Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

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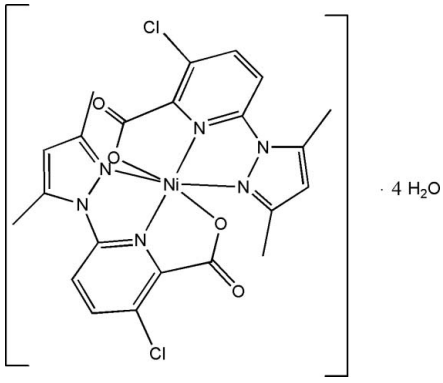
Received 7 November 2007; accepted 24 November 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.040; wR factor = 0.107; data-to-parameter ratio = 13.0.

In the title complex, $[Ni(C_{11}H_9ClN_3O_2)_2]\cdot 4H_2O$, the Ni atom is coordinated by four N atoms and two O atoms derived from two tridentate 3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinate 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 O—H···O hydrogen bonds.

Related literature

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



Experimental

Crystal data

$[Ni(C_{11}H_9ClN_3O_2)_2]\cdot 4H_2O$
M_r = 632.10
Triclinic, $P\overline{1}$
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) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.98 mm^{-1}
T = 298 (2) K
0.52 × 0.49 × 0.37 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.630, T_{max} = 0.713
6957 measured reflections
4644 independent reflections
3549 reflections with $I > 2\sigma(I)$
R_{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
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −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—H···A	D—H	H···A	D···A	D—H···A
O5—H5*A*···O4	0.85	1.96	2.800 (4)	170
O5—H5*B*···O6^{i}	0.85	1.95	2.790 (4)	170
O6—H6*A*···O2^{ii}	0.85	2.21	3.063 (5)	176
O6—H6*B*···O7^{iii}	0.85	1.84	2.693 (4)	176
O7—H7*D*···O4^{iv}	0.85	2.13	2.942 (4)	161
O7—H7*E*···O2^{v}	0.85	1.94	2.758 (4)	160
O8—H8*A*···O5^{vi}	0.85	1.95	2.802 (5)	179
O8—H8*B*···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, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

The authors thank the National Natural Science Foundation of China (grant No. 20761002). This research was sponsored by the Fund of the Talent Highland Research Programme of Guangxi University (grant No. 205121), the Science Foundation of the State Ethnic Affairs Commission (grant No. 07GX05), the Development Foundation of Guangxi Research Institute of Chemical Industry and the Science Foundation of Guangxi University for Nationalities (grant Nos. 0409032, 0409012 and 0509ZD047).

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

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supporting information

Acta Cryst. (2008). E**64**, m64–m65 [https://doi.org/10.1107/S1600536807063003]

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

Kai Zhao, Xian-Hong Yin, Yu Feng, Jie Zhu and Cui-Wu Lin

S1. 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*-N_4O_2 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).

S2. 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 $NiCl_2.6H_2O$ (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%. $C_{22}H_{26}NiN_6O_8$ requires: C 41.80, H 4.15, N 13.30, O 20.25%.

S3. Refinement

C-bound H atoms were included in the riding model approximation with C—H = 0.93 to 0.96 Å, and with U_{iso}(H) = 1.2–1.5U_{eq}(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_{iso}(H) = 1.2U_{eq}(O).

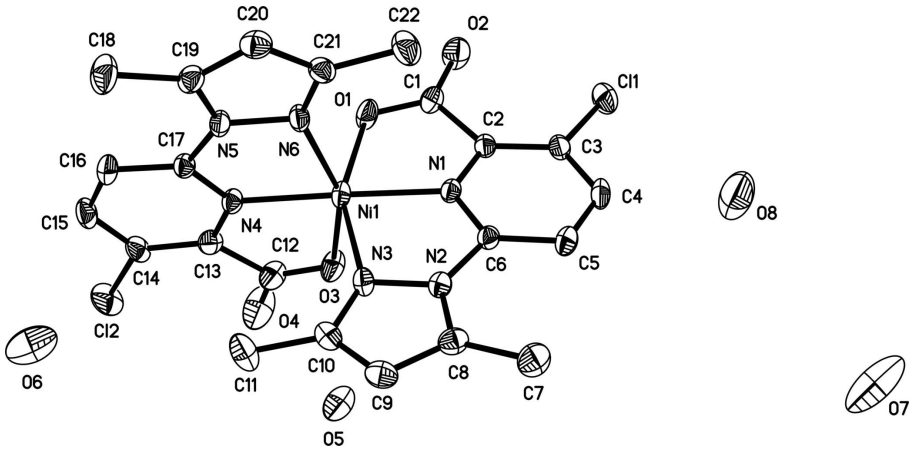

Figure 1

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-1*H*-pyrazol-1-yl)picolinato]nickel(II) tetrahydrate

Crystal data

$[Ni(C_{11}H_9ClN_3O_2)_2]\cdot 4H_2O$
$M_r = 632.10$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 9.5907\ (10)$ Å
$b = 11.2776\ (17)$ Å
$c = 14.2659\ (19)$ Å
$\alpha = 92.593\ (2)°$
$\beta = 105.206\ (3)°$
$\gamma = 113.820\ (3)°$
$V = 1342.0\ (3)$ Å^3
$Z = 2$
$F(000) = 652$
$D_x = 1.564$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3154 reflections
$\theta = 2.4–27.3°$
$\mu = 0.98$ mm^{-1}
$T = 298$ K
Prism, blue
0.52 × 0.49 × 0.37 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
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 $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
$h = -11\rightarrow10$
$k = -13\rightarrow13$
$l = -13\rightarrow16$

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
0 restraints
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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.77264 (5)	0.52387 (4)	0.75140 (3)	0.03203 (14)
Cl1	0.55546 (12)	0.91209 (9)	0.67524 (7)	0.0551 (3)
Cl2	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)
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 (Å²)

	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, º)

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)
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—Cl2	123.2 (3)
C19—N5—N6	110.6 (2)	C15—C14—Cl2	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—Cl1	123.1 (2)	C19—C20—C21	107.5 (3)
C4—C3—Cl1	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—Cl1	176.3 (2)
O3—Ni1—N1—C6	−90.8 (2)	C1—C2—C3—Cl1	−4.7 (5)
N3—Ni1—N1—C6	−1.1 (2)	C2—C3—C4—C5	1.4 (5)
N6—Ni1—N1—C6	90.1 (2)	Cl1—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)
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—Cl2	−178.0 (2)
N1—Ni1—N6—N5	−169.68 (17)	C12—C13—C14—Cl2	0.3 (5)
O1—Ni1—N6—N5	111.03 (18)	C13—C14—C15—C16	−1.6 (5)
O3—Ni1—N6—N5	12.5 (3)	Cl2—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 (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*A*···O4	0.85	1.96	2.800 (4)	170
O5—H5*B*···O6^{i}	0.85	1.95	2.790 (4)	170
O6—H6*A*···O2^{ii}	0.85	2.21	3.063 (5)	176
O6—H6*B*···O7^{iii}	0.85	1.84	2.693 (4)	176
O7—H7*D*···O4^{iv}	0.85	2.13	2.942 (4)	161
O7—H7*E*···O2^{v}	0.85	1.94	2.758 (4)	160
O8—H8*A*···O5^{vi}	0.85	1.95	2.802 (5)	179
O8—H8*B*···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*.