doi:10.1107/S1600536807063003]

Bis[3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinato]nickel(II) tetrahydrate

K. Zhao, X.-H. Yin, Y. Feng, J. Zhu and C.-W. Lin

Comment

Recently we reported the crystal structures of bis[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinato]zinc(II) trihydrate (Yin *et al.*, 2007) and bis[3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinato]cobalt(II) 2.5- hydrate (Zhao *et al.*, 2007). As a continuation of these investigations, the crystal structure of the title complex, (I), is described.

In (I), Fig. 1, the Ni atom is six-coordinated by four N atoms and two O atoms derived from two uninegative tridentate 3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinate ligands. The resultant *cis*-N₄O₂ donor set defines an approximate octahedral geometry with the range of the angles around Ni(II) center being 76.82 (9) to 178.42 (10)°. A complex network of O—H...O hydrogen bonds involving the ligand-O and water molecules of crystallization consolidate the crystal structure (Table 1).

Experimental

6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)picolinic acid (1 mmol, 250 mg) was dissolved in anhydrous alcohol (15 ml) and stirred until a clear solution resulted. A solution of NiCl₂·6H₂O (0.5 mmol, 113 mg) in anhydrous alcohol (10 ml) was then added. After keeping the resulting solution in air to evaporate about half of the volume, blue prisms of (I) formed. The crystals were isolated, washed with ethanol three times and dried in a vacuum desiccator using silica gel as the dessicant; yield 75%. Elemental analysis: Found: C 41.70, H 4.25, N 13.20, O 20.35%. C₂₂H₂₆NiN₆O₈ requires: C 41.80, H 4.15, N 13.30, O 20.25%.

Refinement

C-bound H atoms were included in the riding model approximation with C—H = 0.93 to 0.96 Å, and with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. The water H atoms were located in a difference Fourier map and the O—H distances were constrained to 0.85 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Figures

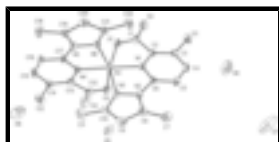


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

Bis[3-chloro-6-(3,5-dimethyl-1H-pyrazol-1-yl)picolinato]nickel(II) tetrahydrate

Crystal data

[Ni(C₁₁H₉ClN₃O₂)₂·4H₂O

M_r = 632.10

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

a = 9.5907 (10) Å

b = 11.2776 (17) Å

c = 14.2659 (19) Å

α = 92.593 (2)°

β = 105.206 (3)°

γ = 113.820 (3)°

V = 1342.0 (3) Å³

Z = 2

*F*₀₀₀ = 652

D_x = 1.564 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 3154 reflections

θ = 2.4–27.3°

μ = 0.98 mm⁻¹

T = 298 (2) K

Prism, blue

0.52 × 0.49 × 0.37 mm

Data collection

Siemens SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 298(2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

*T*_{min} = 0.630, *T*_{max} = 0.713

6957 measured reflections

4644 independent reflections

3549 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.022

θ _{max} = 25.0°

θ _{min} = 2.0°

h = -11→10

k = -13→13

l = -13→16

Refinement

Refinement on *F*²

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.107$

S = 1.01

4644 reflections

356 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.1899P]$

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

(Δ/σ)_{max} < 0.001

$\Delta\rho_{max} = 0.40$ e Å⁻³

$\Delta\rho_{min} = -0.41$ e Å⁻³

Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|--------------|----------------------------------|
| Ni1 | 0.77264 (5) | 0.52387 (4) | 0.75140 (3) | 0.03203 (14) |
| C11 | 0.55546 (12) | 0.91209 (9) | 0.67524 (7) | 0.0551 (3) |
| C12 | 0.57607 (13) | 0.07074 (9) | 0.92174 (8) | 0.0640 (3) |
| N1 | 0.7176 (3) | 0.6405 (2) | 0.66193 (16) | 0.0292 (5) |
| N2 | 0.7517 (3) | 0.5219 (2) | 0.54309 (17) | 0.0337 (6) |
| N3 | 0.7717 (3) | 0.4465 (2) | 0.61479 (18) | 0.0363 (6) |
| N4 | 0.8219 (3) | 0.4031 (2) | 0.83869 (17) | 0.0313 (6) |
| N5 | 1.0849 (3) | 0.5382 (2) | 0.86026 (17) | 0.0326 (6) |
| N6 | 1.0248 (3) | 0.6181 (2) | 0.80948 (18) | 0.0337 (6) |
| O1 | 0.7411 (3) | 0.6477 (2) | 0.84674 (15) | 0.0448 (6) |
| O2 | 0.6899 (3) | 0.8231 (3) | 0.85594 (17) | 0.0582 (7) |
| O3 | 0.5445 (3) | 0.3791 (2) | 0.73513 (17) | 0.0479 (6) |
| O4 | 0.4125 (3) | 0.2055 (3) | 0.7966 (2) | 0.0870 (10) |
| O5 | 0.1053 (4) | 0.1080 (3) | 0.6606 (2) | 0.0812 (9) |
| H5A | 0.2027 | 0.1390 | 0.6960 | 0.097* |
| H5B | 0.0472 | 0.0878 | 0.6985 | 0.097* |
| O6 | 0.9476 (4) | 0.0534 (4) | 0.8033 (2) | 0.0994 (11) |
| H6A | 0.8799 | -0.0101 | 0.8208 | 0.119* |
| H6B | 1.0368 | 0.0837 | 0.8488 | 0.119* |
| O7 | 0.7637 (4) | 0.8418 (4) | 0.0580 (2) | 0.1187 (15) |
| H7D | 0.6933 | 0.8234 | 0.0877 | 0.142* |
| H7E | 0.7179 | 0.8303 | -0.0036 | 0.142* |
| O8 | 0.0584 (6) | 0.8775 (5) | 0.5293 (3) | 0.159 (2) |
| H8A | 0.0092 | 0.8812 | 0.4713 | 0.191* |
| H8B | 0.0733 | 0.9439 | 0.5682 | 0.191* |
| C1 | 0.7039 (4) | 0.7344 (3) | 0.8106 (2) | 0.0371 (7) |
| C2 | 0.6770 (3) | 0.7295 (3) | 0.6994 (2) | 0.0302 (7) |
| C3 | 0.6215 (4) | 0.8021 (3) | 0.6372 (2) | 0.0359 (7) |
| C4 | 0.6125 (4) | 0.7840 (3) | 0.5382 (2) | 0.0439 (8) |
| H4 | 0.5775 | 0.8340 | 0.4964 | 0.053* |
| C5 | 0.6548 (4) | 0.6931 (3) | 0.5015 (2) | 0.0426 (8) |
| H5 | 0.6478 | 0.6797 | 0.4353 | 0.051* |
| C6 | 0.7084 (3) | 0.6222 (3) | 0.5670 (2) | 0.0296 (6) |

supplementary materials

| | | | | |
|------|------------|------------|------------|-------------|
| C7 | 0.7597 (5) | 0.5369 (4) | 0.3668 (2) | 0.0557 (10) |
| H7A | 0.7964 | 0.4988 | 0.3225 | 0.083* |
| H7B | 0.8259 | 0.6300 | 0.3843 | 0.083* |
| H7C | 0.6508 | 0.5212 | 0.3351 | 0.083* |
| C8 | 0.7691 (4) | 0.4755 (3) | 0.4583 (2) | 0.0394 (8) |
| C9 | 0.7988 (4) | 0.3697 (3) | 0.4775 (2) | 0.0455 (8) |
| H9 | 0.8166 | 0.3174 | 0.4341 | 0.055* |
| C10 | 0.7979 (4) | 0.3533 (3) | 0.5734 (2) | 0.0396 (8) |
| C11 | 0.8165 (5) | 0.2478 (4) | 0.6281 (3) | 0.0616 (11) |
| H11A | 0.9201 | 0.2833 | 0.6768 | 0.092* |
| H11B | 0.8063 | 0.1771 | 0.5827 | 0.092* |
| H11C | 0.7350 | 0.2153 | 0.6600 | 0.092* |
| C12 | 0.5349 (4) | 0.2929 (4) | 0.7887 (2) | 0.0465 (9) |
| C13 | 0.6969 (4) | 0.2984 (3) | 0.8487 (2) | 0.0364 (7) |
| C14 | 0.7263 (4) | 0.2110 (3) | 0.9064 (2) | 0.0399 (8) |
| C15 | 0.8827 (4) | 0.2345 (3) | 0.9545 (2) | 0.0451 (9) |
| H15 | 0.9027 | 0.1769 | 0.9947 | 0.054* |
| C16 | 1.0094 (4) | 0.3425 (3) | 0.9436 (2) | 0.0412 (8) |
| H16 | 1.1150 | 0.3592 | 0.9755 | 0.049* |
| C17 | 0.9719 (4) | 0.4250 (3) | 0.8826 (2) | 0.0309 (7) |
| C18 | 1.3525 (4) | 0.5291 (4) | 0.9329 (3) | 0.0599 (11) |
| H18A | 1.4596 | 0.5778 | 0.9307 | 0.090* |
| H18B | 1.3108 | 0.4403 | 0.8998 | 0.090* |
| H18C | 1.3534 | 0.5288 | 1.0004 | 0.090* |
| C19 | 1.2490 (4) | 0.5920 (3) | 0.8830 (2) | 0.0378 (7) |
| C20 | 1.2925 (4) | 0.7063 (3) | 0.8466 (2) | 0.0428 (8) |
| H20 | 1.3962 | 0.7644 | 0.8502 | 0.051* |
| C21 | 1.1525 (4) | 0.7206 (3) | 0.8024 (2) | 0.0362 (7) |
| C22 | 1.1358 (4) | 0.8304 (3) | 0.7544 (3) | 0.0535 (9) |
| H22A | 1.0583 | 0.7956 | 0.6901 | 0.080* |
| H22B | 1.2373 | 0.8890 | 0.7483 | 0.080* |
| H22C | 1.1010 | 0.8774 | 0.7937 | 0.080* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Ni1 | 0.0331 (2) | 0.0372 (2) | 0.0302 (2) | 0.01843 (18) | 0.00948 (17) | 0.01627 (17) |
| Cl1 | 0.0667 (6) | 0.0481 (6) | 0.0634 (6) | 0.0382 (5) | 0.0177 (5) | 0.0138 (4) |
| Cl2 | 0.0823 (8) | 0.0401 (5) | 0.0683 (6) | 0.0134 (5) | 0.0392 (6) | 0.0272 (5) |
| N1 | 0.0298 (14) | 0.0313 (14) | 0.0260 (13) | 0.0131 (12) | 0.0074 (11) | 0.0094 (11) |
| N2 | 0.0381 (15) | 0.0348 (15) | 0.0293 (13) | 0.0165 (12) | 0.0100 (11) | 0.0091 (11) |
| N3 | 0.0433 (16) | 0.0348 (15) | 0.0369 (14) | 0.0211 (13) | 0.0131 (12) | 0.0159 (12) |
| N4 | 0.0318 (14) | 0.0329 (14) | 0.0292 (13) | 0.0131 (12) | 0.0094 (11) | 0.0128 (11) |
| N5 | 0.0324 (15) | 0.0336 (15) | 0.0329 (13) | 0.0172 (12) | 0.0059 (11) | 0.0118 (11) |
| N6 | 0.0357 (15) | 0.0307 (14) | 0.0368 (14) | 0.0161 (12) | 0.0098 (12) | 0.0149 (11) |
| O1 | 0.0596 (15) | 0.0607 (16) | 0.0280 (11) | 0.0382 (13) | 0.0141 (11) | 0.0165 (11) |
| O2 | 0.084 (2) | 0.0719 (18) | 0.0388 (13) | 0.0514 (16) | 0.0211 (13) | 0.0079 (13) |
| O3 | 0.0323 (13) | 0.0596 (16) | 0.0479 (14) | 0.0162 (11) | 0.0093 (11) | 0.0251 (12) |

| | | | | | | |
|-----|-------------|-------------|-------------|-------------|-------------|--------------|
| O4 | 0.0405 (17) | 0.102 (2) | 0.096 (2) | 0.0064 (16) | 0.0172 (16) | 0.059 (2) |
| O5 | 0.071 (2) | 0.100 (2) | 0.0615 (18) | 0.0352 (18) | 0.0067 (15) | 0.0182 (17) |
| O6 | 0.066 (2) | 0.123 (3) | 0.076 (2) | 0.017 (2) | 0.0131 (17) | -0.008 (2) |
| O7 | 0.072 (2) | 0.231 (5) | 0.0458 (17) | 0.063 (3) | 0.0129 (16) | 0.011 (2) |
| O8 | 0.271 (6) | 0.195 (5) | 0.079 (3) | 0.178 (5) | 0.034 (3) | 0.025 (3) |
| C1 | 0.0340 (18) | 0.048 (2) | 0.0336 (17) | 0.0217 (16) | 0.0099 (14) | 0.0101 (15) |
| C2 | 0.0284 (16) | 0.0295 (17) | 0.0323 (16) | 0.0123 (13) | 0.0084 (13) | 0.0090 (13) |
| C3 | 0.0350 (18) | 0.0303 (17) | 0.0409 (18) | 0.0146 (14) | 0.0078 (14) | 0.0112 (14) |
| C4 | 0.056 (2) | 0.044 (2) | 0.0390 (19) | 0.0291 (18) | 0.0120 (16) | 0.0215 (16) |
| C5 | 0.054 (2) | 0.048 (2) | 0.0292 (17) | 0.0240 (18) | 0.0123 (15) | 0.0163 (15) |
| C6 | 0.0300 (16) | 0.0290 (16) | 0.0281 (15) | 0.0112 (13) | 0.0083 (13) | 0.0079 (13) |
| C7 | 0.076 (3) | 0.064 (3) | 0.0370 (19) | 0.034 (2) | 0.0263 (19) | 0.0120 (18) |
| C8 | 0.0387 (19) | 0.043 (2) | 0.0336 (17) | 0.0129 (16) | 0.0137 (14) | 0.0040 (15) |
| C9 | 0.050 (2) | 0.042 (2) | 0.046 (2) | 0.0204 (17) | 0.0167 (17) | -0.0007 (16) |
| C10 | 0.0408 (19) | 0.0324 (18) | 0.049 (2) | 0.0167 (15) | 0.0165 (16) | 0.0089 (15) |
| C11 | 0.082 (3) | 0.049 (2) | 0.076 (3) | 0.042 (2) | 0.035 (2) | 0.024 (2) |
| C12 | 0.036 (2) | 0.052 (2) | 0.0426 (19) | 0.0090 (17) | 0.0119 (16) | 0.0176 (17) |
| C13 | 0.0414 (19) | 0.0356 (18) | 0.0294 (16) | 0.0116 (15) | 0.0136 (14) | 0.0103 (14) |
| C14 | 0.059 (2) | 0.0297 (18) | 0.0356 (17) | 0.0173 (16) | 0.0230 (16) | 0.0147 (14) |
| C15 | 0.070 (3) | 0.042 (2) | 0.0381 (18) | 0.0340 (19) | 0.0213 (18) | 0.0220 (16) |
| C16 | 0.048 (2) | 0.046 (2) | 0.0369 (18) | 0.0271 (17) | 0.0100 (16) | 0.0183 (16) |
| C17 | 0.0360 (18) | 0.0318 (17) | 0.0272 (15) | 0.0164 (14) | 0.0097 (13) | 0.0090 (13) |
| C18 | 0.043 (2) | 0.070 (3) | 0.074 (3) | 0.035 (2) | 0.010 (2) | 0.027 (2) |
| C19 | 0.0325 (18) | 0.044 (2) | 0.0378 (17) | 0.0200 (15) | 0.0061 (14) | 0.0047 (15) |
| C20 | 0.0312 (18) | 0.043 (2) | 0.049 (2) | 0.0114 (16) | 0.0111 (15) | 0.0026 (16) |
| C21 | 0.0370 (18) | 0.0296 (17) | 0.0387 (17) | 0.0104 (14) | 0.0126 (14) | 0.0068 (14) |
| C22 | 0.052 (2) | 0.042 (2) | 0.069 (3) | 0.0179 (18) | 0.022 (2) | 0.0237 (19) |

Geometric parameters (Å, °)

| | | | |
|---------|-----------|----------|-----------|
| Ni1—N4 | 1.998 (2) | C3—C4 | 1.393 (4) |
| Ni1—N1 | 2.000 (2) | C4—C5 | 1.374 (4) |
| Ni1—O1 | 2.069 (2) | C4—H4 | 0.9300 |
| Ni1—O3 | 2.079 (2) | C5—C6 | 1.387 (4) |
| Ni1—N3 | 2.096 (3) | C5—H5 | 0.9300 |
| Ni1—N6 | 2.112 (3) | C7—C8 | 1.505 (5) |
| Cl1—C3 | 1.729 (3) | C7—H7A | 0.9600 |
| Cl2—C14 | 1.726 (3) | C7—H7B | 0.9600 |
| N1—C6 | 1.335 (4) | C7—H7C | 0.9600 |
| N1—C2 | 1.349 (4) | C8—C9 | 1.358 (5) |
| N2—C8 | 1.372 (4) | C9—C10 | 1.390 (5) |
| N2—N3 | 1.384 (3) | C9—H9 | 0.9300 |
| N2—C6 | 1.409 (4) | C10—C11 | 1.497 (4) |
| N3—C10 | 1.323 (4) | C11—H11A | 0.9600 |
| N4—C17 | 1.323 (4) | C11—H11B | 0.9600 |
| N4—C13 | 1.347 (4) | C11—H11C | 0.9600 |
| N5—C19 | 1.377 (4) | C12—C13 | 1.539 (4) |
| N5—N6 | 1.389 (3) | C13—C14 | 1.381 (4) |
| N5—C17 | 1.416 (4) | C14—C15 | 1.383 (5) |

supplementary materials

| | | | |
|------------|-------------|---------------|-----------|
| N6—C21 | 1.333 (4) | C15—C16 | 1.380 (5) |
| O1—C1 | 1.256 (4) | C15—H15 | 0.9300 |
| O2—C1 | 1.238 (4) | C16—C17 | 1.389 (4) |
| O3—C12 | 1.253 (4) | C16—H16 | 0.9300 |
| O4—C12 | 1.228 (4) | C18—C19 | 1.496 (4) |
| O5—H5A | 0.8500 | C18—H18A | 0.9600 |
| O5—H5B | 0.8500 | C18—H18B | 0.9600 |
| O6—H6A | 0.8499 | C18—H18C | 0.9600 |
| O6—H6B | 0.8500 | C19—C20 | 1.359 (5) |
| O7—H7D | 0.8500 | C20—C21 | 1.402 (4) |
| O7—H7E | 0.8499 | C20—H20 | 0.9300 |
| O8—H8A | 0.8500 | C21—C22 | 1.486 (4) |
| O8—H8B | 0.8500 | C22—H22A | 0.9600 |
| C1—C2 | 1.535 (4) | C22—H22B | 0.9600 |
| C2—C3 | 1.382 (4) | C22—H22C | 0.9600 |
| N4—Ni1—N1 | 178.42 (10) | H7A—C7—H7B | 109.5 |
| N4—Ni1—O1 | 101.86 (9) | C8—C7—H7C | 109.5 |
| N1—Ni1—O1 | 78.75 (9) | H7A—C7—H7C | 109.5 |
| N4—Ni1—O3 | 78.49 (9) | H7B—C7—H7C | 109.5 |
| N1—Ni1—O3 | 100.08 (9) | C9—C8—N2 | 105.6 (3) |
| O1—Ni1—O3 | 90.29 (10) | C9—C8—C7 | 129.8 (3) |
| N4—Ni1—N3 | 102.51 (10) | N2—C8—C7 | 124.6 (3) |
| N1—Ni1—N3 | 76.82 (9) | C8—C9—C10 | 108.0 (3) |
| O1—Ni1—N3 | 155.49 (9) | C8—C9—H9 | 126.0 |
| O3—Ni1—N3 | 92.01 (10) | C10—C9—H9 | 126.0 |
| N4—Ni1—N6 | 76.94 (10) | N3—C10—C9 | 110.1 (3) |
| N1—Ni1—N6 | 104.50 (10) | N3—C10—C11 | 120.7 (3) |
| O1—Ni1—N6 | 93.55 (10) | C9—C10—C11 | 129.2 (3) |
| O3—Ni1—N6 | 155.40 (9) | C10—C11—H11A | 109.5 |
| N3—Ni1—N6 | 94.43 (10) | C10—C11—H11B | 109.5 |
| C6—N1—C2 | 121.9 (2) | H11A—C11—H11B | 109.5 |
| C6—N1—Ni1 | 120.58 (19) | C10—C11—H11C | 109.5 |
| C2—N1—Ni1 | 117.24 (18) | H11A—C11—H11C | 109.5 |
| C8—N2—N3 | 110.6 (2) | H11B—C11—H11C | 109.5 |
| C8—N2—C6 | 132.8 (3) | O4—C12—O3 | 127.2 (3) |
| N3—N2—C6 | 116.5 (2) | O4—C12—C13 | 118.0 (3) |
| C10—N3—N2 | 105.6 (2) | O3—C12—C13 | 114.8 (3) |
| C10—N3—Ni1 | 141.3 (2) | N4—C13—C14 | 118.9 (3) |
| N2—N3—Ni1 | 112.77 (17) | N4—C13—C12 | 112.3 (3) |
| C17—N4—C13 | 122.1 (3) | C14—C13—C12 | 128.7 (3) |
| C17—N4—Ni1 | 120.6 (2) | C13—C14—C15 | 119.4 (3) |
| C13—N4—Ni1 | 117.3 (2) | C13—C14—C12 | 123.2 (3) |
| C19—N5—N6 | 110.6 (2) | C15—C14—C12 | 117.4 (2) |
| C19—N5—C17 | 133.0 (2) | C16—C15—C14 | 120.8 (3) |
| N6—N5—C17 | 116.4 (2) | C16—C15—H15 | 119.6 |
| C21—N6—N5 | 105.4 (2) | C14—C15—H15 | 119.6 |
| C21—N6—Ni1 | 141.8 (2) | C15—C16—C17 | 116.9 (3) |
| N5—N6—Ni1 | 111.64 (18) | C15—C16—H16 | 121.5 |
| C1—O1—Ni1 | 116.31 (19) | C17—C16—H16 | 121.5 |

| | | | |
|---------------|--------------|---------------|------------|
| C12—O3—Ni1 | 116.7 (2) | N4—C17—C16 | 121.8 (3) |
| H5A—O5—H5B | 108.1 | N4—C17—N5 | 113.0 (2) |
| H6A—O6—H6B | 108.5 | C16—C17—N5 | 125.2 (3) |
| H7D—O7—H7E | 108.8 | C19—C18—H18A | 109.5 |
| H8A—O8—H8B | 108.4 | C19—C18—H18B | 109.5 |
| O2—C1—O1 | 126.6 (3) | H18A—C18—H18B | 109.5 |
| O2—C1—C2 | 117.7 (3) | C19—C18—H18C | 109.5 |
| O1—C1—C2 | 115.7 (3) | H18A—C18—H18C | 109.5 |
| N1—C2—C3 | 119.0 (3) | H18B—C18—H18C | 109.5 |
| N1—C2—C1 | 111.5 (2) | C20—C19—N5 | 106.2 (3) |
| C3—C2—C1 | 129.4 (3) | C20—C19—C18 | 128.6 (3) |
| C2—C3—C4 | 119.3 (3) | N5—C19—C18 | 125.1 (3) |
| C2—C3—C11 | 123.1 (2) | C19—C20—C21 | 107.5 (3) |
| C4—C3—C11 | 117.5 (2) | C19—C20—H20 | 126.2 |
| C5—C4—C3 | 120.8 (3) | C21—C20—H20 | 126.2 |
| C5—C4—H4 | 119.6 | N6—C21—C20 | 110.3 (3) |
| C3—C4—H4 | 119.6 | N6—C21—C22 | 121.1 (3) |
| C4—C5—C6 | 117.4 (3) | C20—C21—C22 | 128.6 (3) |
| C4—C5—H5 | 121.3 | C21—C22—H22A | 109.5 |
| C6—C5—H5 | 121.3 | C21—C22—H22B | 109.5 |
| N1—C6—C5 | 121.5 (3) | H22A—C22—H22B | 109.5 |
| N1—C6—N2 | 112.5 (2) | C21—C22—H22C | 109.5 |
| C5—C6—N2 | 126.0 (3) | H22A—C22—H22C | 109.5 |
| C8—C7—H7A | 109.5 | H22B—C22—H22C | 109.5 |
| C8—C7—H7B | 109.5 | | |
| O1—Ni1—N1—C6 | -179.1 (2) | N1—C2—C3—C11 | 176.3 (2) |
| O3—Ni1—N1—C6 | -90.8 (2) | C1—C2—C3—C11 | -4.7 (5) |
| N3—Ni1—N1—C6 | -1.1 (2) | C2—C3—C4—C5 | 1.4 (5) |
| N6—Ni1—N1—C6 | 90.1 (2) | C11—C3—C4—C5 | -176.5 (3) |
| O1—Ni1—N1—C2 | -4.8 (2) | C3—C4—C5—C6 | -0.8 (5) |
| O3—Ni1—N1—C2 | 83.5 (2) | C2—N1—C6—C5 | -0.7 (4) |
| N3—Ni1—N1—C2 | 173.2 (2) | Ni1—N1—C6—C5 | 173.4 (2) |
| N6—Ni1—N1—C2 | -95.6 (2) | C2—N1—C6—N2 | -178.1 (3) |
| C8—N2—N3—C10 | -1.2 (3) | Ni1—N1—C6—N2 | -4.1 (3) |
| C6—N2—N3—C10 | 174.8 (3) | C4—C5—C6—N1 | 0.5 (5) |
| C8—N2—N3—Ni1 | 173.52 (19) | C4—C5—C6—N2 | 177.6 (3) |
| C6—N2—N3—Ni1 | -10.5 (3) | C8—N2—C6—N1 | -175.5 (3) |
| N4—Ni1—N3—C10 | -3.4 (4) | N3—N2—C6—N1 | 9.6 (4) |
| N1—Ni1—N3—C10 | 178.0 (4) | C8—N2—C6—C5 | 7.2 (5) |
| O1—Ni1—N3—C10 | -177.2 (3) | N3—N2—C6—C5 | -167.7 (3) |
| O3—Ni1—N3—C10 | -82.1 (4) | N3—N2—C8—C9 | 0.5 (3) |
| N6—Ni1—N3—C10 | 74.1 (4) | C6—N2—C8—C9 | -174.6 (3) |
| N4—Ni1—N3—N2 | -175.31 (19) | N3—N2—C8—C7 | -178.1 (3) |
| N1—Ni1—N3—N2 | 6.15 (19) | C6—N2—C8—C7 | 6.8 (5) |
| O1—Ni1—N3—N2 | 10.9 (4) | N2—C8—C9—C10 | 0.4 (4) |
| O3—Ni1—N3—N2 | 106.0 (2) | C7—C8—C9—C10 | 178.9 (3) |
| N6—Ni1—N3—N2 | -97.7 (2) | N2—N3—C10—C9 | 1.4 (4) |
| O1—Ni1—N4—C17 | -96.3 (2) | Ni1—N3—C10—C9 | -170.8 (3) |
| O3—Ni1—N4—C17 | 175.9 (2) | N2—N3—C10—C11 | -176.7 (3) |

supplementary materials

| | | | |
|---------------|--------------|-----------------|------------|
| N3—Ni1—N4—C17 | 86.3 (2) | Ni1—N3—C10—C11 | 11.1 (6) |
| N6—Ni1—N4—C17 | -5.4 (2) | C8—C9—C10—N3 | -1.2 (4) |
| O1—Ni1—N4—C13 | 85.2 (2) | C8—C9—C10—C11 | 176.7 (4) |
| O3—Ni1—N4—C13 | -2.7 (2) | Ni1—O3—C12—O4 | 173.8 (3) |
| N3—Ni1—N4—C13 | -92.2 (2) | Ni1—O3—C12—C13 | -7.6 (4) |
| N6—Ni1—N4—C13 | 176.1 (2) | C17—N4—C13—C14 | -0.1 (4) |
| C19—N5—N6—C21 | -0.6 (3) | Ni1—N4—C13—C14 | 178.4 (2) |
| C17—N5—N6—C21 | 176.3 (2) | C17—N4—C13—C12 | -178.7 (3) |
| C19—N5—N6—Ni1 | 169.89 (19) | Ni1—N4—C13—C12 | -0.2 (3) |
| C17—N5—N6—Ni1 | -13.2 (3) | O4—C12—C13—N4 | -176.0 (3) |
| N4—Ni1—N6—C21 | 174.8 (4) | O3—C12—C13—N4 | 5.2 (4) |
| N1—Ni1—N6—C21 | -4.6 (4) | O4—C12—C13—C14 | 5.6 (6) |
| O1—Ni1—N6—C21 | -83.9 (3) | O3—C12—C13—C14 | -173.2 (3) |
| O3—Ni1—N6—C21 | 177.6 (3) | N4—C13—C14—C15 | 1.6 (4) |
| N3—Ni1—N6—C21 | 72.9 (3) | C12—C13—C14—C15 | 179.9 (3) |
| N4—Ni1—N6—N5 | 9.66 (17) | N4—C13—C14—C12 | -178.0 (2) |
| N1—Ni1—N6—N5 | -169.68 (17) | C12—C13—C14—C12 | 0.3 (5) |
| O1—Ni1—N6—N5 | 111.03 (18) | C13—C14—C15—C16 | -1.6 (5) |
| O3—Ni1—N6—N5 | 12.5 (3) | C12—C14—C15—C16 | 178.1 (2) |
| N3—Ni1—N6—N5 | -92.17 (18) | C14—C15—C16—C17 | 0.0 (5) |
| N4—Ni1—O1—C1 | -178.3 (2) | C13—N4—C17—C16 | -1.5 (4) |
| N1—Ni1—O1—C1 | 0.2 (2) | Ni1—N4—C17—C16 | -179.9 (2) |
| O3—Ni1—O1—C1 | -100.0 (2) | C13—N4—C17—N5 | 178.3 (2) |
| N3—Ni1—O1—C1 | -4.5 (4) | Ni1—N4—C17—N5 | -0.2 (3) |
| N6—Ni1—O1—C1 | 104.3 (2) | C15—C16—C17—N4 | 1.5 (5) |
| N4—Ni1—O3—C12 | 5.9 (2) | C15—C16—C17—N5 | -178.3 (3) |
| N1—Ni1—O3—C12 | -174.7 (2) | C19—N5—C17—N4 | -174.7 (3) |
| O1—Ni1—O3—C12 | -96.1 (3) | N6—N5—C17—N4 | 9.2 (4) |
| N3—Ni1—O3—C12 | 108.3 (3) | C19—N5—C17—C16 | 5.0 (5) |
| N6—Ni1—O3—C12 | 3.1 (4) | N6—N5—C17—C16 | -171.0 (3) |
| Ni1—O1—C1—O2 | -174.9 (3) | N6—N5—C19—C20 | 0.1 (3) |
| Ni1—O1—C1—C2 | 3.8 (4) | C17—N5—C19—C20 | -176.1 (3) |
| C6—N1—C2—C3 | 1.2 (4) | N6—N5—C19—C18 | -176.8 (3) |
| Ni1—N1—C2—C3 | -173.1 (2) | C17—N5—C19—C18 | 7.0 (5) |
| C6—N1—C2—C1 | -178.0 (3) | N5—C19—C20—C21 | 0.4 (4) |
| Ni1—N1—C2—C1 | 7.7 (3) | C18—C19—C20—C21 | 177.1 (3) |
| O2—C1—C2—N1 | 171.3 (3) | N5—N6—C21—C20 | 0.9 (3) |
| O1—C1—C2—N1 | -7.5 (4) | Ni1—N6—C21—C20 | -164.8 (3) |
| O2—C1—C2—C3 | -7.8 (5) | N5—N6—C21—C22 | -178.3 (3) |
| O1—C1—C2—C3 | 173.4 (3) | Ni1—N6—C21—C22 | 16.1 (5) |
| N1—C2—C3—C4 | -1.5 (5) | C19—C20—C21—N6 | -0.8 (4) |
| C1—C2—C3—C4 | 177.6 (3) | C19—C20—C21—C22 | 178.3 (3) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|-------|-------------|-------------|---------------|
| O5—H5A \cdots O4 | 0.85 | 1.96 | 2.800 (4) | 170 |
| O5—H5B \cdots O6 ⁱ | 0.85 | 1.95 | 2.790 (4) | 170 |
| O6—H6A \cdots O2 ⁱⁱ | 0.85 | 2.21 | 3.063 (5) | 176 |

| | | | | |
|----------------------------|------|------|-----------|-----|
| O6—H6B···O7 ⁱⁱⁱ | 0.85 | 1.84 | 2.693 (4) | 176 |
| O7—H7D···O4 ^{iv} | 0.85 | 2.13 | 2.942 (4) | 161 |
| O7—H7E···O2 ^v | 0.85 | 1.94 | 2.758 (4) | 160 |
| O8—H8A···O5 ^{vi} | 0.85 | 1.95 | 2.802 (5) | 179 |
| O8—H8B···O5 ^{vii} | 0.85 | 2.09 | 2.939 (5) | 178 |

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

Fig. 1

