

Bis[μ_3 -*N'*-oxidopyridine-2-carboximidamido(2-)]bis[μ_2 -*N'*-oxidopyridine-2-carboximidamido(1-)]-tetrapyridentetranickel(II) dinitrate

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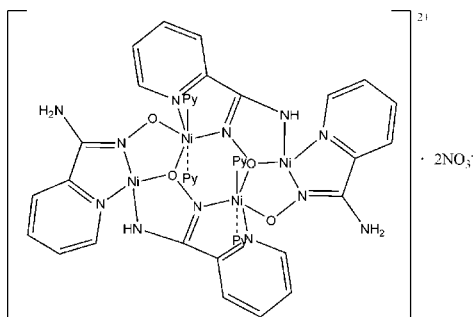
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.041; wR factor = 0.100; data-to-parameter ratio = 12.3.

The title compound, $[\text{Ni}_4(\text{C}_6\text{H}_5\text{N}_3\text{O})_2(\text{C}_6\text{H}_6\text{N}_3\text{O})_2(\text{C}_5\text{H}_5\text{N})_4](\text{NO}_3)_2$, is a tetranuclear nickel complex containing a single-decker cation, located on an inversion center. The two unique Ni^{II} cations are *N,N',N',O*-chelated by carboximidamido(2-) and carboximidamido(1-) anions, forming a distorted four-coordinate planar structure, while the other two Ni^{II} atoms are *N,N',O,O'*-chelated by the same bridging ligands and two pyridine molecules, affording six-coordinated metals in an octahedral geometry. The cation is isostructural with the complex crystallized with perchlorate counter-ions in place of nitrate.

Related literature

For similar metal complexes, see: Kou *et al.* (2010); Papatriantafyllopoulou *et al.* (2008); Inglis *et al.* (2010); Deng & Ran (2011). For the synthesis of the ligand pyridine-2-amidoxine, see: Bernasek (1957).



Experimental

Crystal data

$[\text{Ni}_4(\text{C}_6\text{H}_5\text{N}_3\text{O})_2(\text{C}_6\text{H}_6\text{N}_3\text{O})_2(\text{C}_5\text{H}_5\text{N})_4](\text{NO}_3)_2$
 $M_r = 1217.80$
 Triclinic, $P\bar{1}$
 $a = 10.4356$ (6) Å
 $b = 10.7190$ (8) Å
 $c = 11.2908$ (9) Å
 $\alpha = 92.041$ (6)°
 $\beta = 98.240$ (5)°
 $\gamma = 100.870$ (5)°
 $V = 1224.96$ (15) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 1.59$ mm⁻¹
 $T = 293$ K
 $0.40 \times 0.38 \times 0.35$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2007)
 $T_{\text{min}} = 0.569$, $T_{\text{max}} = 0.606$
 9481 measured reflections
 4286 independent reflections
 3180 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.100$
 $S = 1.03$
 4286 reflections
 349 parameters
 8 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.66$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.52$ e Å⁻³

Data collection: *APEX2* (Bruker, 2007); cell refinement: *S SAINT* (Bruker, 2007); data reduction: *S SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: BH2397).

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 Kou, H.-Z., An, G.-Y., Ji, C.-M., Wang, B.-W. & Cui, A.-L. (2010). *Dalton Trans.* **39**, 9604–9610.
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supplementary materials

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Bis[μ_3 -*N'*-oxidopyridine-2-carboximidamido(2-)]bis[μ_2 -*N'*-oxidopyridine-2-carboximidamido(1-)]tetrapyrinetetranickel(II) dinitrate

X.-H. Deng and J.-W. Ran

Comment

Transition metal compounds have been of great interest for many years. They are very important in the development of coordination chemistry. As an extension of work on the structural characterization of Ni compounds, we report here the crystal structure of a new tetranuclear nickel(II) compound.

The title compound is a tetranuclear nickel(II) complex (Fig. 1). The Ni(II) ions form a central deck, but show different coordinate ways. Two are coordinated by N_{py} , N_{ox} , N_{am} and O_{ox} (where the abbreviations *py*, *ox* and *am* are for the 2-pyridyl, oximate and deprotonated amino donor atoms, respectively), and form square planar geometry. The other two metals are coordinated by two solvent pyridine molecules and two chelating ligands, to form octahedral structures. The different coordinated-nickel(II) ions are bridged by the O_{ox} groups. The Ni1—(N,O) bond lengths are longer than the Ni2—(N,O) bond distances. The angles are also different, as a consequence of the different coordination geometry. The cation is indeed isostructural with that found in the perchlorate complex previously reported (Kou *et al.*, 2010). Related complexes have also been characterized (Papatriantafyllopoulou *et al.*, 2008; Inglis *et al.*, 2010; Deng & Ran, 2011).

Experimental

The synthesis of pyridine-2-amidoxine was carried out according to literature (Bernasek, 1957). The title compound was synthesized by adding a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (290.8 mg, 1 mmol) in H_2O (20 ml) to a solution of the ligand (137 mg, 1 mmol) and NaOH (80 mg, 2 mmol) in ethanol/water (3:1, 20 ml). The mixture was stirred at room temperature. The resulting precipitate was collected and dissolved in a mixture of ethanol and pyridine (3:1 v/v) at 50°C. The solution was allowed to stand in air for one day, and brown crystals were formed at the bottom of the vessel on slow evaporation of the solvent at room temperature. Yield: 56%. Anal. Calcd for $C_{44}H_{42}N_{18}Ni_4O_{10}$: C 43.40, H 3.48, N 20.70. Found: C 43.36, H 3.53, N 20.94. IR (KBr, cm^{-1}): $\nu = 3412$ (w), 3268 (w), 1605 (s), 1552 (s), 1390 (very strong), 1347 (very strong), 1107 (m), 1450 (very strong), 705 (m).

Refinement

H atoms were included in calculated positions with C—H = 0.93, N—H = 0.86 Å. For the terminal amine group N6, H atoms were refined freely, with restrained N—H bond lengths. Other H atoms were refined using a riding-model. Isotropic displacement parameters for H atoms were calculated as $U_{iso}(H) = 1.2 U_{eq}(C,N)$. Anisotropic displacement parameters for nitrate O atoms were restrained.

Figures

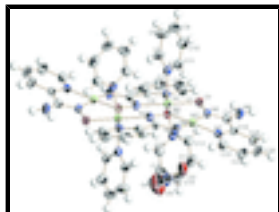


Fig. 1. The molecular structure of the title complex, showing displacement ellipsoids at the 50% probability level.

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Crystal data

$[\text{Ni}_4(\text{C}_6\text{H}_5\text{N}_3\text{O})_2(\text{C}_6\text{H}_6\text{N}_3\text{O})_2(\text{C}_5\text{H}_5\text{N})_4](\text{NO}_3)_2$	$Z = 1$
$M_r = 1217.80$	$F(000) = 624$
Triclinic, $P\bar{1}$	$D_x = 1.651 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 10.4356 (6) \text{ \AA}$	Cell parameters from 1738 reflections
$b = 10.7190 (8) \text{ \AA}$	$\theta = 3.1\text{--}21.8^\circ$
$c = 11.2908 (9) \text{ \AA}$	$\mu = 1.59 \text{ mm}^{-1}$
$\alpha = 92.041 (6)^\circ$	$T = 293 \text{ K}$
$\beta = 98.240 (5)^\circ$	Block, brown
$\gamma = 100.870 (5)^\circ$	$0.40 \times 0.38 \times 0.35 \text{ mm}$
$V = 1224.96 (15) \text{ \AA}^3$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	4286 independent reflections
Radiation source: fine-focus sealed tube graphite	3180 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.039$
Absorption correction: multi-scan (SADABS; Bruker, 2007)	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.5^\circ$
$T_{\text{min}} = 0.569$, $T_{\text{max}} = 0.606$	$h = -12 \rightarrow 12$
9481 measured reflections	$k = -12 \rightarrow 11$
	$l = -9 \rightarrow 13$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.100$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.4034P]$

4286 reflections
 349 parameters
 8 restraints
 0 constraints

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} = 0.001$$

$$\Delta\rho_{\text{max}} = 0.66 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.52 \text{ e } \text{\AA}^{-3}$$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.45373 (3)	0.49188 (3)	0.66926 (3)	0.03132 (8)
Ni2	0.37394 (3)	0.76610 (3)	0.59280 (3)	0.03324 (9)
N1	0.45234 (18)	0.33873 (19)	0.77743 (18)	0.0346 (5)
N2	0.50204 (18)	0.35800 (18)	0.55758 (17)	0.0323 (5)
N3	0.65769 (18)	0.5669 (2)	0.75316 (18)	0.0364 (6)
N4	0.24626 (18)	0.4257 (2)	0.61209 (18)	0.0371 (6)
N5	0.35016 (18)	0.70397 (19)	0.74148 (18)	0.0340 (5)
N6	0.2507 (2)	0.7224 (2)	0.9124 (2)	0.0510 (7)
H6B	0.2906 (19)	0.6662 (16)	0.941 (2)	0.061*
H6A	0.235 (2)	0.7699 (19)	0.9683 (17)	0.061*
N7	0.27188 (19)	0.88369 (19)	0.63555 (19)	0.0384 (6)
N8	0.4142 (2)	0.82419 (19)	0.44897 (19)	0.0419 (6)
H8	0.3973	0.8940	0.4213	0.050*
N9	0.2065 (2)	0.9041 (2)	0.1685 (2)	0.0626 (7)
O1	0.40271 (16)	0.60905 (16)	0.79192 (15)	0.0387 (5)
O2	0.45424 (15)	0.63556 (15)	0.55536 (14)	0.0346 (4)
O3	0.2335 (2)	0.9647 (2)	0.2650 (2)	0.0902 (8)
O4	0.1740 (3)	0.7894 (3)	0.1607 (3)	0.1234 (12)
O5	0.2296 (4)	0.9553 (3)	0.0776 (2)	0.1285 (11)
C1	0.4176 (3)	0.3303 (3)	0.8866 (2)	0.0477 (8)
H1	0.3974	0.4017	0.9234	0.057*
C2	0.4105 (3)	0.2203 (3)	0.9472 (3)	0.0562 (9)
H2	0.3853	0.2171	1.0229	0.067*
C3	0.4416 (3)	0.1151 (3)	0.8929 (3)	0.0532 (9)
H3	0.4352	0.0390	0.9307	0.064*
C4	0.4823 (2)	0.1235 (3)	0.7816 (2)	0.0410 (7)
H4	0.5067	0.0544	0.7447	0.049*
C5	0.4859 (2)	0.2373 (2)	0.7266 (2)	0.0332 (7)
C6	0.5271 (2)	0.2555 (2)	0.6071 (2)	0.0321 (6)
C7	0.7375 (2)	0.4927 (3)	0.8027 (3)	0.0480 (8)
H7	0.7126	0.4051	0.7865	0.058*
C8	0.8551 (3)	0.5403 (3)	0.8767 (3)	0.0612 (10)
H8A	0.9077	0.4856	0.9101	0.073*
C9	0.8934 (3)	0.6691 (3)	0.9002 (3)	0.0651 (11)
H9	0.9709	0.7033	0.9517	0.078*
C10	0.8154 (3)	0.7466 (3)	0.8465 (3)	0.0587 (10)
H10	0.8405	0.8347	0.8585	0.070*
C11	0.6988 (2)	0.6920 (3)	0.7743 (3)	0.0445 (8)
H11	0.6461	0.7455	0.7385	0.053*

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C12	0.1604 (2)	0.4086 (3)	0.6893 (3)	0.0497 (8)
H12	0.1919	0.4291	0.7703	0.060*
C13	0.0283 (3)	0.3623 (3)	0.6558 (3)	0.0654 (10)
H13	-0.0283	0.3513	0.7128	0.079*
C14	-0.0189 (3)	0.3328 (3)	0.5370 (4)	0.0708 (11)
H14	-0.1084	0.3014	0.5114	0.085*
C15	0.0670 (3)	0.3500 (3)	0.4571 (3)	0.0664 (10)
H15	0.0371	0.3309	0.3757	0.080*
C16	0.1994 (3)	0.3960 (3)	0.4975 (3)	0.0503 (8)
H16	0.2577	0.4065	0.4419	0.060*
C17	0.2787 (2)	0.7604 (2)	0.8038 (2)	0.0374 (7)
C18	0.2286 (2)	0.8621 (2)	0.7436 (2)	0.0368 (7)
C19	0.1439 (2)	0.9336 (3)	0.7852 (3)	0.0529 (9)
H19	0.1137	0.9175	0.8577	0.063*
C20	0.1053 (3)	1.0286 (3)	0.7175 (3)	0.0617 (10)
H20	0.0498	1.0780	0.7446	0.074*
C21	0.1495 (3)	1.0495 (3)	0.6102 (3)	0.0585 (9)
H21	0.1239	1.1132	0.5639	0.070*
C22	0.2319 (3)	0.9763 (3)	0.5708 (3)	0.0488 (8)
H22	0.2608	0.9911	0.4975	0.059*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.03287 (15)	0.03169 (17)	0.03126 (17)	0.01043 (13)	0.00592 (13)	0.00101 (13)
Ni2	0.03572 (15)	0.03221 (17)	0.03383 (17)	0.01353 (13)	0.00404 (14)	-0.00190 (14)
N1	0.0353 (10)	0.0386 (12)	0.0312 (11)	0.0102 (9)	0.0055 (9)	0.0022 (9)
N2	0.0389 (10)	0.0305 (11)	0.0292 (11)	0.0082 (9)	0.0091 (9)	0.0017 (9)
N3	0.0362 (10)	0.0368 (11)	0.0378 (12)	0.0088 (9)	0.0088 (9)	0.0010 (10)
N4	0.0353 (10)	0.0417 (12)	0.0359 (11)	0.0088 (9)	0.0094 (9)	0.0008 (10)
N5	0.0349 (10)	0.0352 (11)	0.0342 (11)	0.0131 (9)	0.0061 (9)	-0.0035 (9)
N6	0.0580 (12)	0.0633 (15)	0.0413 (13)	0.0282 (11)	0.0185 (11)	0.0009 (12)
N7	0.0382 (10)	0.0358 (11)	0.0401 (12)	0.0112 (9)	-0.0011 (10)	-0.0057 (10)
N8	0.0565 (12)	0.0310 (11)	0.0451 (13)	0.0210 (10)	0.0133 (10)	0.0057 (10)
N9	0.0837 (15)	0.0704 (16)	0.0504 (15)	0.0439 (13)	0.0246 (13)	0.0175 (13)
O1	0.0458 (9)	0.0395 (10)	0.0345 (9)	0.0176 (8)	0.0066 (8)	0.0013 (8)
O2	0.0448 (8)	0.0347 (9)	0.0299 (9)	0.0180 (7)	0.0107 (7)	0.0037 (7)
O3	0.1267 (16)	0.1144 (18)	0.0461 (13)	0.0744 (14)	0.0053 (13)	-0.0103 (13)
O4	0.151 (2)	0.079 (2)	0.138 (3)	-0.0138 (19)	0.064 (2)	0.0039 (19)
O5	0.243 (3)	0.0930 (18)	0.0743 (17)	0.0774 (19)	0.044 (2)	0.0252 (15)
C1	0.0498 (14)	0.0572 (18)	0.0381 (15)	0.0145 (13)	0.0081 (13)	0.0043 (14)
C2	0.0515 (15)	0.085 (2)	0.0355 (15)	0.0151 (16)	0.0099 (13)	0.0193 (15)
C3	0.0510 (15)	0.0552 (18)	0.0529 (17)	0.0102 (14)	0.0022 (14)	0.0224 (14)
C4	0.0394 (13)	0.0388 (15)	0.0435 (15)	0.0086 (12)	-0.0005 (12)	0.0071 (12)
C5	0.0303 (11)	0.0332 (13)	0.0347 (14)	0.0042 (10)	0.0028 (11)	0.0020 (11)
C6	0.0332 (11)	0.0274 (13)	0.0346 (13)	0.0061 (10)	0.0017 (11)	-0.0005 (11)
C7	0.0384 (13)	0.0400 (15)	0.0642 (19)	0.0097 (12)	0.0004 (14)	0.0037 (14)
C8	0.0447 (15)	0.0564 (18)	0.078 (2)	0.0122 (14)	-0.0111 (16)	0.0107 (17)

C9	0.0421 (15)	0.068 (2)	0.074 (2)	0.0004 (16)	-0.0103 (16)	-0.0087 (18)
C10	0.0466 (15)	0.0435 (17)	0.081 (2)	0.0018 (14)	0.0066 (16)	-0.0128 (16)
C11	0.0408 (13)	0.0436 (15)	0.0519 (17)	0.0136 (12)	0.0096 (13)	0.0020 (13)
C12	0.0398 (13)	0.0613 (18)	0.0474 (17)	0.0088 (13)	0.0082 (13)	-0.0031 (15)
C13	0.0443 (15)	0.060 (2)	0.096 (3)	0.0107 (14)	0.0270 (16)	-0.0007 (19)
C14	0.0370 (14)	0.0539 (19)	0.115 (3)	0.0073 (14)	-0.0030 (17)	-0.021 (2)
C15	0.0554 (17)	0.069 (2)	0.066 (2)	0.0117 (16)	-0.0144 (16)	-0.0184 (18)
C16	0.0502 (15)	0.0569 (18)	0.0431 (16)	0.0117 (14)	0.0049 (13)	-0.0024 (14)
C17	0.0351 (12)	0.0359 (14)	0.0399 (15)	0.0069 (11)	0.0032 (11)	-0.0039 (12)
C18	0.0296 (11)	0.0358 (14)	0.0429 (15)	0.0048 (11)	0.0025 (11)	-0.0080 (12)
C19	0.0429 (13)	0.0549 (17)	0.066 (2)	0.0190 (13)	0.0163 (14)	-0.0062 (15)
C20	0.0542 (15)	0.0575 (18)	0.083 (2)	0.0327 (14)	0.0162 (16)	-0.0032 (17)
C21	0.0596 (15)	0.0522 (17)	0.070 (2)	0.0339 (13)	0.0009 (16)	0.0024 (16)
C22	0.0548 (15)	0.0467 (16)	0.0481 (17)	0.0232 (13)	0.0015 (14)	0.0013 (14)

Geometric parameters (Å, °)

Ni1—O1	2.0295 (17)	C2—H2	0.9300
Ni1—O2	2.0410 (17)	C3—C4	1.383 (4)
Ni1—N2	2.057 (2)	C3—H3	0.9300
Ni1—N1	2.080 (2)	C4—C5	1.386 (4)
Ni1—N4	2.1435 (19)	C4—H4	0.9300
Ni1—N3	2.1900 (18)	C5—C6	1.481 (3)
Ni2—O2	1.8278 (17)	C6—N8 ⁱ	1.333 (3)
Ni2—N8	1.836 (2)	C7—C8	1.381 (4)
Ni2—N5	1.860 (2)	C7—H7	0.9300
Ni2—N7	1.888 (2)	C8—C9	1.368 (4)
N1—C1	1.335 (3)	C8—H8A	0.9300
N1—C5	1.339 (3)	C9—C10	1.367 (4)
N2—C6	1.303 (3)	C9—H9	0.9300
N2—O2 ⁱ	1.414 (3)	C10—C11	1.378 (4)
N3—C11	1.331 (3)	C10—H10	0.9300
N3—C7	1.336 (3)	C11—H11	0.9300
N4—C16	1.321 (3)	C12—C13	1.367 (4)
N4—C12	1.330 (3)	C12—H12	0.9300
N5—C17	1.306 (3)	C13—C14	1.366 (5)
N5—O1	1.350 (3)	C13—H13	0.9300
N6—C17	1.360 (3)	C14—C15	1.354 (5)
N6—H6B	0.843 (15)	C14—H14	0.9300
N6—H6A	0.851 (16)	C15—C16	1.380 (4)
N7—C22	1.347 (3)	C15—H15	0.9300
N7—C18	1.373 (3)	C16—H16	0.9300
N8—C6 ⁱ	1.333 (3)	C17—C18	1.446 (4)
N8—H8	0.8600	C18—C19	1.391 (4)
N9—O4	1.209 (4)	C19—C20	1.381 (4)
N9—O5	1.214 (4)	C19—H19	0.9300
N9—O3	1.217 (3)	C20—C21	1.368 (5)
O2—N2 ⁱ	1.414 (3)	C20—H20	0.9300

supplementary materials

C1—C2	1.380 (4)	C21—C22	1.376 (4)
C1—H1	0.9300	C21—H21	0.9300
C2—C3	1.378 (4)	C22—H22	0.9300
O1—Ni1—O2	87.43 (7)	C2—C3—H3	120.2
O1—Ni1—N2	173.84 (8)	C4—C3—H3	120.2
O2—Ni1—N2	98.68 (7)	C3—C4—C5	118.3 (3)
O1—Ni1—N1	95.46 (8)	C3—C4—H4	120.8
O2—Ni1—N1	176.94 (7)	C5—C4—H4	120.8
N2—Ni1—N1	78.42 (8)	N1—C5—C4	122.4 (2)
O1—Ni1—N4	86.65 (7)	N1—C5—C6	115.2 (2)
O2—Ni1—N4	90.52 (7)	C4—C5—C6	122.4 (2)
N2—Ni1—N4	92.45 (8)	N2—C6—N8 ⁱ	120.5 (2)
N1—Ni1—N4	88.65 (8)	N2—C6—C5	115.1 (2)
O1—Ni1—N3	85.71 (7)	N8 ⁱ —C6—C5	124.5 (2)
O2—Ni1—N3	92.71 (7)	N3—C7—C8	123.0 (3)
N2—Ni1—N3	94.77 (8)	N3—C7—H7	118.5
N1—Ni1—N3	88.52 (7)	C8—C7—H7	118.5
N4—Ni1—N3	171.56 (8)	C9—C8—C7	119.1 (3)
O2—Ni2—N8	84.38 (8)	C9—C8—H8A	120.5
O2—Ni2—N5	91.50 (8)	C7—C8—H8A	120.5
N8—Ni2—N5	174.27 (9)	C10—C9—C8	118.7 (3)
O2—Ni2—N7	172.23 (8)	C10—C9—H9	120.7
N8—Ni2—N7	100.57 (9)	C8—C9—H9	120.7
N5—Ni2—N7	83.96 (9)	C9—C10—C11	118.9 (3)
C1—N1—C5	118.4 (2)	C9—C10—H10	120.6
C1—N1—Ni1	127.43 (19)	C11—C10—H10	120.6
C5—N1—Ni1	114.07 (16)	N3—C11—C10	123.4 (3)
C6—N2—O2 ⁱ	109.62 (19)	N3—C11—H11	118.3
C6—N2—Ni1	115.76 (16)	C10—C11—H11	118.3
O2 ⁱ —N2—Ni1	132.58 (14)	N4—C12—C13	123.4 (3)
C11—N3—C7	116.9 (2)	N4—C12—H12	118.3
C11—N3—Ni1	119.41 (17)	C13—C12—H12	118.3
C7—N3—Ni1	122.75 (16)	C14—C13—C12	118.7 (3)
C16—N4—C12	117.3 (2)	C14—C13—H13	120.7
C16—N4—Ni1	120.50 (18)	C12—C13—H13	120.7
C12—N4—Ni1	122.16 (16)	C15—C14—C13	118.7 (3)
C17—N5—O1	117.4 (2)	C15—C14—H14	120.7
C17—N5—Ni2	116.46 (18)	C13—C14—H14	120.7
O1—N5—Ni2	126.15 (15)	C14—C15—C16	119.5 (3)
C17—N6—H6B	115.2 (18)	C14—C15—H15	120.2
C17—N6—H6A	125.6 (16)	C16—C15—H15	120.2
H6B—N6—H6A	111 (2)	N4—C16—C15	122.4 (3)
C22—N7—C18	118.8 (2)	N4—C16—H16	118.8
C22—N7—Ni2	128.23 (19)	C15—C16—H16	118.8
C18—N7—Ni2	112.85 (17)	N5—C17—N6	122.5 (2)
C6 ⁱ —N8—Ni2	111.45 (17)	N5—C17—C18	113.5 (2)
C6 ⁱ —N8—H8	124.3	N6—C17—C18	123.9 (2)

Ni2—N8—H8	124.3	N7—C18—C19	120.8 (3)
O4—N9—O5	116.9 (3)	N7—C18—C17	113.1 (2)
O4—N9—O3	121.9 (3)	C19—C18—C17	126.1 (3)
O5—N9—O3	120.3 (3)	C20—C19—C18	119.3 (3)
N5—O1—Ni1	112.62 (13)	C20—C19—H19	120.4
N2 ⁱ —O2—Ni2	114.03 (13)	C18—C19—H19	120.4
N2 ⁱ —O2—Ni1	127.93 (13)	C21—C20—C19	119.4 (3)
Ni2—O2—Ni1	117.72 (8)	C21—C20—H20	120.3
N1—C1—C2	122.7 (3)	C19—C20—H20	120.3
N1—C1—H1	118.6	C20—C21—C22	120.0 (3)
C2—C1—H1	118.6	C20—C21—H21	120.0
C3—C2—C1	118.5 (3)	C22—C21—H21	120.0
C3—C2—H2	120.8	N7—C22—C21	121.8 (3)
C1—C2—H2	120.8	N7—C22—H22	119.1
C2—C3—C4	119.5 (3)	C21—C22—H22	119.1

Symmetry codes: (i) $-x+1, -y+1, -z+1$.

Fig. 1

