

(2-Aminobenzoato- κ^2O,O')(*rac*-5,5,7,-
12,12,14-hexamethyl-1,4,8,11-tetraaza-
cyclotetradecane- κ^4N,N',N'',N''')-
nickel(II) perchlorate monohydrate

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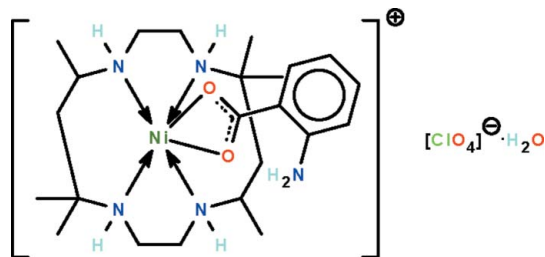
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Key indicators: single-crystal X-ray study; $T = 110$ K; mean $\sigma(C-C) = 0.004$ Å; disorder in solvent or counterion; R factor = 0.023; wR factor = 0.064; data-to-parameter ratio = 9.3.

In the title salt, $[\text{Ni}(\text{C}_7\text{H}_6\text{NO}_2)(\text{C}_{16}\text{H}_{36}\text{N}_4)]\text{ClO}_4 \cdot \text{H}_2\text{O}$, the Ni^{II} cation is O,O' -chelated by the benzoate anion and N,N',N'',N''' -chelated by the macrocycle ligand, conferring a distorted octahedral geometry on the metal atom. The complex cations, perchlorate anions and uncoordinated water molecules are linked by $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds into a three-dimensional network. The perchlorate ion is disordered over two positions in a 0.554 (8):0.446 (8) ratio.

Related literature

For two related structures, see: Ou *et al.* (2008a,b).



Experimental

Crystal data

$[\text{Ni}(\text{C}_7\text{H}_6\text{NO}_2)(\text{C}_{16}\text{H}_{36}\text{N}_4)]\text{ClO}_4 \cdot \text{H}_2\text{O}$	$\beta = 90.784 (1)^\circ$
$M_r = 596.79$	$V = 2805.5 (3) \text{ \AA}^3$
Monoclinic, Cc	$Z = 4$
$a = 9.6452 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 21.5350 (11) \text{ \AA}$	$\mu = 0.84 \text{ mm}^{-1}$
$c = 13.5083 (7) \text{ \AA}$	$T = 110 \text{ K}$
	$0.45 \times 0.20 \times 0.10 \text{ mm}$

Data collection

Bruker SMART APEX diffractometer	6638 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3832 independent reflections
$T_{\min} = 0.818$, $T_{\max} = 1.000$	3667 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.064$	$\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
$S = 1.08$	$\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$
3832 reflections	Absolute structure: Flack (1983), 874 Friedel pairs
410 parameters	Flack parameter: $-0.012 (9)$
142 restraints	

Table 1

Selected bond lengths (Å).

Ni1—N1	2.124 (2)	Ni1—N4	2.087 (2)
Ni1—N2	2.084 (2)	Ni1—O1	2.1659 (17)
Ni1—N3	2.138 (2)	Ni1—O2	2.1280 (16)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots O1w ⁱ	0.86 (2)	2.15 (2)	2.995 (3)	166 (2)
N2—H2 \cdots O5 ⁱⁱ	0.86 (2)	2.35 (2)	3.125 (11)	150 (3)
N3—H3 \cdots O1	0.86 (2)	2.49 (3)	2.885 (3)	109 (2)
N4—H4 \cdots O6 ⁱⁱ	0.86 (3)	2.40 (2)	3.195 (6)	155 (3)
N5—H51 \cdots O2	0.85 (3)	2.13 (3)	2.751 (3)	129 (2)
N5—H52 \cdots O4 ⁱ	0.85 (1)	2.32 (1)	3.155 (6)	168 (3)
O1w—H11 \cdots O1	0.84 (2)	1.96 (2)	2.795 (2)	172 (3)
O1w—H12 \cdots O3	0.83 (2)	2.26 (2)	3.077 (9)	167 (3)
O1w—H12 \cdots O3'	0.83 (2)	2.09 (2)	2.890 (9)	160 (3)

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

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5028).

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supplementary materials

Acta Cryst. (2010). E66, m1295-m1296 [doi:10.1107/S1600536810037116]

(2-Aminobenzoato- κ^2O,O')(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- κ^4N,N',N'',N''')nickel(II) perchlorate monohydrate

G.-C. Ou and S. W. Ng

Comment

Previous studies on (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel benzoate perchlorate salts have documented a chelating mode for the carboxylate ion. The perchlorate counterion is not directly involved in coordination but forms hydrogen bonds with the amino portions of the macrocycle (Ou *et al.*, 2008*a*, 2008*b*). The title substituted benzoate has an additional amino unit that also engages in hydrogen bonding. In the salt, $[\text{Ni}(\text{C}_{16}\text{H}_{36}\text{N}_4)(\text{C}_7\text{H}_6\text{NO}_2)][\text{ClO}_4]\cdot\text{H}_2\text{O}$ (Scheme I, Fig. 1), the metal atom is *O,O'*-chelated by the carboxylate anion and *N,N',N'',N'''*-chelated by the macrocycle to confer an octahedral geometry to the metal center. The cation, anion and lattice water molecules are linked by N–H \cdots O and O–H \cdots O hydrogen bonds into a three-dimensional network.

Experimental

Anthranilic acid (0.27 g, 2 mmol) and sodium hydroxide (0.08 g, 2 mmol) were dissolved in water (15 ml). To this solution was added (*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel diperchlorate (0.11 g, 2 mmol) dissolved in acetonitrile (10 ml). The solution was set aside for the growth of violet crystals after a few days.

Refinement

Carbon-bound H-atoms were placed in calculated positions (C–H 0.95–1.00 Å) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to 1.2–1.5 $U(\text{C})$.

The water and amino H atoms were located in a difference Fourier map, and were refined with distance restraints of O–H 0.84±0.01 Å and N–H 0.86±0.01 Å. For the water molecule, the H \cdots H distance was restrained to 1.37±0.01 Å. The temperature factors were tied to those of the parent atoms by a factor of 1.2–1.5 times.

The perchlorate is disordered over two positions in a 0.554 (8):0.446 (8) ratio. All Cl–O distances were restrained to within 0.01 Å of each other as were the O \cdots O distances. The anisotropic temperature factors of the O atoms were restrained to be nearly isotropic.

Figures

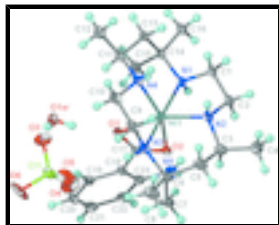


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $[\text{Ni}(\text{C}_{16}\text{H}_{36}\text{N}_4)(\text{C}_7\text{H}_6\text{NO}_2)][\text{ClO}_4]\cdot\text{H}_2\text{O}$ at the 50% probability level; hydrogen atoms are shown as spheres of arbitrary radius. The disorder in the perchlorate is not shown.

(2-Aminobenzoato- $\kappa^2\text{O},\text{O}'$)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- $\kappa^4\text{N},\text{N}',\text{N}'',\text{N}'''$)nickel(II) perchlorate monohydrate

Crystal data

$[\text{Ni}(\text{C}_7\text{H}_6\text{NO}_2)(\text{C}_{16}\text{H}_{36}\text{N}_4)]\text{ClO}_4\cdot\text{H}_2\text{O}$

$M_r = 596.79$

Monoclinic, *Cc*

Hall symbol: C -2yc

$a = 9.6452$ (5) Å

$b = 21.5350$ (11) Å

$c = 13.5083$ (7) Å

$\beta = 90.784$ (1)°

$V = 2805.5$ (3) Å³

$Z = 4$

$F(000) = 1272$

$D_x = 1.413$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5267 reflections

$\theta = 2.3$ – 27.0 °

$\mu = 0.84$ mm⁻¹

$T = 110$ K

Prism, violet

$0.45 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART APEX
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

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

$T_{\min} = 0.818$, $T_{\max} = 1.000$

6638 measured reflections

3832 independent reflections

3667 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 27.0$ °, $\theta_{\min} = 1.9$ °

$h = -11 \rightarrow 12$

$k = -26 \rightarrow 26$

$l = -8 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.064$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.1275P]$

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

$S = 1.08$ $(\Delta/\sigma)_{\max} = 0.001$
 3832 reflections $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
 410 parameters $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$
 142 restraints Absolute structure: Flack (1983), 874 Friedel pairs
 Primary atom site location: structure-invariant direct methods Flack parameter: $-0.012(9)$

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ni1	0.50011 (3)	0.399116 (12)	0.49992 (3)	0.01859 (8)	
O1	0.58175 (16)	0.44546 (8)	0.37089 (12)	0.0219 (4)	
O2	0.66792 (16)	0.46225 (7)	0.51979 (12)	0.0201 (3)	
Cl1	0.6956 (5)	0.2675 (2)	0.1539 (3)	0.0295 (7)	0.554 (8)
O3	0.5575 (5)	0.2886 (4)	0.1347 (6)	0.0444 (19)	0.554 (8)
O4	0.7620 (5)	0.3111 (2)	0.2197 (4)	0.0581 (17)	0.554 (8)
O5	0.6945 (9)	0.2080 (2)	0.2001 (5)	0.0439 (19)	0.554 (8)
O6	0.7708 (7)	0.2650 (3)	0.0641 (4)	0.070 (2)	0.554 (8)
Cl1'	0.6956 (6)	0.2641 (3)	0.1262 (4)	0.0311 (10)	0.446 (8)
O3'	0.5794 (8)	0.2974 (4)	0.1623 (6)	0.042 (2)	0.446 (8)
O4'	0.8213 (6)	0.2957 (3)	0.1496 (6)	0.060 (3)	0.446 (8)
O5'	0.6992 (12)	0.2028 (3)	0.1656 (9)	0.057 (3)	0.446 (8)
O6'	0.6838 (8)	0.2577 (3)	0.0218 (4)	0.058 (2)	0.446 (8)
O1W	0.5173 (2)	0.42855 (9)	0.17034 (14)	0.0296 (4)	
H11	0.545 (3)	0.4343 (13)	0.2291 (11)	0.044*	
H12	0.537 (4)	0.3925 (8)	0.153 (2)	0.044*	
N1	0.3714 (2)	0.46844 (10)	0.56243 (16)	0.0190 (4)	
H1	0.423 (2)	0.4982 (10)	0.585 (2)	0.023*	
N2	0.4909 (2)	0.35763 (9)	0.63905 (16)	0.0211 (4)	
H2	0.428 (2)	0.3296 (10)	0.636 (2)	0.025*	
N3	0.6127 (2)	0.32080 (10)	0.44631 (17)	0.0243 (4)	
H3	0.652 (3)	0.3351 (13)	0.3944 (14)	0.029*	
N4	0.3296 (2)	0.36063 (10)	0.42555 (16)	0.0242 (4)	
H4	0.280 (3)	0.3380 (12)	0.4632 (19)	0.029*	
N5	0.7978 (2)	0.57537 (11)	0.53966 (18)	0.0289 (5)	
H51	0.739 (3)	0.5514 (12)	0.567 (2)	0.035*	
H52	0.814 (3)	0.6115 (8)	0.563 (2)	0.035*	
C1	0.3207 (3)	0.44029 (12)	0.65532 (18)	0.0245 (5)	
H1A	0.2438	0.4112	0.6402	0.029*	
H1B	0.2852	0.4732	0.6995	0.029*	
C2	0.4374 (3)	0.40601 (11)	0.70620 (19)	0.0253 (5)	
H2A	0.5126	0.4354	0.7241	0.030*	
H2B	0.4037	0.3866	0.7678	0.030*	
C3	0.6234 (3)	0.33020 (13)	0.6779 (2)	0.0282 (6)	
H3a	0.6968	0.3629	0.6751	0.034*	
C4	0.6109 (3)	0.30893 (15)	0.7856 (2)	0.0378 (7)	
H4A	0.5814	0.3440	0.8265	0.057*	
H4B	0.7011	0.2937	0.8096	0.057*	

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H4C	0.5423	0.2755	0.7895	0.057*
C5	0.6684 (3)	0.27612 (12)	0.6133 (2)	0.0293 (6)
H5A	0.5883	0.2477	0.6059	0.035*
H5B	0.7418	0.2532	0.6499	0.035*
C6	0.7230 (3)	0.28992 (12)	0.5088 (2)	0.0298 (6)
C7	0.8464 (3)	0.33447 (13)	0.5146 (2)	0.0353 (7)
H7A	0.8832	0.3409	0.4481	0.053*
H7B	0.9188	0.3167	0.5575	0.053*
H7C	0.8162	0.3743	0.5418	0.053*
C8	0.7727 (3)	0.22831 (14)	0.4626 (3)	0.0393 (7)
H8A	0.7921	0.2348	0.3923	0.059*
H8B	0.7003	0.1967	0.4692	0.059*
H8C	0.8573	0.2143	0.4969	0.059*
C9	0.5037 (3)	0.27846 (12)	0.4086 (2)	0.0297 (6)
H9A	0.4632	0.2551	0.4643	0.036*
H9B	0.5444	0.2483	0.3620	0.036*
C10	0.3920 (3)	0.31573 (13)	0.3564 (2)	0.0288 (6)
H10A	0.4324	0.3383	0.2998	0.035*
H10B	0.3194	0.2874	0.3304	0.035*
C11	0.2384 (3)	0.40671 (11)	0.37461 (19)	0.0241 (5)
H11A	0.2979	0.4328	0.3310	0.029*
C12	0.1271 (3)	0.37581 (15)	0.3090 (2)	0.0335 (6)
H12A	0.1719	0.3517	0.2568	0.050*
H12B	0.0680	0.4078	0.2788	0.050*
H12C	0.0704	0.3481	0.3494	0.050*
C13	0.1684 (2)	0.45014 (12)	0.44934 (19)	0.0238 (5)
H13A	0.1253	0.4240	0.5007	0.029*
H13B	0.0923	0.4722	0.4142	0.029*
C14	0.2594 (2)	0.49930 (12)	0.50235 (18)	0.0217 (5)
C15	0.3297 (3)	0.54169 (12)	0.42814 (19)	0.0237 (5)
H15A	0.3819	0.5740	0.4637	0.036*
H15B	0.2592	0.5611	0.3853	0.036*
H15C	0.3932	0.5173	0.3876	0.036*
C16	0.1671 (3)	0.54025 (13)	0.5675 (2)	0.0259 (6)
H16A	0.2256	0.5678	0.6079	0.039*
H16B	0.1117	0.5138	0.6109	0.039*
H16C	0.1053	0.5652	0.5253	0.039*
C17	0.6690 (2)	0.47306 (11)	0.42754 (19)	0.0186 (5)
C18	0.7701 (2)	0.51743 (11)	0.38477 (18)	0.0198 (5)
C19	0.8068 (2)	0.51078 (12)	0.28554 (19)	0.0234 (5)
H19	0.7678	0.4777	0.2479	0.028*
C20	0.8984 (3)	0.55104 (13)	0.2407 (2)	0.0292 (6)
H20	0.9247	0.5450	0.1739	0.035*
C21	0.9514 (3)	0.60087 (12)	0.2959 (2)	0.0301 (6)
H21	1.0125	0.6296	0.2657	0.036*
C22	0.9161 (3)	0.60871 (12)	0.3934 (2)	0.0276 (6)
H22	0.9532	0.6430	0.4292	0.033*
C23	0.8259 (2)	0.56699 (12)	0.4417 (2)	0.0219 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01972 (13)	0.01555 (14)	0.02064 (13)	-0.00292 (12)	0.00605 (9)	-0.00109 (13)
O1	0.0225 (8)	0.0217 (9)	0.0217 (8)	-0.0068 (7)	0.0050 (7)	-0.0017 (7)
O2	0.0227 (8)	0.0171 (9)	0.0207 (8)	-0.0015 (6)	0.0043 (7)	-0.0002 (7)
Cl1	0.0273 (9)	0.0245 (10)	0.0371 (17)	0.0031 (6)	0.0107 (11)	0.0046 (11)
O3	0.036 (2)	0.035 (3)	0.062 (4)	0.005 (2)	-0.007 (2)	-0.016 (3)
O4	0.053 (3)	0.045 (3)	0.075 (4)	-0.004 (2)	-0.017 (3)	-0.008 (2)
O5	0.055 (3)	0.015 (2)	0.062 (4)	0.000 (2)	0.014 (3)	0.010 (2)
O6	0.071 (4)	0.077 (4)	0.065 (4)	0.031 (3)	0.052 (4)	0.012 (3)
Cl1'	0.0308 (12)	0.0213 (12)	0.041 (3)	0.0025 (8)	0.0045 (16)	0.0042 (15)
O3'	0.048 (4)	0.033 (4)	0.047 (4)	0.016 (3)	0.024 (3)	0.001 (3)
O4'	0.055 (3)	0.038 (3)	0.087 (6)	-0.014 (3)	-0.021 (3)	0.020 (3)
O5'	0.051 (4)	0.027 (4)	0.094 (7)	0.008 (3)	0.017 (5)	0.010 (4)
O6'	0.055 (4)	0.079 (4)	0.041 (3)	0.016 (3)	0.009 (3)	-0.017 (3)
O1W	0.0405 (11)	0.0243 (10)	0.0239 (9)	0.0039 (8)	-0.0026 (8)	0.0000 (7)
N1	0.0222 (10)	0.0145 (10)	0.0205 (10)	-0.0003 (8)	0.0027 (8)	0.0008 (8)
N2	0.0208 (10)	0.0180 (10)	0.0248 (10)	0.0008 (8)	0.0057 (8)	0.0009 (8)
N3	0.0254 (10)	0.0186 (11)	0.0291 (11)	-0.0042 (8)	0.0107 (9)	-0.0014 (9)
N4	0.0258 (10)	0.0228 (11)	0.0242 (10)	-0.0061 (8)	0.0086 (8)	-0.0022 (9)
N5	0.0337 (12)	0.0215 (11)	0.0315 (12)	-0.0095 (9)	0.0063 (9)	-0.0075 (9)
C1	0.0287 (12)	0.0262 (13)	0.0187 (11)	0.0058 (10)	0.0078 (10)	0.0013 (10)
C2	0.0314 (13)	0.0246 (13)	0.0202 (11)	0.0062 (10)	0.0056 (10)	0.0018 (10)
C3	0.0250 (12)	0.0240 (14)	0.0356 (15)	0.0034 (10)	0.0030 (11)	0.0032 (11)
C4	0.0416 (16)	0.0366 (16)	0.0353 (15)	0.0169 (13)	0.0014 (13)	0.0070 (13)
C5	0.0295 (13)	0.0180 (12)	0.0406 (15)	0.0043 (10)	0.0081 (11)	0.0038 (11)
C6	0.0245 (13)	0.0232 (14)	0.0420 (16)	0.0016 (10)	0.0122 (11)	-0.0024 (12)
C7	0.0229 (13)	0.0326 (16)	0.0507 (17)	0.0009 (11)	0.0090 (12)	-0.0002 (13)
C8	0.0370 (16)	0.0235 (15)	0.058 (2)	0.0074 (12)	0.0127 (15)	-0.0063 (14)
C9	0.0347 (13)	0.0181 (13)	0.0368 (14)	-0.0057 (10)	0.0146 (11)	-0.0073 (11)
C10	0.0315 (14)	0.0250 (14)	0.0301 (14)	-0.0081 (10)	0.0079 (11)	-0.0125 (11)
C11	0.0247 (12)	0.0247 (13)	0.0232 (12)	-0.0063 (9)	0.0049 (10)	-0.0010 (10)
C12	0.0295 (13)	0.0429 (17)	0.0282 (13)	-0.0081 (12)	0.0010 (11)	-0.0065 (12)
C13	0.0193 (11)	0.0276 (13)	0.0245 (12)	-0.0013 (9)	0.0031 (10)	0.0017 (10)
C14	0.0229 (11)	0.0224 (12)	0.0200 (11)	0.0015 (9)	0.0040 (9)	0.0031 (10)
C15	0.0278 (12)	0.0222 (12)	0.0212 (11)	0.0021 (9)	0.0048 (10)	0.0034 (10)
C16	0.0263 (13)	0.0259 (15)	0.0256 (13)	0.0059 (10)	0.0062 (10)	0.0040 (11)
C17	0.0197 (11)	0.0140 (11)	0.0222 (12)	0.0024 (9)	0.0045 (9)	-0.0008 (9)
C18	0.0190 (11)	0.0170 (12)	0.0236 (12)	0.0000 (8)	0.0017 (9)	0.0014 (9)
C19	0.0210 (12)	0.0238 (13)	0.0255 (12)	-0.0011 (9)	0.0037 (10)	0.0014 (10)
C20	0.0253 (12)	0.0355 (15)	0.0269 (13)	0.0006 (10)	0.0083 (10)	0.0080 (11)
C21	0.0210 (12)	0.0288 (14)	0.0405 (15)	-0.0034 (9)	0.0045 (11)	0.0131 (12)
C22	0.0249 (12)	0.0199 (13)	0.0378 (15)	-0.0048 (9)	-0.0005 (11)	0.0034 (11)
C23	0.0194 (11)	0.0193 (12)	0.0269 (12)	0.0015 (9)	0.0022 (10)	0.0017 (10)

supplementary materials

Geometric parameters (Å, °)

Ni1—N1	2.124 (2)	C5—C6	1.541 (4)
Ni1—N2	2.084 (2)	C5—H5A	0.9900
Ni1—N3	2.138 (2)	C5—H5B	0.9900
Ni1—N4	2.087 (2)	C6—C7	1.530 (4)
Ni1—O1	2.1659 (17)	C6—C8	1.546 (4)
Ni1—O2	2.1280 (16)	C7—H7A	0.9800
O1—C17	1.276 (3)	C7—H7B	0.9800
O2—C17	1.268 (3)	C7—H7C	0.9800
Cl1—O6	1.423 (4)	C8—H8A	0.9800
Cl1—O5	1.425 (5)	C8—H8B	0.9800
Cl1—O3	1.427 (5)	C8—H8C	0.9800
Cl1—O4	1.437 (5)	C9—C10	1.510 (4)
Cl1'—O6'	1.421 (5)	C9—H9A	0.9900
Cl1'—O5'	1.423 (6)	C9—H9B	0.9900
Cl1'—O3'	1.422 (5)	C10—H10A	0.9900
Cl1'—O4'	1.422 (6)	C10—H10B	0.9900
O1W—H11	0.843 (10)	C11—C12	1.534 (4)
O1W—H12	0.833 (10)	C11—C13	1.539 (3)
N1—C1	1.482 (3)	C11—H11A	1.0000
N1—C14	1.498 (3)	C12—H12A	0.9800
N1—H1	0.861 (10)	C12—H12B	0.9800
N2—C2	1.479 (3)	C12—H12C	0.9800
N2—C3	1.496 (3)	C13—C14	1.545 (3)
N2—H2	0.858 (10)	C13—H13A	0.9900
N3—C9	1.477 (3)	C13—H13B	0.9900
N3—C6	1.504 (4)	C14—C15	1.522 (3)
N3—H3	0.860 (10)	C14—C16	1.538 (3)
N4—C10	1.478 (3)	C15—H15A	0.9800
N4—C11	1.489 (3)	C15—H15B	0.9800
N4—H4	0.86 (3)	C15—H15C	0.9800
N5—C23	1.366 (3)	C16—H16A	0.9800
N5—H51	0.86 (3)	C16—H16B	0.9800
N5—H52	0.854 (10)	C16—H16C	0.9800
C1—C2	1.504 (3)	C17—C18	1.487 (3)
C1—H1A	0.9900	C18—C19	1.399 (3)
C1—H1B	0.9900	C18—C23	1.418 (3)
C2—H2A	0.9900	C19—C20	1.383 (3)
C2—H2B	0.9900	C19—H19	0.9500
C3—C5	1.522 (4)	C20—C21	1.400 (4)
C3—C4	1.532 (4)	C20—H20	0.9500
C3—H3a	1.0000	C21—C22	1.375 (4)
C4—H4A	0.9800	C21—H21	0.9500
C4—H4B	0.9800	C22—C23	1.416 (4)
C4—H4C	0.9800	C22—H22	0.9500
N2—Ni1—N4	102.76 (8)	N3—C6—C7	107.2 (2)
N2—Ni1—N1	84.86 (8)	N3—C6—C5	110.60 (19)

N4—Ni1—N1	90.54 (8)	C7—C6—C5	110.5 (2)
N2—Ni1—O2	101.64 (7)	N3—C6—C8	111.9 (2)
N4—Ni1—O2	155.16 (8)	C7—C6—C8	108.2 (2)
N1—Ni1—O2	87.05 (7)	C5—C6—C8	108.4 (2)
N2—Ni1—N3	89.73 (8)	C6—C7—H7A	109.5
N4—Ni1—N3	85.66 (8)	C6—C7—H7B	109.5
N1—Ni1—N3	172.56 (8)	H7A—C7—H7B	109.5
O2—Ni1—N3	99.07 (7)	C6—C7—H7C	109.5
N2—Ni1—O1	160.67 (7)	H7A—C7—H7C	109.5
N4—Ni1—O1	95.07 (7)	H7B—C7—H7C	109.5
N1—Ni1—O1	102.53 (7)	C6—C8—H8A	109.5
O2—Ni1—O1	61.50 (6)	C6—C8—H8B	109.5
N3—Ni1—O1	84.20 (7)	H8A—C8—H8B	109.5
C17—O1—Ni1	88.63 (14)	C6—C8—H8C	109.5
C17—O2—Ni1	90.56 (14)	H8A—C8—H8C	109.5
O6—C11—O5	110.2 (4)	H8B—C8—H8C	109.5
O6—C11—O3	110.1 (4)	N3—C9—C10	109.4 (2)
O5—C11—O3	110.7 (4)	N3—C9—H9A	109.8
O6—C11—O4	108.9 (4)	C10—C9—H9A	109.8
O5—C11—O4	108.8 (4)	N3—C9—H9B	109.8
O3—C11—O4	108.1 (4)	C10—C9—H9B	109.8
O6'—C11'—O5'	106.4 (7)	H9A—C9—H9B	108.2
O6'—C11'—O3'	109.6 (5)	N4—C10—C9	110.3 (2)
O5'—C11'—O3'	110.8 (5)	N4—C10—H10A	109.6
O6'—C11'—O4'	108.9 (5)	C9—C10—H10A	109.6
O5'—C11'—O4'	110.2 (5)	N4—C10—H10B	109.6
O3'—C11'—O4'	110.8 (5)	C9—C10—H10B	109.6
H11—O1W—H12	109.4 (17)	H10A—C10—H10B	108.1
C1—N1—C14	113.35 (19)	N4—C11—C12	112.5 (2)
C1—N1—Ni1	104.50 (15)	N4—C11—C13	111.3 (2)
C14—N1—Ni1	121.17 (16)	C12—C11—C13	109.5 (2)
C1—N1—H1	101.7 (19)	N4—C11—H11A	107.8
C14—N1—H1	105.3 (19)	C12—C11—H11A	107.8
Ni1—N1—H1	109.1 (18)	C13—C11—H11A	107.8
C2—N2—C3	111.5 (2)	C11—C12—H12A	109.5
C2—N2—Ni1	105.70 (15)	C11—C12—H12B	109.5
C3—N2—Ni1	116.01 (15)	H12A—C12—H12B	109.5
C2—N2—H2	106 (2)	C11—C12—H12C	109.5
C3—N2—H2	110 (2)	H12A—C12—H12C	109.5
Ni1—N2—H2	107 (2)	H12B—C12—H12C	109.5
C9—N3—C6	114.5 (2)	C11—C13—C14	117.97 (19)
C9—N3—Ni1	103.96 (15)	C11—C13—H13A	107.8
C6—N3—Ni1	121.14 (16)	C14—C13—H13A	107.8
C9—N3—H3	105 (2)	C11—C13—H13B	107.8
C6—N3—H3	107 (2)	C14—C13—H13B	107.8
Ni1—N3—H3	103 (2)	H13A—C13—H13B	107.2
C10—N4—C11	112.8 (2)	N1—C14—C15	107.37 (19)
C10—N4—Ni1	103.81 (15)	N1—C14—C16	111.3 (2)
C11—N4—Ni1	114.50 (15)	C15—C14—C16	107.4 (2)

supplementary materials

C10—N4—H4	104 (2)	N1—C14—C13	110.4 (2)
C11—N4—H4	109 (2)	C15—C14—C13	111.2 (2)
Ni1—N4—H4	113 (2)	C16—C14—C13	109.19 (19)
C23—N5—H51	119 (2)	C14—C15—H15A	109.5
C23—N5—H52	116 (2)	C14—C15—H15B	109.5
H51—N5—H52	121 (3)	H15A—C15—H15B	109.5
N1—C1—C2	109.5 (2)	C14—C15—H15C	109.5
N1—C1—H1A	109.8	H15A—C15—H15C	109.5
C2—C1—H1A	109.8	H15B—C15—H15C	109.5
N1—C1—H1B	109.8	C14—C16—H16A	109.5
C2—C1—H1B	109.8	C14—C16—H16B	109.5
H1A—C1—H1B	108.2	H16A—C16—H16B	109.5
N2—C2—C1	109.3 (2)	C14—C16—H16C	109.5
N2—C2—H2A	109.8	H16A—C16—H16C	109.5
C1—C2—H2A	109.8	H16B—C16—H16C	109.5
N2—C2—H2B	109.8	O2—C17—O1	119.3 (2)
C1—C2—H2B	109.8	O2—C17—C18	120.9 (2)
H2A—C2—H2B	108.3	O1—C17—C18	119.8 (2)
N2—C3—C5	110.5 (2)	C19—C18—C23	119.9 (2)
N2—C3—C4	111.9 (2)	C19—C18—C17	118.9 (2)
C5—C3—C4	110.0 (2)	C23—C18—C17	121.3 (2)
N2—C3—H3a	108.1	C20—C19—C18	121.8 (2)
C5—C3—H3a	108.1	C20—C19—H19	119.1
C4—C3—H3a	108.1	C18—C19—H19	119.1
C3—C4—H4A	109.5	C19—C20—C21	118.6 (2)
C3—C4—H4B	109.5	C19—C20—H20	120.7
H4A—C4—H4B	109.5	C21—C20—H20	120.7
C3—C4—H4C	109.5	C22—C21—C20	120.7 (2)
H4A—C4—H4C	109.5	C22—C21—H21	119.6
H4B—C4—H4C	109.5	C20—C21—H21	119.6
C3—C5—C6	118.7 (2)	C21—C22—C23	121.7 (3)
C3—C5—H5A	107.6	C21—C22—H22	119.1
C6—C5—H5A	107.6	C23—C22—H22	119.1
C3—C5—H5B	107.6	N5—C23—C18	123.1 (2)
C6—C5—H5B	107.6	N5—C23—C22	119.6 (2)
H5A—C5—H5B	107.1	C18—C23—C22	117.3 (2)
N2—Ni1—O1—C17	-31.3 (3)	C2—N2—C3—C4	51.2 (3)
N4—Ni1—O1—C17	171.28 (14)	Ni1—N2—C3—C4	172.23 (19)
N1—Ni1—O1—C17	79.59 (14)	N2—C3—C5—C6	71.2 (3)
O2—Ni1—O1—C17	0.00 (13)	C4—C3—C5—C6	-164.7 (2)
N3—Ni1—O1—C17	-103.62 (14)	C9—N3—C6—C7	163.1 (2)
N2—Ni1—O2—C17	169.89 (14)	Ni1—N3—C6—C7	-71.0 (2)
N4—Ni1—O2—C17	-21.1 (2)	C9—N3—C6—C5	-76.4 (3)
N1—Ni1—O2—C17	-105.97 (14)	Ni1—N3—C6—C5	49.4 (3)
N3—Ni1—O2—C17	78.28 (15)	C9—N3—C6—C8	44.6 (3)
O1—Ni1—O2—C17	0.00 (13)	Ni1—N3—C6—C8	170.46 (18)
N2—Ni1—N1—C1	-14.19 (16)	C3—C5—C6—N3	-61.6 (3)
N4—Ni1—N1—C1	88.57 (16)	C3—C5—C6—C7	56.8 (3)
O2—Ni1—N1—C1	-116.17 (16)	C3—C5—C6—C8	175.3 (2)

O1—Ni1—N1—C1	-176.11 (15)	C6—N3—C9—C10	174.1 (2)
N2—Ni1—N1—C14	-143.61 (18)	Ni1—N3—C9—C10	39.7 (2)
N4—Ni1—N1—C14	-40.84 (18)	C11—N4—C10—C9	169.1 (2)
O2—Ni1—N1—C14	114.42 (17)	Ni1—N4—C10—C9	44.6 (2)
O1—Ni1—N1—C14	54.48 (18)	N3—C9—C10—N4	-59.9 (3)
N4—Ni1—N2—C2	-104.54 (16)	C10—N4—C11—C12	53.3 (3)
N1—Ni1—N2—C2	-15.15 (16)	Ni1—N4—C11—C12	171.73 (16)
O2—Ni1—N2—C2	70.77 (16)	C10—N4—C11—C13	176.57 (19)
N3—Ni1—N2—C2	169.98 (16)	Ni1—N4—C11—C13	-65.0 (2)
O1—Ni1—N2—C2	98.6 (2)	N4—C11—C13—C14	71.8 (3)
N4—Ni1—N2—C3	131.31 (17)	C12—C11—C13—C14	-163.2 (2)
N1—Ni1—N2—C3	-139.30 (18)	C1—N1—C14—C15	163.3 (2)
O2—Ni1—N2—C3	-53.38 (18)	Ni1—N1—C14—C15	-71.2 (2)
N3—Ni1—N2—C3	45.83 (18)	C1—N1—C14—C16	46.1 (3)
O1—Ni1—N2—C3	-25.6 (3)	Ni1—N1—C14—C16	171.49 (16)
N2—Ni1—N3—C9	90.51 (16)	C1—N1—C14—C13	-75.4 (2)
N4—Ni1—N3—C9	-12.31 (16)	Ni1—N1—C14—C13	50.1 (2)
O2—Ni1—N3—C9	-167.74 (16)	C11—C13—C14—N1	-61.3 (3)
O1—Ni1—N3—C9	-107.87 (16)	C11—C13—C14—C15	57.7 (3)
N2—Ni1—N3—C6	-40.04 (18)	C11—C13—C14—C16	176.0 (2)
N4—Ni1—N3—C6	-142.86 (18)	Ni1—O2—C17—O1	0.0 (2)
O2—Ni1—N3—C6	61.70 (18)	Ni1—O2—C17—C18	179.87 (19)
O1—Ni1—N3—C6	121.58 (18)	Ni1—O1—C17—O2	0.0 (2)
N2—Ni1—N4—C10	-105.88 (17)	Ni1—O1—C17—C18	-179.88 (19)
N1—Ni1—N4—C10	169.26 (17)	O2—C17—C18—C19	155.0 (2)
O2—Ni1—N4—C10	85.1 (2)	O1—C17—C18—C19	-25.2 (3)
N3—Ni1—N4—C10	-17.14 (17)	O2—C17—C18—C23	-26.9 (3)
O1—Ni1—N4—C10	66.63 (17)	O1—C17—C18—C23	152.9 (2)
N2—Ni1—N4—C11	130.71 (15)	C23—C18—C19—C20	0.8 (4)
N1—Ni1—N4—C11	45.86 (16)	C17—C18—C19—C20	178.9 (2)
O2—Ni1—N4—C11	-38.3 (3)	C18—C19—C20—C21	-2.2 (4)
N3—Ni1—N4—C11	-140.55 (16)	C19—C20—C21—C22	1.7 (4)
O1—Ni1—N4—C11	-56.77 (16)	C20—C21—C22—C23	0.3 (4)
C14—N1—C1—C2	175.3 (2)	C19—C18—C23—N5	-178.1 (2)
Ni1—N1—C1—C2	41.4 (2)	C17—C18—C23—N5	3.8 (4)
C3—N2—C2—C1	169.3 (2)	C19—C18—C23—C22	1.1 (3)
Ni1—N2—C2—C1	42.4 (2)	C17—C18—C23—C22	-176.9 (2)
N1—C1—C2—N2	-58.6 (3)	C21—C22—C23—N5	177.6 (2)
C2—N2—C3—C5	174.1 (2)	C21—C22—C23—C18	-1.7 (4)
Ni1—N2—C3—C5	-64.8 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O1w ⁱ	0.86 (2)	2.15 (2)	2.995 (3)	166 (2)
N2—H2 \cdots O5 ⁱⁱ	0.86 (2)	2.56 (2)	3.304 (8)	147 (2)
N2—H2 \cdots O5 ⁱⁱⁱ	0.86 (2)	2.35 (2)	3.125 (11)	150 (3)
N3—H3 \cdots O1	0.86 (2)	2.49 (3)	2.885 (3)	109 (2)

supplementary materials

N4—H4…O6 ⁱⁱ	0.86 (3)	2.61 (2)	3.343 (6)	145 (3)
N4—H4…O6 ⁱⁱ	0.86 (3)	2.40 (2)	3.195 (6)	155 (3)
N5—H51…O2	0.85 (3)	2.13 (3)	2.751 (3)	129 (2)
N5—H52…O4 ⁱ	0.85 (1)	2.32 (1)	3.155 (6)	168 (3)
O1w—H11…O1	0.84 (2)	1.96 (2)	2.795 (2)	172 (3)
O1w—H12…O3	0.83 (2)	2.26 (2)	3.077 (9)	167 (3)
O1w—H12…O3'	0.83 (2)	2.09 (2)	2.890 (9)	160 (3)

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

Fig. 1

