

Ammonium tris(3-aminopyrazine-2-carboxylato- κ^2N^1,O)nickelate(II) trihydrate

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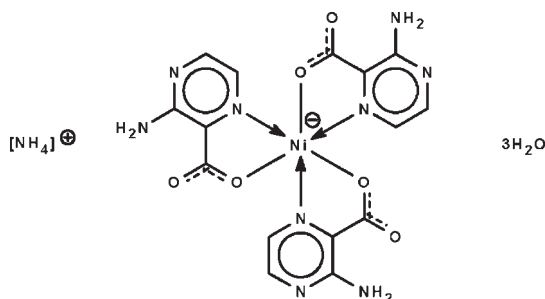
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.035; wR factor = 0.096; data-to-parameter ratio = 13.5.

The Ni^{II} atom in the title hydrated salt, (NH₄)[Ni(C₅H₄N₃O₂)₃·3H₂O], is *N,O*-chelated by the three 3-aminopyrazine-2-carboxylate ligands, resulting in a distorted octahedral *mer*-NiN₃O₃ geometry for the metal. In the crystal, the complex anion, ammonium cation and uncoordinated water molecules are linked by extensive N—H...N, N—H...O, O—H...N and O—H...O hydrogen bonds, forming a three-dimensional network.

Related literature

For the crystal structure of diaquabis(3-aminopyrazine-2-carboxylato)nickel(II), see: Ptasiwicz-Bak & Leciejewicz (1999).



Experimental

Crystal data

 (NH₄)[Ni(C₅H₄N₃O₂)₃·3H₂O

 $M_r = 545.14$

 Monoclinic, $P2_1/n$
 $a = 11.2092$ (3) Å

 $b = 14.7061$ (4) Å

 $c = 13.7540$ (4) Å

 $\beta = 97.5214$ (8)°

 $V = 2247.75$ (11) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.93$ mm⁻¹
 $T = 293$ K

 $0.28 \times 0.22 \times 0.19$ mm

Data collection

Rigaku R-Axis RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
 $T_{\min} = 0.780$, $T_{\max} = 0.843$

21341 measured reflections
5114 independent reflections
4322 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.096$
 $S = 1.02$

5114 reflections

380 parameters

25 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.26$ e Å⁻³
Table 1

Selected bond lengths (Å).

Ni1—O1	2.0476 (13)	Ni1—N7	2.0561 (14)
Ni1—O3	2.0526 (13)	Ni1—N4	2.0805 (14)
Ni1—O5	2.0567 (13)	Ni1—N1	2.0857 (15)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H31...O2	0.85 (1)	2.08 (2)	2.740 (3)	134 (2)
N6—H61...O4	0.85 (1)	2.01 (2)	2.701 (3)	138 (2)
N6—H62...N5 ⁱ	0.85 (1)	2.15 (1)	2.992 (2)	175 (2)
N9—H91...O6	0.86 (1)	2.07 (2)	2.733 (2)	134 (2)
N9—H92...O3 ⁱⁱ	0.85 (1)	2.10 (1)	2.924 (2)	164 (2)
N10—H101...O2	0.86 (1)	1.91 (1)	2.756 (3)	169 (3)
N10—H102...O1 ^w	0.86 (1)	1.94 (1)	2.779 (3)	164 (3)
N10—H103...O2 ^w	0.85 (1)	2.07 (1)	2.919 (3)	172 (3)
N10—H104...N8 ⁱⁱⁱ	0.84 (1)	2.36 (2)	3.018 (3)	135 (2)
O1 ^w —H1 ^w ...O1	0.84 (1)	2.25 (2)	2.964 (3)	143 (4)
O1 ^w —H1 ^w 2...N2 ^{iv}	0.85 (1)	2.00 (1)	2.842 (3)	171 (4)
O2 ^w —H2 ^w 1...O5 ^v	0.85 (1)	2.03 (1)	2.869 (2)	168 (3)
O2 ^w —H2 ^w 2...O6 ^{vi}	0.84 (1)	1.96 (1)	2.766 (2)	159 (3)
O3 ^w —H3 ^w 1...O4	0.85 (1)	2.39 (5)	2.812 (3)	111 (4)

Symmetry codes: (i) $-x, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (v) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO* data reduction: *CrystalClear* (Rigaku/MSK, 2002); 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: *pubCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5228).

References

- Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Ptasiewicz-Bak, H. & Leciejewicz, B. (1999). *Pol. J. Chem.* **73**, 717–725.
- Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSK (2002). *CrystalClear*. Rigaku/MSK Inc., The Woodlands, Texas, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Westrip, S. P. (2009). *publCIF*. In preparation.

supplementary materials

Acta Cryst. (2009). E65, m1631-m1632 [doi:10.1107/S1600536809048363]

Ammonium tris(3-aminopyrazine-2-carboxylato- κ^2N^1,O)nickelate(II) trihydrate

X.-L. Cheng, S. Gao and S. W. Ng

Experimental

Nickel dichloride hexahydrate (0.48 g, 2 mmol), 3-aminopyrazine-2-carboxylic acid (0.56 g, 4 mmol) and sodium hydroxide (0.16 g 4 mmol) were dissolved in a water/DMF ($v/v = 10\text{ ml}:1\text{ ml}$) mixture. The solution was sealed in a 50 ml Teflon-lined stainless steel bomb and held at 443 K for 3 days. The bomb was gradually cooled to room temperature, and green blocks of (I) were obtained after several days. The presence of the ammonium counterion is explained by the decomposition of DMF.

Refinement

Carbon-bound H-atoms were placed in calculated positions (C–H 0.93 Å) and were included in the refinement in the riding model approximation, with $U(\text{H}) = 1.2U(\text{C})$. The amino and water H-atoms were located in a difference Fourier map, and were refined with a distance restraint of N–H = O–H = 0.85±0.01 Å; their U_{iso} values were refined.

Figures

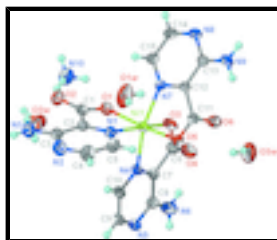


Fig. 1. The molecular structure of (I) at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

Ammonium tris(3-aminopyrazine-2-carboxylato- κ^2N^1,O)nickelate(II) trihydrate

Crystal data

$(\text{NH}_4)[\text{Ni}(\text{C}_5\text{H}_4\text{N}_3\text{O}_2)_3]\cdot 3\text{H}_2\text{O}$

$M_r = 545.14$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 11.2092\ (3)\ \text{\AA}$

$b = 14.7061\ (4)\ \text{\AA}$

$c = 13.7540\ (4)\ \text{\AA}$

$\beta = 97.5214\ (8)^\circ$

$V = 2247.75\ (11)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1128$

$D_x = 1.611\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 17239 reflections

$\theta = 3.2\text{--}27.5^\circ$

$\mu = 0.93\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, green

$0.28 \times 0.22 \times 0.19\ \text{mm}$

supplementary materials

Data collection

Rigaku R-Axis RAPID IP diffractometer	5114 independent reflections
Radiation source: fine-focus sealed tube	4322 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.028$
$T = 293$ K	$\theta_{\text{max}} = 27.4^\circ$
ω scan	$\theta_{\text{min}} = 3.2^\circ$
Absorption correction: Multi-scan (ABSCOR; Higashi, 1995)	$h = -14 \rightarrow 14$
$T_{\text{min}} = 0.780$, $T_{\text{max}} = 0.843$	$k = -19 \rightarrow 19$
21341 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.096$	$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 0.5222P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
5114 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
380 parameters	$\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{\AA}^{-3}$
25 restraints	$\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.31748 (2)	0.668273 (15)	0.689311 (16)	0.03143 (9)
O1	0.42705 (12)	0.74401 (9)	0.78914 (10)	0.0399 (3)
O2	0.46912 (13)	0.77268 (10)	0.94948 (10)	0.0483 (3)
O3	0.37891 (13)	0.72843 (9)	0.57068 (10)	0.0446 (3)
O4	0.33775 (17)	0.83556 (12)	0.45711 (12)	0.0616 (5)
O5	0.21564 (11)	0.57245 (9)	0.60709 (9)	0.0391 (3)
O6	0.22619 (12)	0.43404 (11)	0.54208 (12)	0.0536 (4)
O1W	0.5686 (2)	0.8674 (2)	0.67787 (15)	0.0930 (8)
O2W	0.53958 (16)	1.06663 (15)	0.88906 (13)	0.0643 (5)
O3W	0.3437 (3)	0.8148 (3)	0.25454 (17)	0.0980 (8)
N1	0.25466 (14)	0.62854 (10)	0.81904 (11)	0.0341 (3)
N2	0.15754 (17)	0.62107 (13)	0.99403 (13)	0.0500 (4)
N3	0.2905 (2)	0.73064 (15)	1.06019 (13)	0.0525 (5)
N4	0.19233 (13)	0.77229 (10)	0.65903 (10)	0.0327 (3)
N5	0.03798 (15)	0.91375 (11)	0.59648 (12)	0.0410 (4)

N6	0.14458 (19)	0.94291 (14)	0.46855 (15)	0.0560 (5)
N7	0.44529 (13)	0.56953 (10)	0.67977 (10)	0.0307 (3)
N8	0.60635 (14)	0.44427 (11)	0.62184 (12)	0.0389 (4)
N9	0.45018 (16)	0.36067 (12)	0.54171 (13)	0.0418 (4)
N10	0.6367 (2)	0.88322 (17)	0.87878 (16)	0.0609 (5)
C1	0.40689 (16)	0.73693 (12)	0.87734 (13)	0.0352 (4)
C2	0.30163 (16)	0.67882 (12)	0.89515 (13)	0.0331 (4)
C3	0.25094 (18)	0.67630 (13)	0.98471 (14)	0.0389 (4)
C4	0.1158 (2)	0.56992 (16)	0.91715 (16)	0.0528 (5)
H4	0.0521	0.5307	0.9229	0.063*
C5	0.16254 (19)	0.57242 (14)	0.82959 (15)	0.0429 (4)
H5	0.1305	0.5354	0.7778	0.052*
C6	0.31612 (18)	0.79401 (13)	0.53101 (13)	0.0385 (4)
C7	0.21035 (17)	0.82128 (11)	0.58056 (13)	0.0321 (4)
C8	0.13109 (17)	0.89357 (12)	0.54759 (13)	0.0368 (4)
C9	0.02365 (18)	0.86309 (14)	0.67384 (14)	0.0413 (4)
H9	-0.0410	0.8758	0.7077	0.050*
C10	0.09911 (17)	0.79277 (14)	0.70670 (13)	0.0390 (4)
H10	0.0855	0.7596	0.7618	0.047*
C11	0.27182 (16)	0.50055 (13)	0.58777 (13)	0.0345 (4)
C12	0.40521 (15)	0.49993 (12)	0.62341 (12)	0.0294 (3)
C13	0.48649 (16)	0.43358 (12)	0.59462 (12)	0.0316 (4)
C14	0.64164 (17)	0.51541 (14)	0.67792 (15)	0.0418 (4)
H14	0.7237	0.5235	0.6970	0.050*
C15	0.56347 (16)	0.57786 (13)	0.70937 (14)	0.0379 (4)
H15	0.5924	0.6252	0.7507	0.045*
H1W1	0.518 (4)	0.826 (3)	0.681 (3)	0.16 (2)*
H1W2	0.587 (4)	0.871 (3)	0.6200 (14)	0.138 (16)*
H2W1	0.4664 (10)	1.071 (2)	0.8988 (19)	0.079 (10)*
H2W2	0.586 (2)	1.078 (3)	0.9408 (15)	0.123 (15)*
H3W1	0.366 (6)	0.861 (2)	0.290 (3)	0.20 (3)*
H3W2	0.325 (6)	0.772 (3)	0.292 (3)	0.21 (3)*
H31	0.3539 (16)	0.7617 (16)	1.056 (2)	0.064 (8)*
H32	0.259 (2)	0.724 (2)	1.1133 (13)	0.076 (9)*
H61	0.2078 (15)	0.9305 (16)	0.4426 (16)	0.054 (7)*
H62	0.0924 (18)	0.9821 (13)	0.4466 (18)	0.058 (7)*
H91	0.3745 (10)	0.3567 (18)	0.5212 (19)	0.059 (7)*
H92	0.5008 (17)	0.3270 (13)	0.5183 (17)	0.048 (7)*
H101	0.592 (2)	0.8458 (15)	0.9058 (17)	0.079 (10)*
H102	0.627 (3)	0.871 (2)	0.8169 (8)	0.106 (13)*
H103	0.612 (3)	0.9371 (9)	0.887 (2)	0.16 (2)*
H104	0.7095 (10)	0.876 (2)	0.902 (2)	0.124 (15)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.03054 (14)	0.03344 (14)	0.03110 (13)	0.00615 (9)	0.00699 (9)	0.00153 (9)
O1	0.0392 (7)	0.0421 (7)	0.0402 (7)	-0.0052 (6)	0.0123 (6)	-0.0010 (6)

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O2	0.0463 (8)	0.0536 (8)	0.0440 (7)	-0.0107 (7)	0.0029 (6)	-0.0063 (7)
O3	0.0452 (8)	0.0472 (7)	0.0454 (7)	0.0188 (6)	0.0214 (6)	0.0114 (6)
O4	0.0649 (11)	0.0760 (11)	0.0496 (9)	0.0243 (9)	0.0285 (8)	0.0262 (8)
O5	0.0292 (6)	0.0472 (7)	0.0400 (7)	0.0099 (6)	0.0012 (5)	-0.0059 (6)
O6	0.0326 (7)	0.0540 (9)	0.0713 (10)	0.0016 (6)	-0.0046 (7)	-0.0237 (8)
O1W	0.0979 (17)	0.131 (2)	0.0520 (11)	-0.0539 (16)	0.0174 (11)	-0.0013 (12)
O2W	0.0414 (9)	0.0925 (13)	0.0577 (10)	-0.0038 (9)	0.0021 (8)	-0.0103 (10)
O3W	0.0917 (18)	0.144 (2)	0.0590 (12)	-0.0021 (17)	0.0121 (12)	-0.0216 (15)
N1	0.0345 (8)	0.0350 (8)	0.0325 (7)	0.0019 (6)	0.0037 (6)	0.0027 (6)
N2	0.0528 (11)	0.0581 (11)	0.0419 (9)	-0.0058 (9)	0.0163 (8)	0.0059 (8)
N3	0.0585 (12)	0.0643 (12)	0.0360 (9)	-0.0039 (10)	0.0113 (9)	-0.0049 (9)
N4	0.0335 (8)	0.0342 (7)	0.0312 (7)	0.0067 (6)	0.0067 (6)	-0.0003 (6)
N5	0.0408 (9)	0.0391 (8)	0.0427 (8)	0.0131 (7)	0.0042 (7)	-0.0013 (7)
N6	0.0556 (12)	0.0564 (11)	0.0582 (11)	0.0224 (10)	0.0161 (10)	0.0245 (10)
N7	0.0276 (7)	0.0340 (7)	0.0303 (7)	0.0042 (6)	0.0032 (6)	0.0011 (6)
N8	0.0298 (8)	0.0432 (8)	0.0443 (8)	0.0071 (7)	0.0074 (7)	0.0015 (7)
N9	0.0349 (9)	0.0419 (9)	0.0498 (9)	0.0042 (7)	0.0107 (8)	-0.0092 (8)
N10	0.0507 (12)	0.0779 (16)	0.0551 (12)	-0.0199 (11)	0.0108 (10)	-0.0007 (11)
C1	0.0343 (9)	0.0340 (9)	0.0374 (9)	0.0032 (7)	0.0053 (7)	-0.0006 (8)
C2	0.0325 (9)	0.0349 (9)	0.0317 (8)	0.0058 (7)	0.0037 (7)	0.0029 (7)
C3	0.0408 (10)	0.0432 (10)	0.0329 (9)	0.0067 (8)	0.0054 (8)	0.0042 (8)
C4	0.0518 (13)	0.0584 (13)	0.0501 (12)	-0.0145 (11)	0.0138 (10)	0.0067 (11)
C5	0.0442 (11)	0.0436 (10)	0.0407 (10)	-0.0084 (9)	0.0046 (8)	0.0021 (8)
C6	0.0408 (10)	0.0426 (10)	0.0335 (9)	0.0070 (8)	0.0104 (8)	0.0023 (8)
C7	0.0338 (9)	0.0319 (8)	0.0306 (8)	0.0043 (7)	0.0039 (7)	-0.0011 (7)
C8	0.0387 (10)	0.0340 (9)	0.0368 (9)	0.0043 (8)	0.0014 (8)	0.0007 (7)
C9	0.0376 (10)	0.0478 (11)	0.0393 (9)	0.0113 (9)	0.0084 (8)	-0.0069 (9)
C10	0.0387 (10)	0.0461 (10)	0.0339 (9)	0.0089 (8)	0.0111 (8)	-0.0001 (8)
C11	0.0280 (8)	0.0433 (10)	0.0321 (8)	0.0044 (7)	0.0036 (7)	-0.0003 (8)
C12	0.0269 (8)	0.0330 (8)	0.0288 (8)	0.0038 (7)	0.0050 (6)	0.0027 (7)
C13	0.0315 (9)	0.0335 (8)	0.0306 (8)	0.0042 (7)	0.0076 (7)	0.0037 (7)
C14	0.0253 (9)	0.0500 (11)	0.0496 (11)	0.0033 (8)	0.0027 (8)	-0.0003 (9)
C15	0.0304 (9)	0.0412 (10)	0.0409 (9)	0.0008 (8)	0.0006 (7)	-0.0029 (8)

Geometric parameters (Å, °)

Ni1—O1	2.0476 (13)	N6—C8	1.332 (3)
Ni1—O3	2.0526 (13)	N6—H61	0.853 (10)
Ni1—O5	2.0567 (13)	N6—H62	0.849 (10)
Ni1—N7	2.0561 (14)	N7—C12	1.326 (2)
Ni1—N4	2.0805 (14)	N7—C15	1.340 (2)
Ni1—N1	2.0857 (15)	N8—C14	1.329 (3)
O1—C1	1.267 (2)	N8—C13	1.356 (2)
O2—C1	1.252 (2)	N9—C13	1.329 (2)
O3—C6	1.274 (2)	N9—H91	0.860 (10)
O4—C6	1.237 (2)	N9—H92	0.848 (10)
O5—C11	1.276 (2)	N10—H101	0.861 (9)
O6—C11	1.237 (2)	N10—H102	0.861 (9)
O1W—H1W1	0.84 (1)	N10—H103	0.853 (9)

O1W—H1W2	0.85 (1)	N10—H104	0.844 (9)
O2W—H2W1	0.85 (1)	C1—C2	1.503 (3)
O2W—H2W2	0.84 (1)	C2—C3	1.423 (3)
O3W—H3W1	0.85 (1)	C4—C5	1.375 (3)
O3W—H3W2	0.86 (1)	C4—H4	0.9300
N1—C2	1.332 (2)	C5—H5	0.9300
N1—C5	1.345 (3)	C6—C7	1.498 (3)
N2—C4	1.332 (3)	C7—C8	1.421 (2)
N2—C3	1.344 (3)	C9—C10	1.374 (3)
N3—C3	1.339 (3)	C9—H9	0.9300
N3—H31	0.854 (10)	C10—H10	0.9300
N3—H32	0.858 (10)	C11—C12	1.511 (2)
N4—C7	1.335 (2)	C12—C13	1.426 (2)
N4—C10	1.339 (2)	C14—C15	1.377 (3)
N5—C9	1.326 (3)	C14—H14	0.9300
N5—C8	1.347 (3)	C15—H15	0.9300
O1—Ni1—O3	93.69 (6)	H103—N10—H104	111.9 (14)
O1—Ni1—O5	169.25 (5)	O2—C1—O1	125.01 (18)
O3—Ni1—O5	94.48 (6)	O2—C1—C2	118.53 (16)
O1—Ni1—N7	93.74 (6)	O1—C1—C2	116.43 (16)
O3—Ni1—N7	86.83 (5)	N1—C2—C3	120.28 (17)
O5—Ni1—N7	79.76 (5)	N1—C2—C1	115.18 (16)
O1—Ni1—N4	93.66 (6)	C3—C2—C1	124.54 (17)
O3—Ni1—N4	79.14 (5)	N3—C3—N2	118.03 (19)
O5—Ni1—N4	94.73 (6)	N3—C3—C2	121.75 (19)
N7—Ni1—N4	164.51 (6)	N2—C3—C2	120.16 (18)
O1—Ni1—N1	79.56 (6)	N2—C4—C5	123.1 (2)
O3—Ni1—N1	170.67 (6)	N2—C4—H4	118.5
O5—Ni1—N1	93.05 (6)	C5—C4—H4	118.5
N7—Ni1—N1	99.95 (6)	N1—C5—C4	119.79 (19)
N4—Ni1—N1	94.76 (6)	N1—C5—H5	120.1
C1—O1—Ni1	115.52 (12)	C4—C5—H5	120.1
C6—O3—Ni1	116.28 (12)	O4—C6—O3	124.70 (18)
C11—O5—Ni1	115.38 (11)	O4—C6—C7	119.59 (17)
H1W1—O1W—H1W2	111 (2)	O3—C6—C7	115.71 (16)
H2W1—O2W—H2W2	111 (2)	N4—C7—C8	120.49 (17)
H3W1—O3W—H3W2	108 (2)	N4—C7—C6	115.85 (15)
C2—N1—C5	119.07 (16)	C8—C7—C6	123.65 (17)
C2—N1—Ni1	111.95 (12)	N6—C8—N5	117.76 (17)
C5—N1—Ni1	127.91 (13)	N6—C8—C7	122.34 (18)
C4—N2—C3	117.56 (18)	N5—C8—C7	119.90 (17)
C3—N3—H31	117.1 (19)	N5—C9—C10	123.55 (18)
C3—N3—H32	118 (2)	N5—C9—H9	118.2
H31—N3—H32	124 (3)	C10—C9—H9	118.2
C7—N4—C10	119.01 (15)	N4—C10—C9	119.64 (18)
C7—N4—Ni1	112.91 (12)	N4—C10—H10	120.2
C10—N4—Ni1	128.06 (13)	C9—C10—H10	120.2
C9—N5—C8	117.40 (16)	O6—C11—O5	125.35 (17)
C8—N6—H61	114.4 (17)	O6—C11—C12	119.08 (16)

supplementary materials

C8—N6—H62	120.9 (18)	O5—C11—C12	115.57 (16)
H61—N6—H62	125 (2)	N7—C12—C13	120.69 (15)
C12—N7—C15	119.61 (15)	N7—C12—C11	115.47 (15)
C12—N7—Ni1	113.37 (11)	C13—C12—C11	123.71 (16)
C15—N7—Ni1	125.84 (12)	N9—C13—N8	117.77 (16)
C14—N8—C13	117.41 (16)	N9—C13—C12	122.88 (16)
C13—N9—H91	116.9 (18)	N8—C13—C12	119.35 (16)
C13—N9—H92	120.5 (17)	N8—C14—C15	123.63 (17)
H91—N9—H92	121 (2)	N8—C14—H14	118.2
H101—N10—H102	107.1 (13)	C15—C14—H14	118.2
H101—N10—H103	108.6 (14)	N7—C15—C14	119.21 (17)
H102—N10—H103	108.8 (13)	N7—C15—H15	120.4
H101—N10—H104	110.0 (13)	C14—C15—H15	120.4
H102—N10—H104	110.3 (14)		
O3—Ni1—O1—C1	170.89 (13)	O1—C1—C2—C3	-167.48 (17)
O5—Ni1—O1—C1	-49.7 (3)	C4—N2—C3—N3	177.4 (2)
N7—Ni1—O1—C1	-102.05 (13)	C4—N2—C3—C2	0.1 (3)
N4—Ni1—O1—C1	91.56 (13)	N1—C2—C3—N3	-175.23 (18)
N1—Ni1—O1—C1	-2.61 (13)	C1—C2—C3—N3	3.6 (3)
O1—Ni1—O3—C6	-96.17 (15)	N1—C2—C3—N2	2.0 (3)
O5—Ni1—O3—C6	90.82 (15)	C1—C2—C3—N2	-179.12 (17)
N7—Ni1—O3—C6	170.28 (15)	C3—N2—C4—C5	-1.0 (3)
N4—Ni1—O3—C6	-3.15 (14)	C2—N1—C5—C4	2.1 (3)
O1—Ni1—O5—C11	-53.7 (3)	Ni1—N1—C5—C4	-164.99 (16)
O3—Ni1—O5—C11	85.68 (13)	N2—C4—C5—N1	0.0 (4)
N7—Ni1—O5—C11	-0.27 (13)	Ni1—O3—C6—O4	-177.33 (18)
N4—Ni1—O5—C11	165.13 (13)	Ni1—O3—C6—C7	3.5 (2)
N1—Ni1—O5—C11	-99.84 (13)	C10—N4—C7—C8	-0.6 (3)
O1—Ni1—N1—C2	8.76 (12)	Ni1—N4—C7—C8	178.20 (13)
O5—Ni1—N1—C2	-179.11 (12)	C10—N4—C7—C6	-179.78 (17)
N7—Ni1—N1—C2	100.76 (12)	Ni1—N4—C7—C6	-1.0 (2)
N4—Ni1—N1—C2	-84.10 (13)	O4—C6—C7—N4	179.16 (19)
O1—Ni1—N1—C5	176.63 (17)	O3—C6—C7—N4	-1.6 (3)
O5—Ni1—N1—C5	-11.24 (17)	O4—C6—C7—C8	0.0 (3)
N7—Ni1—N1—C5	-91.37 (17)	O3—C6—C7—C8	179.19 (17)
N4—Ni1—N1—C5	83.77 (17)	C9—N5—C8—N6	178.60 (19)
O1—Ni1—N4—C7	95.17 (13)	C9—N5—C8—C7	-1.0 (3)
O3—Ni1—N4—C7	2.10 (12)	N4—C7—C8—N6	-178.67 (19)
O5—Ni1—N4—C7	-91.56 (13)	C6—C7—C8—N6	0.5 (3)
N7—Ni1—N4—C7	-23.2 (3)	N4—C7—C8—N5	0.9 (3)
N1—Ni1—N4—C7	174.97 (12)	C6—C7—C8—N5	-179.97 (17)
O1—Ni1—N4—C10	-86.20 (16)	C8—N5—C9—C10	0.8 (3)
O3—Ni1—N4—C10	-179.26 (17)	C7—N4—C10—C9	0.4 (3)
O5—Ni1—N4—C10	87.08 (16)	Ni1—N4—C10—C9	-178.17 (14)
N7—Ni1—N4—C10	155.4 (2)	N5—C9—C10—N4	-0.5 (3)
N1—Ni1—N4—C10	-6.39 (17)	Ni1—O5—C11—O6	177.70 (16)
O1—Ni1—N7—C12	175.68 (12)	Ni1—O5—C11—C12	-3.4 (2)
O3—Ni1—N7—C12	-90.82 (12)	C15—N7—C12—C13	0.5 (2)
O5—Ni1—N7—C12	4.31 (12)	Ni1—N7—C12—C13	168.81 (12)

N4—Ni1—N7—C12	-65.9 (3)	C15—N7—C12—C11	-175.57 (16)
N1—Ni1—N7—C12	95.64 (12)	Ni1—N7—C12—C11	-7.23 (18)
O1—Ni1—N7—C15	-16.83 (15)	O6—C11—C12—N7	-173.77 (17)
O3—Ni1—N7—C15	76.67 (15)	O5—C11—C12—N7	7.2 (2)
O5—Ni1—N7—C15	171.80 (16)	O6—C11—C12—C13	10.3 (3)
N4—Ni1—N7—C15	101.6 (2)	O5—C11—C12—C13	-168.66 (16)
N1—Ni1—N7—C15	-96.87 (15)	C14—N8—C13—N9	-177.44 (18)
Ni1—O1—C1—O2	174.82 (15)	C14—N8—C13—C12	2.5 (3)
Ni1—O1—C1—C2	-3.5 (2)	N7—C12—C13—N9	177.08 (17)
C5—N1—C2—C3	-3.1 (3)	C11—C12—C13—N9	-7.2 (3)
Ni1—N1—C2—C3	166.01 (13)	N7—C12—C13—N8	-2.9 (2)
C5—N1—C2—C1	177.96 (16)	C11—C12—C13—N8	172.81 (16)
Ni1—N1—C2—C1	-12.97 (18)	C13—N8—C14—C15	0.1 (3)
O2—C1—C2—N1	-166.99 (16)	C12—N7—C15—C14	2.1 (3)
O1—C1—C2—N1	11.5 (2)	Ni1—N7—C15—C14	-164.65 (14)
O2—C1—C2—C3	14.1 (3)	N8—C14—C15—N7	-2.5 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H31...O2	0.85 (1)	2.08 (2)	2.740 (3)	134 (2)
N6—H61...O4	0.85 (1)	2.01 (2)	2.701 (3)	138 (2)
N6—H62...N5 ⁱ	0.85 (1)	2.15 (1)	2.992 (2)	175 (2)
N9—H91...O6	0.86 (1)	2.07 (2)	2.733 (2)	134 (2)
N9—H92...O3 ⁱⁱ	0.85 (1)	2.10 (1)	2.924 (2)	164 (2)
N10—H101...O2	0.86 (1)	1.91 (1)	2.756 (3)	169 (3)
N10—H102...O1w	0.86 (1)	1.94 (1)	2.779 (3)	164 (3)
N10—H103...O2w	0.85 (1)	2.07 (1)	2.919 (3)	172 (3)
N10—H104...N8 ⁱⁱⁱ	0.84 (1)	2.36 (2)	3.018 (3)	135 (2)
O1w—H1w1...O1	0.84 (1)	2.25 (2)	2.964 (3)	143 (4)
O1w—H1w2...N2 ^{iv}	0.85 (1)	2.00 (1)	2.842 (3)	171 (4)
O2w—H2w1...O5 ^v	0.85 (1)	2.03 (1)	2.869 (2)	168 (3)
O2w—H2w2...O6 ^{vi}	0.84 (1)	1.96 (1)	2.766 (2)	159 (3)
O3w—H3w1...O4	0.85 (1)	2.39 (5)	2.812 (3)	111 (4)

Symmetry codes: (i) $-x, -y+2, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+3/2, y+1/2, -z+3/2$; (iv) $x+1/2, -y+3/2, z-1/2$; (v) $-x+1/2, y+1/2, -z+3/2$; (vi) $x+1/2, -y+3/2, z+1/2$.

Fig. 1

