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Bis[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-picolinato]nickel(II)–aqua[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid]dithiocyanatonickel(II) (1/1)

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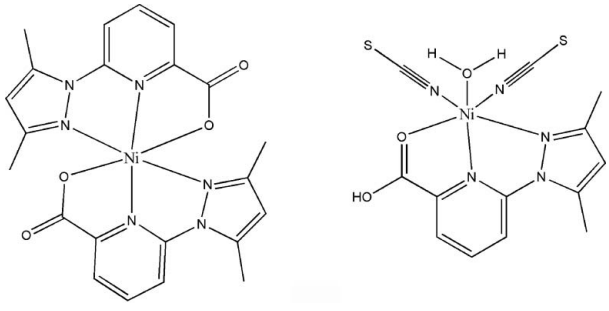
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.007 Å; R factor = 0.048; wR factor = 0.114; data-to-parameter ratio = 13.4.

In the title cocrystal, $[Ni(C_{11}H_{10}N_3O_2)_2]\cdot[Ni(NCS)_2(C_{11}H_{11}N_3O_2)(H_2O)]$, both Ni^{II} ions are in disorted octahedral coordination environments. One Ni^{II} ion is coordinated by four N atoms and two O atoms from two tridentate 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinate (DPP) ligands, while the other Ni^{II} ion is coordinated by a tridentate 6-((3,5-dimethyl-1*H*-pyrazol-1-yl))picolinic acid (DPPH) ligand and by two N atoms and one O atom from two thiocyanate and one water ligand, respectively. In the crystal structure, molecules are linked by intermolecular O—H···O and O—H···S hydrogen bonds, forming extended chains along [010].

Related literature

For related literature, see: Bhatia *et al.* (1981); Costamagna *et al.* (1992); Yin *et al.* (2007).



Experimental

Crystal data

$[Ni(C_{11}H_{10}N_3O_2)_2]\cdot[Ni(NCS)_2(C_{11}H_{11}N_3O_2)(H_2O)]$
M_r = 901.26
Monoclinic, $P2_1/c$
a = 13.8022 (11) Å
b = 9.0399 (10) Å
c = 31.836 (2) Å
β = 99.086 (2)°
V = 3922.4 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.13 mm^{-1}
T = 298 (2) K
0.48 × 0.33 × 0.27 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.613, T_{max} = 0.750
19154 measured reflections
6905 independent reflections
4381 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.114
S = 1.03
6905 reflections
514 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—N5	1.998 (4)	Ni2—N9	1.983 (3)
Ni1—N1	2.025 (3)	Ni2—N6	1.991 (3)
Ni1—N4	2.060 (4)	Ni2—O6	2.074 (3)
Ni1—N3	2.111 (3)	Ni2—N8	2.114 (4)
Ni1—O3	2.121 (3)	Ni2—O4	2.119 (3)
Ni1—O1	2.168 (3)	Ni2—N11	2.140 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O5^{i}	0.82	1.67	2.479 (4)	170
O3—H3A···O7^{ii}	0.85	1.82	2.674 (4)	180
O3—H3B···S1^{iii}	0.85	2.38	3.221 (3)	173

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

Data collection: *SMART* (Bruker, 1996); cell refinement: *SAINT* (Bruker, 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2574).

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supporting information

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S1. Comment

In recent years, there has been an increasing interest in coordination chemistry due to the increased recognition of it's role in catalysis, enzymatic reactions, magnetism and molecular architectures (Costamagna *et al.*, 1992; Bhatia *et al.*, 1981). Recently we reported the crystal structure of bis(6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinato)zinc(II) trihydrate (Yin *et al.*, 2007). As a continuation of our investigations, we report herein the crystal structure of the title co-crystal (I).

The title co-crystal consists of two neutral mononuclear Ni(II) complex molecules, shown in Fig. 1. In one molecule the Ni^{II} ion is six-coordinated by four N atoms and two O atoms from two tridentate DDP ligands that define a distorted octahedral *cis*-N_4O_2 donor set and in the other molecule the Ni^{II} ion is six-coordinated by four N atoms and two O atoms from one tridentate DDPH ligand, two thiocyanate ligands and one water ligand which again defines a distorted octahedral *cis*-N_4O_2 donor set. In the crystal structure, molecules are connected, by intermolecular O—H···O and O—H···S hydrogen bonds (Fig. 2).

S2. Experimental

6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid, KSCN and $NiCl_2$. $6H_2O$ were available commercially and were used without further purification. Equimolar 6-(3,5-dimethyl-1*H*-pyrazol-1-yl) picolinic acid (1 mmol, 217 mg) and KSCN (2 mmol, 194 mg) was dissolved in anhydrous alcohol (15 ml). The mixture was stirred to give a clear solution, To this solution was added $NiCl_2.6H_2O$ (1 mmol, 231 mg) in anhydrous alcohol (10 ml). After keeping the resulting solution in air to evaporate about half of the solvents, blue prisms of the title compound were formed. The crystals were isolated, washed with alcohol three times and dried in a vacuum desiccator using silica gel (Yield 75%). Elemental analysis: found: C, 46.54; H, 3.79; N, 17.00; O, 12.53.; calc. for $C_{35}H_{33}Ni_N11_O7_S2$: C, 46.64; H, 3.69; N, 17.10; O, 12.43.

S3. Refinement

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with O—H and C—H distances of 0.82–0.85 Å and 0.93–0.96 Å, respectively. They were treated as riding atoms, with U_{iso}(H) = 1.2U_{eq}(C or water O atoms) and and U_{iso}(H) = 1.5U_{eq}(hydroxyl O or methyl C atoms).

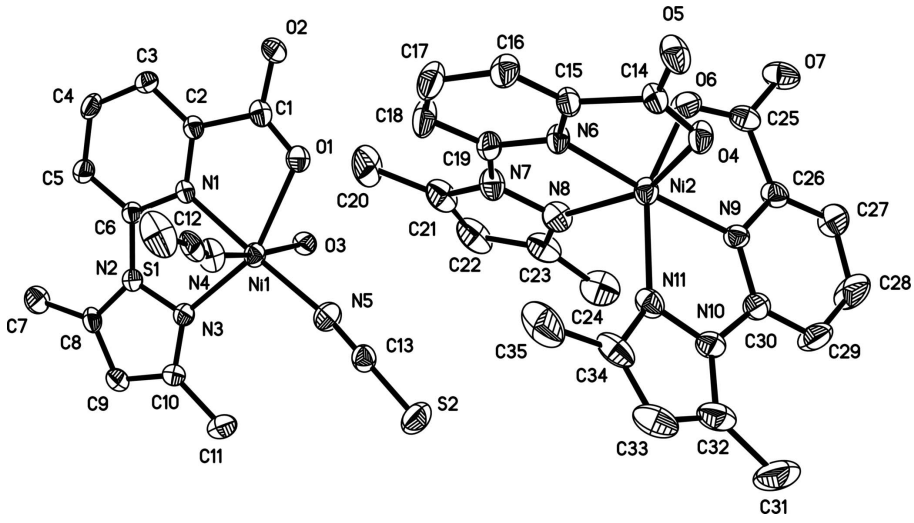

Figure 1

The asymmetric unit of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

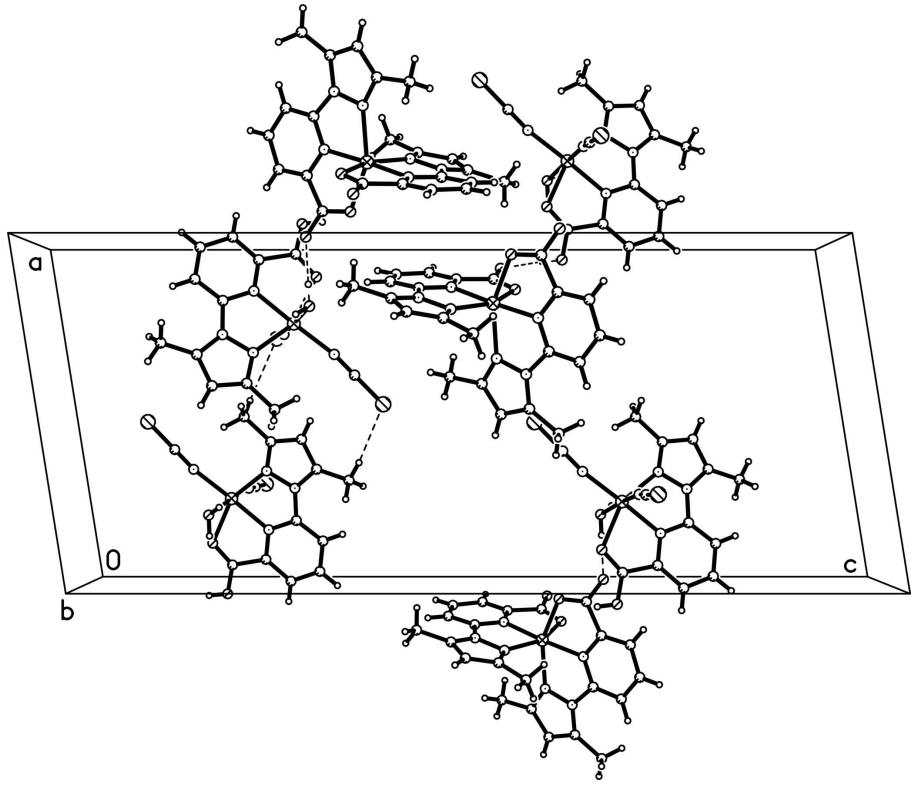

Figure 2

Part of the crystal structure showing the hydrogen bonded interactions as dashed lines.

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Crystal data

$[Ni(C_{11}H_{10}N_3O_2)_2]\cdot[Ni(NCS)_2(C_{11}H_{11}N_3O_2)(H_2O)]$
$M_r = 901.26$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 13.8022\ (11)$ Å
$b = 9.0399\ (10)$ Å
$c = 31.836\ (2)$ Å
$\beta = 99.086\ (2)°$
$V = 3922.4\ (6)$ Å^3
$Z = 4$
$F(000) = 1856$
$D_x = 1.526$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3753 reflections
$\theta = 2.6–22.9°$
$\mu = 1.13$ mm^{-1}
$T = 298$ K
Prism, blue
0.48 × 0.33 × 0.27 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.613$, $T_{max} = 0.750$
19154 measured reflections
6905 independent reflections
4381 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.5°$
$h = -12\rightarrow16$
$k = -10\rightarrow10$
$l = -37\rightarrow37$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.114$
$S = 1.03$
6905 reflections
514 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
$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 2.9546P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ 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	0.24058 (4)	0.42965 (6)	0.686675 (15)	0.03842 (17)
Ni2	0.19482 (4)	1.00803 (6)	0.438647 (16)	0.03771 (17)
N1	0.1467 (2)	0.4084 (4)	0.72917 (9)	0.0320 (8)

N2	0.2749 (2)	0.3082 (4)	0.77386 (9)	0.0358 (8)
N3	0.3262 (2)	0.3327 (4)	0.74042 (10)	0.0390 (9)
N4	0.2669 (3)	0.6460 (5)	0.70537 (12)	0.0549 (11)
N5	0.3293 (3)	0.4463 (5)	0.64300 (12)	0.0596 (11)
N6	0.1458 (2)	1.1195 (4)	0.48498 (10)	0.0371 (8)
N7	0.1818 (3)	0.9150 (4)	0.52584 (11)	0.0464 (9)
N8	0.2156 (3)	0.8587 (4)	0.49037 (11)	0.0480 (10)
N9	0.2380 (2)	0.9084 (4)	0.38931 (10)	0.0350 (8)
N10	0.3919 (2)	0.9966 (4)	0.41309 (11)	0.0456 (9)
N11	0.3475 (3)	1.0611 (4)	0.44472 (11)	0.0445 (9)
O1	0.1022 (2)	0.5021 (3)	0.65064 (8)	0.0431 (7)
O2	−0.0545 (2)	0.5399 (3)	0.65829 (9)	0.0503 (8)
H2	−0.0607	0.5608	0.6329	0.075*
O3	0.1967 (2)	0.2198 (3)	0.66053 (8)	0.0434 (7)
H3A	0.1346	0.2126	0.6575	0.052*
H3B	0.2214	0.1521	0.6774	0.052*
O4	0.1493 (2)	1.2102 (3)	0.40810 (8)	0.0443 (8)
O5	0.0809 (2)	1.4260 (4)	0.41996 (9)	0.0555 (9)
O6	0.0634 (2)	0.9185 (4)	0.40887 (10)	0.0503 (8)
O7	−0.0013 (2)	0.8022 (4)	0.34892 (10)	0.0617 (9)
S1	0.27353 (13)	0.94691 (16)	0.72189 (5)	0.0834 (5)
S2	0.47389 (11)	0.47417 (19)	0.59247 (5)	0.0798 (5)
C1	0.0358 (3)	0.5031 (5)	0.67191 (13)	0.0390 (10)
C2	0.0546 (3)	0.4568 (4)	0.71798 (12)	0.0335 (10)
C3	−0.0118 (3)	0.4582 (5)	0.74606 (13)	0.0398 (11)
H3	−0.0753	0.4936	0.7381	0.048*
C4	0.0204 (3)	0.4045 (5)	0.78678 (12)	0.0445 (11)
H4	−0.0223	0.4035	0.8066	0.053*
C5	0.1146 (3)	0.3528 (5)	0.79809 (13)	0.0420 (11)
H5	0.1361	0.3167	0.8253	0.050*
C6	0.1763 (3)	0.3558 (4)	0.76794 (12)	0.0321 (9)
C7	0.3009 (4)	0.1860 (6)	0.84664 (13)	0.0617 (15)
H7A	0.2817	0.2689	0.8623	0.093*
H7B	0.3541	0.1348	0.8637	0.093*
H7C	0.2463	0.1200	0.8397	0.093*
C8	0.3330 (3)	0.2391 (5)	0.80689 (12)	0.0399 (11)
C9	0.4223 (3)	0.2198 (5)	0.79409 (13)	0.0508 (13)
H9	0.4774	0.1756	0.8097	0.061*
C10	0.4148 (3)	0.2792 (5)	0.75302 (13)	0.0463 (12)
C11	0.4895 (3)	0.2788 (7)	0.72406 (15)	0.0754 (17)
H11A	0.4582	0.2991	0.6955	0.113*
H11B	0.5206	0.1836	0.7250	0.113*
H11C	0.5379	0.3534	0.7330	0.113*
C12	0.2685 (3)	0.7709 (6)	0.71093 (13)	0.0510 (13)
C13	0.3893 (3)	0.4586 (5)	0.62209 (14)	0.0462 (12)
C14	0.1163 (3)	1.3025 (5)	0.43136 (13)	0.0401 (11)
C15	0.1182 (3)	1.2592 (5)	0.47733 (12)	0.0381 (10)
C16	0.0964 (3)	1.3499 (5)	0.50913 (13)	0.0508 (12)

H16	0.0774	1.4475	0.5035	0.061*
C17	0.1033 (4)	1.2930 (6)	0.54967 (15)	0.0628 (15)
H17	0.0903	1.3531	0.5718	0.075*
C18	0.1292 (4)	1.1482 (6)	0.55737 (14)	0.0615 (14)
H18	0.1324	1.1080	0.5844	0.074*
C19	0.1505 (3)	1.0632 (5)	0.52399 (12)	0.0418 (11)
C20	0.1528 (4)	0.8318 (6)	0.59934 (14)	0.0778 (18)
H20A	0.1516	0.7380	0.6134	0.117*
H20B	0.0881	0.8735	0.5948	0.117*
H20C	0.1968	0.8975	0.6168	0.117*
C21	0.1873 (4)	0.8106 (6)	0.55735 (15)	0.0553 (13)
C22	0.2273 (4)	0.6904 (6)	0.54170 (17)	0.0657 (16)
H22	0.2416	0.6013	0.5559	0.079*
C23	0.2435 (3)	0.7226 (5)	0.50052 (16)	0.0541 (13)
C24	0.2874 (4)	0.6305 (6)	0.46946 (17)	0.0754 (16)
H24A	0.2416	0.6219	0.4435	0.113*
H24B	0.3024	0.5339	0.4812	0.113*
H24C	0.3465	0.6766	0.4636	0.113*
C25	0.0685 (3)	0.8525 (5)	0.37462 (15)	0.0445 (11)
C26	0.1699 (3)	0.8374 (5)	0.36265 (13)	0.0414 (11)
C27	0.1926 (4)	0.7616 (6)	0.32851 (15)	0.0631 (15)
H27	0.1443	0.7141	0.3096	0.076*
C28	0.2895 (4)	0.7578 (7)	0.32308 (17)	0.090 (2)
H28	0.3074	0.7037	0.3007	0.108*
C29	0.3604 (4)	0.8323 (7)	0.35006 (16)	0.0724 (17)
H29	0.4258	0.8304	0.3463	0.087*
C30	0.3305 (3)	0.9101 (5)	0.38296 (13)	0.0432 (11)
C31	0.5563 (4)	0.9984 (8)	0.3858 (2)	0.101 (2)
H31A	0.6165	1.0528	0.3925	0.152*
H31B	0.5267	1.0195	0.3571	0.152*
H31C	0.5697	0.8944	0.3887	0.152*
C32	0.4878 (3)	1.0429 (6)	0.41551 (18)	0.0625 (15)
C33	0.5031 (4)	1.1323 (6)	0.44985 (19)	0.0762 (17)
H33	0.5619	1.1792	0.4604	0.091*
C34	0.4170 (4)	1.1430 (6)	0.46687 (16)	0.0598 (14)
C35	0.3967 (4)	1.2296 (7)	0.50418 (18)	0.092 (2)
H35A	0.3399	1.2905	0.4960	0.139*
H35B	0.4522	1.2911	0.5143	0.139*
H35C	0.3850	1.1632	0.5264	0.139*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0413 (3)	0.0431 (4)	0.0317 (3)	−0.0045 (3)	0.0085 (2)	0.0046 (3)
Ni2	0.0444 (3)	0.0363 (4)	0.0326 (3)	0.0026 (3)	0.0067 (2)	−0.0028 (3)
N1	0.038 (2)	0.032 (2)	0.0249 (17)	0.0001 (16)	0.0012 (14)	0.0001 (15)
N2	0.037 (2)	0.041 (2)	0.0298 (18)	0.0009 (17)	0.0051 (15)	0.0014 (16)
N3	0.036 (2)	0.051 (3)	0.0311 (19)	−0.0031 (17)	0.0079 (16)	0.0024 (17)

N4	0.072 (3)	0.044 (3)	0.048 (2)	−0.011 (2)	0.005 (2)	0.004 (2)
N5	0.056 (3)	0.075 (3)	0.052 (2)	−0.011 (2)	0.019 (2)	0.011 (2)
N6	0.049 (2)	0.035 (2)	0.0282 (18)	0.0041 (17)	0.0076 (16)	0.0030 (16)
N7	0.062 (3)	0.041 (3)	0.036 (2)	0.001 (2)	0.0063 (18)	0.0093 (19)
N8	0.056 (2)	0.036 (2)	0.052 (2)	0.0029 (19)	0.0059 (19)	0.0076 (19)
N9	0.0298 (19)	0.038 (2)	0.0371 (19)	−0.0013 (16)	0.0039 (15)	−0.0049 (16)
N10	0.035 (2)	0.052 (3)	0.048 (2)	−0.0079 (19)	0.0024 (17)	−0.005 (2)
N11	0.047 (2)	0.042 (2)	0.042 (2)	−0.0011 (19)	−0.0036 (17)	−0.0094 (18)
O1	0.0486 (18)	0.0445 (19)	0.0367 (16)	0.0003 (15)	0.0083 (14)	0.0117 (14)
O2	0.053 (2)	0.057 (2)	0.0382 (16)	0.0213 (16)	0.0000 (14)	0.0132 (15)
O3	0.0409 (17)	0.047 (2)	0.0415 (17)	0.0019 (14)	0.0045 (13)	0.0029 (14)
O4	0.062 (2)	0.0406 (19)	0.0318 (16)	0.0103 (16)	0.0115 (14)	0.0055 (14)
O5	0.081 (2)	0.041 (2)	0.0403 (17)	0.0192 (18)	−0.0033 (16)	0.0046 (16)
O6	0.0394 (18)	0.058 (2)	0.0552 (19)	−0.0019 (16)	0.0116 (15)	−0.0110 (17)
O7	0.0389 (19)	0.062 (2)	0.079 (2)	−0.0089 (17)	−0.0065 (17)	−0.0135 (19)
S1	0.1254 (14)	0.0401 (9)	0.0742 (10)	−0.0016 (9)	−0.0166 (9)	0.0096 (7)
S2	0.0663 (9)	0.1134 (14)	0.0672 (9)	−0.0227 (9)	0.0334 (7)	−0.0160 (9)
C1	0.053 (3)	0.028 (3)	0.034 (2)	0.005 (2)	0.002 (2)	0.002 (2)
C2	0.041 (3)	0.029 (3)	0.030 (2)	0.0036 (19)	0.0027 (19)	−0.0012 (18)
C3	0.037 (2)	0.044 (3)	0.039 (2)	0.008 (2)	0.0085 (19)	0.000 (2)
C4	0.050 (3)	0.055 (3)	0.033 (2)	0.001 (2)	0.020 (2)	−0.001 (2)
C5	0.044 (3)	0.049 (3)	0.034 (2)	0.005 (2)	0.010 (2)	0.002 (2)
C6	0.036 (2)	0.029 (2)	0.031 (2)	0.0036 (19)	0.0049 (18)	−0.0006 (18)
C7	0.066 (3)	0.079 (4)	0.039 (3)	0.024 (3)	0.003 (2)	0.021 (3)
C8	0.051 (3)	0.041 (3)	0.026 (2)	0.007 (2)	0.000 (2)	0.001 (2)
C9	0.041 (3)	0.069 (4)	0.039 (3)	0.011 (2)	−0.004 (2)	−0.003 (2)
C10	0.033 (3)	0.066 (3)	0.040 (3)	−0.002 (2)	0.005 (2)	−0.004 (2)
C11	0.045 (3)	0.122 (5)	0.062 (3)	0.011 (3)	0.018 (3)	0.008 (3)
C12	0.057 (3)	0.058 (4)	0.033 (3)	−0.004 (3)	−0.008 (2)	0.013 (2)
C13	0.049 (3)	0.049 (3)	0.040 (3)	−0.010 (2)	0.006 (2)	−0.003 (2)
C14	0.046 (3)	0.041 (3)	0.031 (2)	0.001 (2)	−0.001 (2)	−0.001 (2)
C15	0.044 (3)	0.041 (3)	0.028 (2)	0.003 (2)	0.0025 (19)	0.000 (2)
C16	0.066 (3)	0.044 (3)	0.044 (3)	0.020 (2)	0.013 (2)	−0.003 (2)
C17	0.086 (4)	0.065 (4)	0.042 (3)	0.017 (3)	0.026 (3)	−0.004 (3)
C18	0.090 (4)	0.067 (4)	0.032 (3)	0.009 (3)	0.022 (3)	0.006 (3)
C19	0.046 (3)	0.047 (3)	0.033 (2)	0.002 (2)	0.009 (2)	0.007 (2)
C20	0.100 (4)	0.086 (5)	0.048 (3)	−0.016 (3)	0.012 (3)	0.034 (3)
C21	0.061 (3)	0.048 (3)	0.053 (3)	−0.009 (3)	−0.004 (3)	0.026 (3)
C22	0.074 (4)	0.044 (4)	0.070 (4)	−0.014 (3)	−0.016 (3)	0.029 (3)
C23	0.054 (3)	0.033 (3)	0.070 (3)	0.000 (2)	−0.007 (3)	0.010 (3)
C24	0.083 (4)	0.041 (3)	0.100 (4)	0.011 (3)	0.008 (3)	0.002 (3)
C25	0.038 (3)	0.037 (3)	0.056 (3)	−0.001 (2)	−0.001 (2)	0.003 (2)
C26	0.037 (3)	0.042 (3)	0.042 (3)	−0.003 (2)	−0.002 (2)	−0.009 (2)
C27	0.059 (3)	0.078 (4)	0.052 (3)	−0.016 (3)	0.006 (3)	−0.032 (3)
C28	0.071 (4)	0.134 (6)	0.071 (4)	−0.017 (4)	0.030 (3)	−0.062 (4)
C29	0.044 (3)	0.110 (5)	0.068 (3)	−0.007 (3)	0.024 (3)	−0.035 (3)
C30	0.040 (3)	0.047 (3)	0.042 (2)	−0.002 (2)	0.006 (2)	−0.006 (2)
C31	0.045 (3)	0.144 (6)	0.120 (5)	−0.025 (4)	0.029 (3)	−0.015 (5)

C32	0.038 (3)	0.065 (4)	0.079 (4)	−0.011 (3)	−0.005 (3)	0.014 (3)
C33	0.051 (4)	0.070 (4)	0.098 (4)	−0.018 (3)	−0.018 (3)	−0.010 (4)
C34	0.060 (4)	0.043 (3)	0.065 (3)	0.001 (3)	−0.024 (3)	−0.008 (3)
C35	0.103 (5)	0.075 (5)	0.085 (4)	0.009 (4)	−0.029 (4)	−0.041 (4)

Geometric parameters (Å, º)

Ni1—N5	1.998 (4)	C5—H5	0.9300
Ni1—N1	2.025 (3)	C7—C8	1.485 (6)
Ni1—N4	2.060 (4)	C7—H7A	0.9600
Ni1—N3	2.111 (3)	C7—H7B	0.9600
Ni1—O3	2.121 (3)	C7—H7C	0.9600
Ni1—O1	2.168 (3)	C8—C9	1.369 (6)
Ni2—N9	1.983 (3)	C9—C10	1.402 (6)
Ni2—N6	1.991 (3)	C9—H9	0.9300
Ni2—O6	2.074 (3)	C10—C11	1.488 (6)
Ni2—N8	2.114 (4)	C11—H11A	0.9600
Ni2—O4	2.119 (3)	C11—H11B	0.9600
Ni2—N11	2.140 (4)	C11—H11C	0.9600
N1—C6	1.325 (4)	C14—C15	1.511 (5)
N1—C2	1.339 (5)	C15—C16	1.372 (5)
N2—C8	1.369 (5)	C16—C17	1.378 (6)
N2—N3	1.387 (4)	C16—H16	0.9300
N2—C6	1.411 (5)	C17—C18	1.369 (7)
N3—C10	1.316 (5)	C17—H17	0.9300
N4—C12	1.143 (6)	C18—C19	1.380 (6)
N5—C13	1.147 (5)	C18—H18	0.9300
N6—C15	1.331 (5)	C20—C21	1.501 (6)
N6—C19	1.334 (5)	C20—H20A	0.9600
N7—C21	1.370 (5)	C20—H20B	0.9600
N7—N8	1.385 (5)	C20—H20C	0.9600
N7—C19	1.406 (5)	C21—C22	1.349 (7)
N8—C23	1.313 (5)	C22—C23	1.395 (7)
N9—C30	1.324 (5)	C22—H22	0.9300
N9—C26	1.328 (5)	C23—C24	1.493 (7)
N10—C32	1.379 (5)	C24—H24A	0.9600
N10—N11	1.387 (5)	C24—H24B	0.9600
N10—C30	1.411 (5)	C24—H24C	0.9600
N11—C34	1.324 (5)	C25—C26	1.513 (6)
O1—C1	1.223 (5)	C26—C27	1.362 (6)
O2—C1	1.296 (5)	C27—C28	1.376 (7)
O2—H2	0.8200	C27—H27	0.9300
O3—H3A	0.8500	C28—C29	1.372 (7)
O3—H3B	0.8500	C28—H28	0.9300
O4—C14	1.248 (5)	C29—C30	1.377 (6)
O5—C14	1.250 (5)	C29—H29	0.9300
O6—C25	1.255 (5)	C31—C32	1.494 (7)
O7—C25	1.248 (5)	C31—H31A	0.9600

S1—C12	1.628 (6)	C31—H31B	0.9600
S2—C13	1.618 (5)	C31—H31C	0.9600
C1—C2	1.508 (5)	C32—C33	1.349 (7)
C2—C3	1.377 (5)	C33—C34	1.386 (7)
C3—C4	1.390 (5)	C33—H33	0.9300
C3—H3	0.9300	C34—C35	1.486 (7)
C4—C5	1.374 (6)	C35—H35A	0.9600
C4—H4	0.9300	C35—H35B	0.9600
C5—C6	1.380 (5)	C35—H35C	0.9600

N5—Ni1—N1	177.66 (14)	C8—C9—C10	106.9 (4)
N5—Ni1—N4	91.74 (17)	C8—C9—H9	126.5
N1—Ni1—N4	89.96 (14)	C10—C9—H9	126.5
N5—Ni1—N3	105.60 (15)	N3—C10—C9	110.7 (4)
N1—Ni1—N3	75.79 (12)	N3—C10—C11	120.9 (4)
N4—Ni1—N3	96.29 (14)	C9—C10—C11	128.3 (4)
N5—Ni1—O3	87.85 (14)	C10—C11—H11A	109.5
N1—Ni1—O3	90.23 (12)	C10—C11—H11B	109.5
N4—Ni1—O3	171.48 (13)	H11A—C11—H11B	109.5
N3—Ni1—O3	92.01 (12)	C10—C11—H11C	109.5
N5—Ni1—O1	101.21 (14)	H11A—C11—H11C	109.5
N1—Ni1—O1	77.24 (11)	H11B—C11—H11C	109.5
N4—Ni1—O1	88.07 (14)	N4—C12—S1	176.5 (4)
N3—Ni1—O1	152.66 (12)	N5—C13—S2	179.4 (5)
O3—Ni1—O1	83.67 (11)	O4—C14—O5	126.0 (4)
N9—Ni2—N6	175.49 (14)	O4—C14—C15	116.7 (4)
N9—Ni2—O6	79.14 (12)	O5—C14—C15	117.3 (4)
N6—Ni2—O6	99.25 (13)	N6—C15—C16	121.4 (4)
N9—Ni2—N8	107.83 (14)	N6—C15—C14	112.6 (4)
N6—Ni2—N8	76.48 (14)	C16—C15—C14	126.0 (4)
O6—Ni2—N8	96.22 (13)	C15—C16—C17	118.5 (4)
N9—Ni2—O4	97.64 (12)	C15—C16—H16	120.7
N6—Ni2—O4	78.03 (12)	C17—C16—H16	120.7
O6—Ni2—O4	87.26 (12)	C18—C17—C16	120.1 (4)
N8—Ni2—O4	154.51 (13)	C18—C17—H17	119.9
N9—Ni2—N11	76.01 (13)	C16—C17—H17	119.9
N6—Ni2—N11	105.36 (14)	C17—C18—C19	118.4 (4)
O6—Ni2—N11	155.04 (13)	C17—C18—H18	120.8
N8—Ni2—N11	93.56 (14)	C19—C18—H18	120.8
O4—Ni2—N11	93.71 (13)	N6—C19—C18	121.3 (4)
C6—N1—C2	120.3 (3)	N6—C19—N7	111.8 (4)
C6—N1—Ni1	121.4 (3)	C18—C19—N7	126.8 (4)
C2—N1—Ni1	118.2 (2)	C21—C20—H20A	109.5
C8—N2—N3	110.7 (3)	C21—C20—H20B	109.5
C8—N2—C6	132.7 (3)	H20A—C20—H20B	109.5
N3—N2—C6	116.6 (3)	C21—C20—H20C	109.5
C10—N3—N2	105.7 (3)	H20A—C20—H20C	109.5
C10—N3—Ni1	140.7 (3)	H20B—C20—H20C	109.5

N2—N3—Ni1	113.6 (2)	C22—C21—N7	105.2 (4)
C12—N4—Ni1	168.9 (4)	C22—C21—C20	129.6 (5)
C13—N5—Ni1	171.5 (4)	N7—C21—C20	125.1 (5)
C15—N6—C19	120.2 (4)	C21—C22—C23	108.3 (4)
C15—N6—Ni2	117.7 (3)	C21—C22—H22	125.8
C19—N6—Ni2	121.6 (3)	C23—C22—H22	125.8
C21—N7—N8	110.9 (4)	N8—C23—C22	110.0 (5)
C21—N7—C19	131.9 (4)	N8—C23—C24	119.5 (5)
N8—N7—C19	117.2 (3)	C22—C23—C24	130.4 (5)
C23—N8—N7	105.5 (4)	C23—C24—H24A	109.5
C23—N8—Ni2	142.0 (3)	C23—C24—H24B	109.5
N7—N8—Ni2	112.3 (3)	H24A—C24—H24B	109.5
C30—N9—C26	120.7 (4)	C23—C24—H24C	109.5
C30—N9—Ni2	122.3 (3)	H24A—C24—H24C	109.5
C26—N9—Ni2	117.0 (3)	H24B—C24—H24C	109.5
C32—N10—N11	111.2 (4)	O7—C25—O6	126.8 (4)
C32—N10—C30	132.4 (4)	O7—C25—C26	116.8 (4)
N11—N10—C30	116.1 (3)	O6—C25—C26	116.3 (4)
C34—N11—N10	104.8 (4)	N9—C26—C27	121.6 (4)
C34—N11—Ni2	142.5 (4)	N9—C26—C25	112.6 (4)
N10—N11—Ni2	112.4 (2)	C27—C26—C25	125.8 (4)
C1—O1—Ni1	112.6 (3)	C26—C27—C28	117.6 (4)
C1—O2—H2	109.5	C26—C27—H27	121.2
Ni1—O3—H3A	109.5	C28—C27—H27	121.2
Ni1—O3—H3B	109.6	C29—C28—C27	121.4 (5)
H3A—O3—H3B	108.2	C29—C28—H28	119.3
C14—O4—Ni2	114.4 (3)	C27—C28—H28	119.3
C25—O6—Ni2	114.7 (3)	C28—C29—C30	117.2 (5)
O1—C1—O2	125.6 (4)	C28—C29—H29	121.4
O1—C1—C2	120.5 (4)	C30—C29—H29	121.4
O2—C1—C2	113.9 (4)	N9—C30—C29	121.5 (4)
N1—C2—C3	122.1 (3)	N9—C30—N10	113.1 (4)
N1—C2—C1	111.1 (3)	C29—C30—N10	125.5 (4)
C3—C2—C1	126.8 (4)	C32—C31—H31A	109.5
C2—C3—C4	117.1 (4)	C32—C31—H31B	109.5
C2—C3—H3	121.5	H31A—C31—H31B	109.5
C4—C3—H3	121.5	C32—C31—H31C	109.5
C5—C4—C3	120.8 (4)	H31A—C31—H31C	109.5
C5—C4—H4	119.6	H31B—C31—H31C	109.5
C3—C4—H4	119.6	C33—C32—N10	104.7 (5)
C4—C5—C6	118.2 (4)	C33—C32—C31	129.8 (5)
C4—C5—H5	120.9	N10—C32—C31	125.5 (5)
C6—C5—H5	120.9	C32—C33—C34	108.9 (5)
N1—C6—C5	121.4 (4)	C32—C33—H33	125.5
N1—C6—N2	112.5 (3)	C34—C33—H33	125.5
C5—C6—N2	126.1 (3)	N11—C34—C33	110.3 (5)
C8—C7—H7A	109.5	N11—C34—C35	120.6 (5)
C8—C7—H7B	109.5	C33—C34—C35	129.1 (5)

H7A—C7—H7B	109.5	C34—C35—H35A	109.5
C8—C7—H7C	109.5	C34—C35—H35B	109.5
H7A—C7—H7C	109.5	H35A—C35—H35B	109.5
H7B—C7—H7C	109.5	C34—C35—H35C	109.5
N2—C8—C9	106.0 (4)	H35A—C35—H35C	109.5
N2—C8—C7	125.8 (4)	H35B—C35—H35C	109.5
C9—C8—C7	128.0 (4)		

N4—Ni1—N1—C6	−93.8 (3)	C2—C3—C4—C5	0.1 (6)
N3—Ni1—N1—C6	2.7 (3)	C3—C4—C5—C6	0.1 (7)
O3—Ni1—N1—C6	94.7 (3)	C2—N1—C6—C5	−1.6 (6)
O1—Ni1—N1—C6	178.1 (3)	Ni1—N1—C6—C5	174.5 (3)
N4—Ni1—N1—C2	82.4 (3)	C2—N1—C6—N2	179.2 (3)
N3—Ni1—N1—C2	178.9 (3)	Ni1—N1—C6—N2	−4.6 (5)
O3—Ni1—N1—C2	−89.1 (3)	C4—C5—C6—N1	0.7 (6)
O1—Ni1—N1—C2	−5.6 (3)	C4—C5—C6—N2	179.7 (4)
C8—N2—N3—C10	−0.1 (4)	C8—N2—C6—N1	−175.0 (4)
C6—N2—N3—C10	−179.7 (4)	N3—N2—C6—N1	4.4 (5)
C8—N2—N3—Ni1	177.2 (3)	C8—N2—C6—C5	5.8 (7)
C6—N2—N3—Ni1	−2.4 (4)	N3—N2—C6—C5	−174.7 (4)
N5—Ni1—N3—C10	−2.2 (5)	N3—N2—C8—C9	0.0 (5)
N1—Ni1—N3—C10	175.9 (5)	C6—N2—C8—C9	179.5 (4)
N4—Ni1—N3—C10	−95.7 (5)	N3—N2—C8—C7	−175.4 (4)
O3—Ni1—N3—C10	86.2 (5)	C6—N2—C8—C7	4.1 (7)
O1—Ni1—N3—C10	166.3 (4)	N2—C8—C9—C10	0.1 (5)
N5—Ni1—N3—N2	−178.1 (3)	C7—C8—C9—C10	175.3 (4)
N1—Ni1—N3—N2	0.0 (2)	N2—N3—C10—C9	0.2 (5)
N4—Ni1—N3—N2	88.3 (3)	Ni1—N3—C10—C9	−175.9 (4)
O3—Ni1—N3—N2	−89.8 (3)	N2—N3—C10—C11	176.7 (4)
O1—Ni1—N3—N2	−9.7 (4)	Ni1—N3—C10—C11	0.6 (8)
N5—Ni1—N4—C12	91 (2)	C8—C9—C10—N3	−0.2 (5)
N1—Ni1—N4—C12	−87 (2)	C8—C9—C10—C11	−176.3 (5)
N3—Ni1—N4—C12	−163 (2)	Ni2—O4—C14—O5	−176.4 (4)
O1—Ni1—N4—C12	−10 (2)	Ni2—O4—C14—C15	2.7 (5)
O6—Ni2—N6—C15	−90.5 (3)	C19—N6—C15—C16	1.6 (6)
N8—Ni2—N6—C15	175.3 (3)	Ni2—N6—C15—C16	−170.9 (3)
O4—Ni2—N6—C15	−5.3 (3)	C19—N6—C15—C14	−179.4 (4)
N11—Ni2—N6—C15	85.2 (3)	Ni2—N6—C15—C14	8.0 (5)
O6—Ni2—N6—C19	97.0 (3)	O4—C14—C15—N6	−7.0 (6)
N8—Ni2—N6—C19	2.8 (3)	O5—C14—C15—N6	172.2 (4)
O4—Ni2—N6—C19	−177.8 (3)	O4—C14—C15—C16	172.0 (4)
N11—Ni2—N6—C19	−87.2 (3)	O5—C14—C15—C16	−8.9 (7)
C21—N7—N8—C23	−1.4 (5)	N6—C15—C16—C17	−0.2 (7)
C19—N7—N8—C23	177.7 (4)	C14—C15—C16—C17	−179.0 (4)
C21—N7—N8—Ni2	174.0 (3)	C15—C16—C17—C18	−1.5 (8)
C19—N7—N8—Ni2	−6.9 (4)	C16—C17—C18—C19	1.7 (8)
N9—Ni2—N8—C23	−3.5 (5)	C15—N6—C19—C18	−1.4 (6)
N6—Ni2—N8—C23	175.1 (5)	Ni2—N6—C19—C18	170.9 (4)

O6—Ni2—N8—C23	77.0 (5)	C15—N6—C19—N7	−179.4 (4)
O4—Ni2—N8—C23	173.7 (4)	Ni2—N6—C19—N7	−7.2 (5)
N11—Ni2—N8—C23	−80.0 (5)	C17—C18—C19—N6	−0.3 (7)
N9—Ni2—N8—N7	−176.3 (3)	C17—C18—C19—N7	177.4 (5)
N6—Ni2—N8—N7	2.3 (3)	C21—N7—C19—N6	−172.1 (4)
O6—Ni2—N8—N7	−95.7 (3)	N8—N7—C19—N6	9.0 (5)
O4—Ni2—N8—N7	1.0 (5)	C21—N7—C19—C18	10.0 (8)
N11—Ni2—N8—N7	107.3 (3)	N8—N7—C19—C18	−168.9 (4)
O6—Ni2—N9—C30	−179.3 (4)	N8—N7—C21—C22	1.7 (5)
N8—Ni2—N9—C30	−86.2 (3)	C19—N7—C21—C22	−177.3 (4)
O4—Ni2—N9—C30	95.0 (3)	N8—N7—C21—C20	−177.2 (4)
N11—Ni2—N9—C30	3.0 (3)	C19—N7—C21—C20	3.9 (8)
O6—Ni2—N9—C26	0.0 (3)	N7—C21—C22—C23	−1.3 (6)
N8—Ni2—N9—C26	93.1 (3)	C20—C21—C22—C23	177.5 (5)
O4—Ni2—N9—C26	−85.8 (3)	N7—N8—C23—C22	0.5 (5)
N11—Ni2—N9—C26	−177.7 (3)	Ni2—N8—C23—C22	−172.5 (4)
C32—N10—N11—C34	−1.6 (5)	N7—N8—C23—C24	−178.0 (4)
C30—N10—N11—C34	−175.9 (4)	Ni2—N8—C23—C24	9.0 (8)
C32—N10—N11—Ni2	174.7 (3)	C21—C22—C23—N8	0.5 (6)
C30—N10—N11—Ni2	0.3 (4)	C21—C22—C23—C24	178.8 (5)
N9—Ni2—N11—C34	172.4 (5)	Ni2—O6—C25—O7	−172.6 (4)
N6—Ni2—N11—C34	−3.1 (5)	Ni2—O6—C25—C26	5.1 (5)
O6—Ni2—N11—C34	167.0 (4)	C30—N9—C26—C27	1.4 (7)
N8—Ni2—N11—C34	−80.1 (5)	Ni2—N9—C26—C27	−177.9 (4)
O4—Ni2—N11—C34	75.5 (5)	C30—N9—C26—C25	−178.2 (4)
N9—Ni2—N11—N10	−1.6 (3)	Ni2—N9—C26—C25	2.5 (5)
N6—Ni2—N11—N10	−177.2 (3)	O7—C25—C26—N9	172.8 (4)
O6—Ni2—N11—N10	−7.1 (5)	O6—C25—C26—N9	−5.1 (6)
N8—Ni2—N11—N10	105.9 (3)	O7—C25—C26—C27	−6.7 (7)
O4—Ni2—N11—N10	−98.6 (3)	O6—C25—C26—C27	175.3 (5)
N5—Ni1—O1—C1	−178.8 (3)	N9—C26—C27—C28	1.6 (8)
N1—Ni1—O1—C1	3.0 (3)	C25—C26—C27—C28	−178.9 (5)
N4—Ni1—O1—C1	−87.4 (3)	C26—C27—C28—C29	−2.4 (9)
N3—Ni1—O1—C1	12.5 (4)	C27—C28—C29—C30	0.4 (10)
O3—Ni1—O1—C1	94.6 (3)	C26—N9—C30—C29	−3.5 (7)
N9—Ni2—O4—C14	179.9 (3)	Ni2—N9—C30—C29	175.7 (4)
N6—Ni2—O4—C14	1.2 (3)	C26—N9—C30—N10	177.0 (4)
O6—Ni2—O4—C14	101.2 (3)	Ni2—N9—C30—N10	−3.7 (5)
N8—Ni2—O4—C14	2.5 (5)	C28—C29—C30—N9	2.6 (8)
N11—Ni2—O4—C14	−103.8 (3)	C28—C29—C30—N10	−178.1 (5)
N9—Ni2—O6—C25	−3.0 (3)	C32—N10—C30—N9	−170.9 (4)
N6—Ni2—O6—C25	172.8 (3)	N11—N10—C30—N9	1.9 (5)
N8—Ni2—O6—C25	−110.0 (3)	C32—N10—C30—C29	9.7 (8)
O4—Ni2—O6—C25	95.4 (3)	N11—N10—C30—C29	−177.5 (5)
N11—Ni2—O6—C25	2.5 (5)	N11—N10—C32—C33	2.1 (5)
Ni1—O1—C1—O2	−179.1 (3)	C30—N10—C32—C33	175.2 (5)
Ni1—O1—C1—C2	−0.2 (5)	N11—N10—C32—C31	−178.4 (5)
C6—N1—C2—C3	1.8 (6)	C30—N10—C32—C31	−5.3 (8)

Ni1—N1—C2—C3	−174.4 (3)	N10—C32—C33—C34	−1.8 (6)
C6—N1—C2—C1	−176.8 (3)	C31—C32—C33—C34	178.7 (6)
Ni1—N1—C2—C1	7.0 (4)	N10—N11—C34—C33	0.4 (5)
O1—C1—C2—N1	−4.3 (6)	Ni2—N11—C34—C33	−173.9 (4)
O2—C1—C2—N1	174.7 (3)	N10—N11—C34—C35	−179.6 (4)
O1—C1—C2—C3	177.1 (4)	Ni2—N11—C34—C35	6.0 (8)
O2—C1—C2—C3	−3.8 (6)	C32—C33—C34—N11	0.9 (7)
N1—C2—C3—C4	−1.1 (6)	C32—C33—C34—C35	−179.0 (5)
C1—C2—C3—C4	177.3 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O5^{i}	0.82	1.67	2.479 (4)	170
O3—H3*A*···O7^{ii}	0.85	1.82	2.674 (4)	180
O3—H3*B*···S1^{iii}	0.85	2.38	3.221 (3)	173

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