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Crystal structure of a binuclear nickel(II) complex constructed of 1*H*-imidazo-[4,5-*f*][1,10]phenanthroline and doubly deprotonated benzene-1,3,5-tricarboxylic acid

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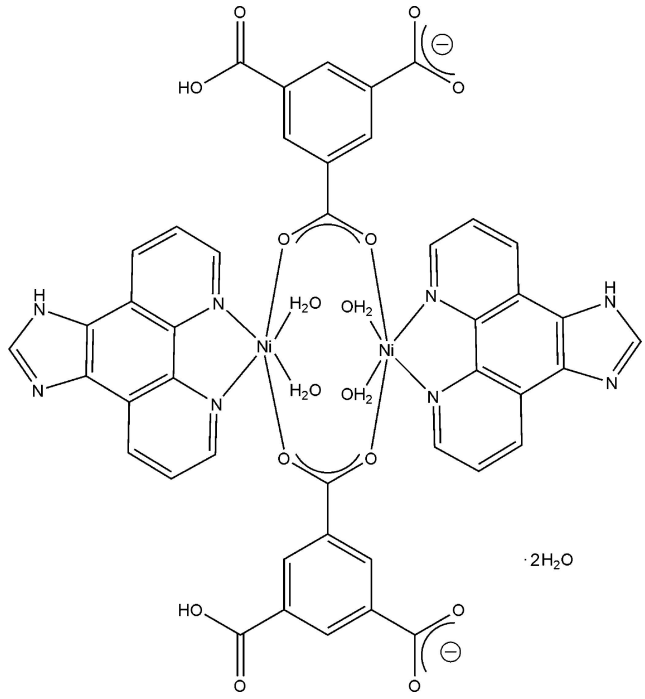
The title complex, $[Ni_2(C_9H_4O_6)_2(C_{13}H_8N_4)_2(H_2O)_4]\cdot 2H_2O$, bis($\mu$-5-carboxybenzene-1,3-dicarboxylato-κ^2O^1:$O^{1'}$)bis[diaqua-(1*H*-imidazo[4,5-*f*][1,10]phenanthroline-κ^2N^7,N^8)nickel(II)] dihydrate, was obtained under solvothermal conditions by the reaction of benzene-1,3,5-tricarboxylic acid (H_3BTC) with $Ni(NO_3)_2$ in the presence of 1*H*-imidazo[4,5-*f*][1,10]phenanthroline (IP). The crystal has triclinic ($P\overline{1}$) symmetry with a centrosymmetric binuclear nickel(II) cluster. The Ni^{II} atom is coordinated by two N atoms from a chelating 1*H*-imidazo-[4,5-*f*][1,10]phenanthroline ligand, two carboxylate O atoms from two 5-carboxybenzene-1,3-dicarboxylate ligands and two water molecules in a slightly distorted octahedral geometry. Two carboxylate groups bridge two Ni^{II} cations, forming the binuclear complex. Extensive N—H···O, O—H···O and O—H···N hydrogen bonding is present in the crystal structure, forming a three-dimensional supermolecular framework. Weak π–π stacking is observed between parallel $HBTC^{2-}$ and IP ring systems, the face-to-face separation being 3.695 (2) Å.

Keywords: crystal structure; nickel(II) complex; binuclear cluster; 1*H*-imidazo[4,5-*f*][1,10]phenanthroline; benzene-1,3,5-tricarboxylic acid; hydrogen bonding; π–π stacking.

CCDC reference: 1051597

1. Related literature

For general background, see: Stephenson *et al.* (2008). For details of the synthesis, see: Liu *et al.* (2009); Wu *et al.* (1997); Yang *et al.* (2010); Che *et al.* (2013).



2. Experimental

2.1. Crystal data

$[Ni_2(C_9H_4O_6)_2(C_{13}H_8N_4)_2(H_2O)_4]\cdot 2H_2O$
M_r = 1082.22
Triclinic, $P\overline{1}$
a = 8.581 (5) Å
b = 9.032 (5) Å
c = 14.278 (5) Å
α = 82.222 (5)°
β = 87.729 (5)°
γ = 73.117 (5)°
V = 1049.2 (9) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.99 mm^{-1}
T = 293 K
0.28 × 0.16 × 0.15 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.805, T_{max} = 0.867
5594 measured reflections
3851 independent reflections
3050 reflections with $I > 2\sigma(I)$
R_{int} = 0.048

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.072
S = 0.95
3851 reflections
325 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O6^{i}	0.86	1.93	2.772 (3)	165
O1—H1*WA*···O5^{ii}	0.88	1.82	2.676 (2)	165
O1—H1*WB*···O8^{iii}	0.84	1.94	2.741 (2)	161
O2—H2*WA*···N3^{iv}	0.89	1.94	2.798 (3)	160
O2—H2*WB*···O4	0.89	1.86	2.630 (2)	144
O7—H7*O*···O9^{iii}	0.85	1.72	2.558 (2)	166
O9—H9*WA*···O5^{ii}	0.86	1.88	2.684 (2)	153

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9WB···O6^{v}	0.87	1.99	2.813 (3)	159

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: ZP2016).

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supporting information

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Crystal structure of a binuclear nickel(II) complex constructed of 1*H*-imidazo[4,5-*f*][1,10]phenanthroline and doubly deprotonated benzene-1,3,5-tricarboxylic acid

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S1. Introduction

Imidazo[4,5-*f*][1,10]phenanthroline (IP) derivatives have been used to recognize the secondary structure of DNA in Ru(II) complexes. IP also an important heteroaromatic N-donor ligands for the construction of coordination polymers. A handful of comcpounds based on IP and carboxylate ligands have been described (Liu *et al.*, 2009; Stephenson *et al.*, 2008; Wu *et al.*, 1997; Yang *et al.*, 2010). The title compound was prepared during an attempt to prepare a coordination polymer containing both benzenetricarboxylate (BTC) and IP ligands, however, an simple dinuclear complex obtained.

S2. Synthesis and crystallization

Nickel nitrate hexahydrate and benzenetricarboxylate acid were obtained commercially. imidazo[4,5-*f*][1,10]phenanthroline was prepared *via* a published procedure (Wu *et al.* (1997). A mixture of Nickel nitrate hexahydrate (133 mg, 0.50 mmol), benzenetricarboxylate acid (105 mg, 0.50 mmol), imidazo[4,5-*f*][1,10]phenanthroline (0.110 g,0.5 mmol) and 10.0 g water (550 mmol) was placed into a 23 ml Teflon-lined Parr Acid Digestion bomb, which was then heated under autogenous pressure at 398 K for 72 h, then cooled to RT at a rate of 5 °c/h. The resulting green crystals of the title compound were obtained.

S3. Refinement

All H atoms were found in a difference Fourier map. The H atoms bound to C or N atoms were placed in calculated positions, with C—H= 0.93Å (CH) or N—H=0.86Å (NH)), U_{iso}(H)= 1.2 times U_{eq}(C or N). The H atoms bound to O atoms were restrained with O—H = 0.85 Å, and refined with U_{iso}(H)= 1.5 times U_{eq}(O).

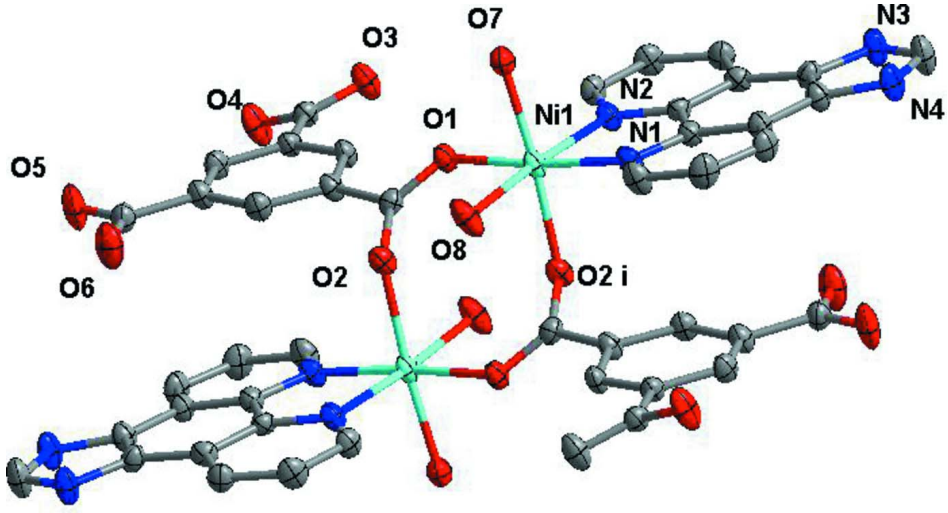

Figure 1

The molecular structure of the title compound, showing 30% probability displacement ellipsoids with the atom numbering. H atoms have been omitted for clarity. [Symmetry code: (i) -*x* + 1, -*y* + 1, -*z* + 1.]

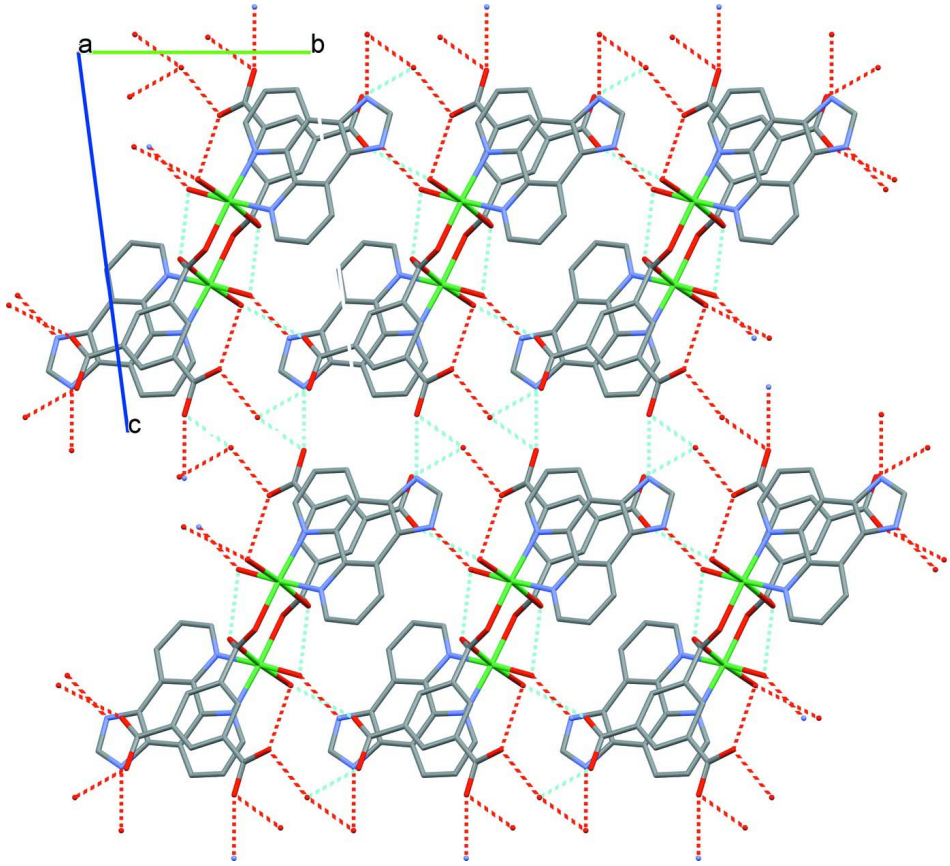

Figure 2

A packing view of the three-dimensional supermolecular framework of the title compound viewed along the *a* axis.

Bis(μ-5-carboxybenzene-1,3-dicarboxylato-κ²*O*¹:*O*¹′)bis[diaqua(1*H*-imidazo[4,5-*f*][1,10]phenanthroline-κ²*N*⁷,*N*⁸)nickel(II)] dihydrate

Crystal data

$[Ni_2(C_9H_4O_6)_2(C_{13}H_8N_4)_2(H_2O)_4]\cdot 2H_2O$
M_r = 1082.22
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.581 (5) Å
b = 9.032 (5) Å
c = 14.278 (5) Å
α = 82.222 (5)°
β = 87.729 (5)°
γ = 73.117 (5)°
V = 1049.2 (9) Å^3
Z = 1
$F(000)$ = 556
D_x = 1.713 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 2586 reflections
θ = 3.6–24.9°
μ = 0.99 mm^{-1}
T = 293 K
Block, yellow-green
0.28 × 0.16 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.805, T_{max} = 0.867
5594 measured reflections
3851 independent reflections
3050 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 25.5°, θ_{min} = 2.4°
h = −6→10
k = −10→10
l = −16→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.072
S = 0.95
3851 reflections
325 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
$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
C1	0.6312 (3)	0.3200 (3)	0.81421 (15)	0.0288 (6)
H1	0.5473	0.4127	0.8124	0.035*

C2	0.6567 (3)	0.2172 (3)	0.89778 (16)	0.0338 (6)
H2	0.5912	0.2413	0.9503	0.041*
C3	0.7796 (3)	0.0801 (3)	0.90156 (16)	0.0310 (6)
H3	0.7976	0.0092	0.9565	0.037*
C4	0.8778 (3)	0.0478 (3)	0.82195 (15)	0.0227 (5)
C5	0.8443 (3)	0.1596 (2)	0.74049 (15)	0.0209 (5)
C6	0.9472 (3)	0.1389 (2)	0.65729 (15)	0.0207 (5)
C7	1.0812 (3)	0.0055 (3)	0.65371 (15)	0.0231 (5)
C8	1.1781 (3)	−0.0002 (3)	0.57196 (16)	0.0270 (5)
H8	1.2676	−0.0861	0.5664	0.032*
C9	1.1399 (3)	0.1215 (3)	0.50060 (16)	0.0280 (6)
H9	1.2038	0.1190	0.4464	0.034*
C10	1.0050 (3)	0.2493 (3)	0.50942 (15)	0.0258 (5)
H10	0.9811	0.3315	0.4605	0.031*
C11	1.1089 (3)	−0.1101 (3)	0.73572 (15)	0.0252 (5)
C12	1.0117 (3)	−0.0873 (3)	0.81472 (15)	0.0243 (5)
C13	1.2023 (3)	−0.3077 (3)	0.83840 (17)	0.0369 (6)
H13	1.2656	−0.4031	0.8682	0.044*
C14	0.5942 (3)	0.6540 (2)	0.43305 (15)	0.0220 (5)
C15	0.6305 (3)	0.7419 (3)	0.34261 (15)	0.0212 (5)
C16	0.7606 (3)	0.6785 (3)	0.28582 (15)	0.0234 (5)
H16	0.8326	0.5814	0.3061	0.028*
C17	0.7849 (3)	0.7588 (3)	0.19821 (15)	0.0223 (5)
C18	0.6787 (3)	0.9059 (3)	0.17046 (16)	0.0264 (5)
H18	0.6933	0.9601	0.1122	0.032*
C19	0.5521 (3)	0.9727 (3)	0.22814 (15)	0.0243 (5)
C20	0.5259 (3)	0.8897 (3)	0.31353 (15)	0.0249 (5)
H20	0.4384	0.9329	0.3515	0.030*
C22	0.9187 (3)	0.6874 (3)	0.13265 (15)	0.0240 (5)
C23	0.4356 (3)	1.1296 (3)	0.19953 (17)	0.0288 (6)
Ni1	0.70279 (4)	0.43502 (3)	0.609962 (19)	0.02230 (10)
N1	0.7200 (2)	0.2927 (2)	0.73743 (12)	0.0229 (4)
N2	0.9089 (2)	0.2582 (2)	0.58513 (12)	0.0217 (4)
N3	1.2298 (2)	−0.2516 (2)	0.75156 (13)	0.0329 (5)
N4	1.0757 (2)	−0.2163 (2)	0.88009 (13)	0.0315 (5)
H4	1.0409	−0.2341	0.9366	0.038*
O1	0.83799 (18)	0.55829 (17)	0.66524 (10)	0.0274 (4)
H1WA	0.8974	0.5175	0.7162	0.041*
H1WB	0.7704	0.6288	0.6903	0.041*
O2	0.48839 (19)	0.60135 (19)	0.63947 (11)	0.0368 (4)
H2WA	0.4226	0.6611	0.6785	0.055*
H2WB	0.4306	0.6295	0.5865	0.055*
O3	0.71191 (18)	0.56435 (17)	0.48112 (10)	0.0257 (4)
O4	0.44422 (18)	0.67849 (17)	0.45611 (10)	0.0249 (4)
O5	1.0320 (2)	0.57271 (19)	0.16548 (11)	0.0346 (4)
O6	0.9071 (2)	0.74669 (19)	0.04712 (11)	0.0365 (4)
O7	0.4671 (2)	1.19600 (19)	0.11669 (12)	0.0474 (5)
H7O	0.3828	1.2679	0.0956	0.071*

O8	0.3214 (2)	1.18626 (19)	0.24846 (12)	0.0436 (5)
O9	0.7523 (2)	0.56589 (19)	0.96006 (11)	0.0404 (5)
H9WA	0.8263	0.5505	0.9168	0.061*
H9WB	0.7762	0.6295	0.9933	0.061*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0238 (13)	0.0318 (14)	0.0252 (13)	−0.0005 (11)	0.0062 (11)	−0.0021 (10)
C2	0.0336 (15)	0.0396 (15)	0.0225 (12)	−0.0044 (12)	0.0105 (11)	−0.0014 (11)
C3	0.0342 (15)	0.0327 (14)	0.0205 (12)	−0.0051 (12)	0.0044 (11)	0.0044 (10)
C4	0.0225 (12)	0.0254 (12)	0.0193 (11)	−0.0073 (10)	0.0023 (10)	0.0007 (9)
C5	0.0202 (12)	0.0238 (12)	0.0181 (11)	−0.0062 (10)	0.0009 (10)	−0.0007 (9)
C6	0.0190 (12)	0.0242 (12)	0.0186 (11)	−0.0064 (10)	0.0004 (9)	−0.0010 (9)
C7	0.0211 (12)	0.0260 (12)	0.0216 (12)	−0.0066 (10)	0.0024 (10)	−0.0027 (10)
C8	0.0240 (13)	0.0257 (13)	0.0286 (13)	−0.0039 (11)	0.0050 (11)	−0.0028 (10)
C9	0.0266 (13)	0.0334 (14)	0.0217 (12)	−0.0068 (11)	0.0088 (10)	−0.0021 (10)
C10	0.0276 (13)	0.0297 (13)	0.0192 (11)	−0.0090 (11)	0.0029 (10)	0.0012 (10)
C11	0.0252 (13)	0.0224 (12)	0.0252 (12)	−0.0040 (11)	0.0023 (11)	−0.0001 (10)
C12	0.0249 (13)	0.0258 (12)	0.0201 (11)	−0.0061 (11)	0.0023 (10)	0.0009 (10)
C13	0.0355 (15)	0.0277 (14)	0.0354 (15)	0.0038 (12)	0.0040 (12)	0.0084 (11)
C14	0.0252 (13)	0.0221 (12)	0.0179 (11)	−0.0054 (11)	0.0030 (10)	−0.0034 (9)
C15	0.0205 (12)	0.0250 (12)	0.0171 (11)	−0.0063 (10)	0.0003 (10)	0.0005 (9)
C16	0.0212 (12)	0.0223 (12)	0.0224 (12)	−0.0016 (10)	−0.0021 (10)	0.0024 (9)
C17	0.0197 (12)	0.0258 (12)	0.0198 (11)	−0.0051 (10)	0.0002 (10)	0.0003 (9)
C18	0.0273 (13)	0.0277 (13)	0.0208 (12)	−0.0062 (11)	0.0017 (10)	0.0037 (10)
C19	0.0229 (13)	0.0240 (12)	0.0235 (12)	−0.0046 (11)	−0.0003 (10)	0.0013 (10)
C20	0.0214 (12)	0.0286 (13)	0.0228 (12)	−0.0045 (11)	0.0051 (10)	−0.0041 (10)
C22	0.0237 (13)	0.0253 (13)	0.0224 (12)	−0.0071 (11)	0.0016 (10)	−0.0010 (10)
C23	0.0291 (14)	0.0255 (13)	0.0290 (13)	−0.0050 (11)	−0.0001 (12)	−0.0003 (11)
Ni1	0.01924 (16)	0.02540 (17)	0.01782 (16)	−0.00195 (13)	0.00227 (12)	0.00200 (12)
N1	0.0193 (10)	0.0253 (10)	0.0215 (10)	−0.0036 (9)	0.0017 (8)	−0.0006 (8)
N2	0.0219 (10)	0.0243 (10)	0.0166 (9)	−0.0055 (9)	0.0021 (8)	0.0017 (8)
N3	0.0295 (12)	0.0291 (11)	0.0283 (11)	0.0053 (10)	0.0070 (9)	0.0043 (9)
N4	0.0333 (12)	0.0313 (12)	0.0214 (10)	−0.0019 (10)	0.0070 (9)	0.0077 (9)
O1	0.0260 (9)	0.0286 (9)	0.0230 (8)	−0.0014 (7)	−0.0001 (7)	−0.0022 (7)
O2	0.0285 (10)	0.0466 (11)	0.0211 (9)	0.0106 (8)	0.0009 (7)	−0.0027 (8)
O3	0.0202 (8)	0.0312 (9)	0.0202 (8)	−0.0030 (7)	0.0009 (7)	0.0065 (7)
O4	0.0200 (8)	0.0314 (9)	0.0201 (8)	−0.0044 (7)	0.0038 (7)	−0.0001 (7)
O5	0.0287 (10)	0.0391 (10)	0.0238 (9)	0.0074 (8)	0.0002 (7)	0.0006 (8)
O6	0.0357 (10)	0.0424 (11)	0.0201 (9)	0.0012 (9)	0.0069 (8)	0.0063 (8)
O7	0.0398 (11)	0.0397 (11)	0.0407 (11)	0.0114 (9)	0.0098 (9)	0.0172 (9)
O8	0.0469 (12)	0.0290 (10)	0.0425 (11)	0.0061 (9)	0.0138 (10)	−0.0032 (8)
O9	0.0411 (11)	0.0382 (10)	0.0320 (10)	0.0021 (9)	0.0049 (8)	−0.0016 (8)

Geometric parameters (Å, º)

C1—N1	1.319 (3)	C15—C16	1.384 (3)
C1—C2	1.392 (3)	C15—C20	1.394 (3)
C1—H1	0.9300	C16—C17	1.399 (3)
C2—C3	1.370 (3)	C16—H16	0.9300
C2—H2	0.9300	C17—C18	1.391 (3)
C3—C4	1.399 (3)	C17—C22	1.503 (3)
C3—H3	0.9300	C18—C19	1.381 (3)
C4—C5	1.413 (3)	C18—H18	0.9300
C4—C12	1.425 (3)	C19—C20	1.388 (3)
C5—N1	1.353 (3)	C19—C23	1.492 (3)
C5—C6	1.451 (3)	C20—H20	0.9300
C6—N2	1.361 (3)	C22—O5	1.248 (3)
C6—C7	1.408 (3)	C22—O6	1.261 (3)
C7—C8	1.404 (3)	C23—O8	1.209 (3)
C7—C11	1.437 (3)	C23—O7	1.307 (3)
C8—C9	1.367 (3)	Ni1—O3	2.0531 (16)
C8—H8	0.9300	Ni1—N1	2.0652 (19)
C9—C10	1.392 (3)	Ni1—N2	2.066 (2)
C9—H9	0.9300	Ni1—O1	2.0662 (17)
C10—N2	1.330 (3)	Ni1—O2	2.0794 (18)
C10—H10	0.9300	Ni1—O4^{i}	2.1540 (17)
C11—C12	1.378 (3)	N4—H4	0.8600
C11—N3	1.390 (3)	O1—H1WA	0.8794
C12—N4	1.380 (3)	O1—H1WB	0.8376
C13—N3	1.314 (3)	O2—H2WA	0.8944
C13—N4	1.333 (3)	O2—H2WB	0.8873
C13—H13	0.9300	O4—Ni1^{i}	2.1540 (17)
C14—O3	1.255 (3)	O7—H7O	0.8528
C14—O4	1.279 (3)	O9—H9WA	0.8627
C14—C15	1.493 (3)	O9—H9WB	0.8651
N1—C1—C2	123.3 (2)	C19—C18—C17	121.0 (2)
N1—C1—H1	118.3	C19—C18—H18	119.5
C2—C1—H1	118.3	C17—C18—H18	119.5
C3—C2—C1	119.0 (2)	C18—C19—C20	119.7 (2)
C3—C2—H2	120.5	C18—C19—C23	122.0 (2)
C1—C2—H2	120.5	C20—C19—C23	118.2 (2)
C2—C3—C4	119.3 (2)	C19—C20—C15	120.2 (2)
C2—C3—H3	120.3	C19—C20—H20	119.9
C4—C3—H3	120.3	C15—C20—H20	119.9
C3—C4—C5	117.8 (2)	O5—C22—O6	124.3 (2)
C3—C4—C12	126.4 (2)	O5—C22—C17	118.4 (2)
C5—C4—C12	115.84 (19)	O6—C22—C17	117.2 (2)
N1—C5—C4	122.0 (2)	O8—C23—O7	124.1 (2)
N1—C5—C6	117.03 (19)	O8—C23—C19	122.2 (2)
C4—C5—C6	120.9 (2)	O7—C23—C19	113.7 (2)

N2—C6—C7	122.7 (2)	O3—Ni1—N1	173.78 (7)
N2—C6—C5	115.78 (19)	O3—Ni1—N2	94.05 (7)
C7—C6—C5	121.52 (19)	N1—Ni1—N2	80.10 (7)
C8—C7—C6	117.2 (2)	O3—Ni1—O1	88.33 (7)
C8—C7—C11	126.1 (2)	N1—Ni1—O1	89.79 (7)
C6—C7—C11	116.7 (2)	N2—Ni1—O1	92.10 (8)
C9—C8—C7	119.5 (2)	O3—Ni1—O2	89.01 (6)
C9—C8—H8	120.2	N1—Ni1—O2	96.93 (7)
C7—C8—H8	120.2	N2—Ni1—O2	176.09 (7)
C8—C9—C10	119.8 (2)	O1—Ni1—O2	90.43 (8)
C8—C9—H9	120.1	O3—Ni1—O4^{i}	87.63 (6)
C10—C9—H9	120.1	N1—Ni1—O4^{i}	94.41 (7)
N2—C10—C9	122.6 (2)	N2—Ni1—O4^{i}	89.96 (8)
N2—C10—H10	118.7	O1—Ni1—O4^{i}	175.58 (6)
C9—C10—H10	118.7	O2—Ni1—O4^{i}	87.72 (8)
C12—C11—N3	109.89 (19)	C1—N1—C5	118.49 (19)
C12—C11—C7	121.0 (2)	C1—N1—Ni1	128.11 (16)
N3—C11—C7	129.1 (2)	C5—N1—Ni1	113.32 (14)
C11—C12—N4	105.6 (2)	C10—N2—C6	118.2 (2)
C11—C12—C4	123.9 (2)	C10—N2—Ni1	128.14 (16)
N4—C12—C4	130.4 (2)	C6—N2—Ni1	113.64 (14)
N3—C13—N4	114.2 (2)	C13—N3—C11	103.84 (19)
N3—C13—H13	122.9	C13—N4—C12	106.45 (19)
N4—C13—H13	122.9	C13—N4—H4	126.8
O3—C14—O4	125.1 (2)	C12—N4—H4	126.8
O3—C14—C15	118.1 (2)	Ni1—O1—H1WA	120.3
O4—C14—C15	116.79 (19)	Ni1—O1—H1WB	105.6
C16—C15—C20	119.6 (2)	H1WA—O1—H1WB	96.1
C16—C15—C14	121.87 (19)	Ni1—O2—H2WA	152.1
C20—C15—C14	118.51 (19)	Ni1—O2—H2WB	106.7
C15—C16—C17	120.7 (2)	H2WA—O2—H2WB	101.2
C15—C16—H16	119.7	C14—O3—Ni1	127.43 (14)
C17—C16—H16	119.7	C14—O4—Ni1^{i}	119.27 (14)
C18—C17—C16	118.7 (2)	C23—O7—H7O	109.8
C18—C17—C22	119.7 (2)	H9WA—O9—H9WB	105.2
C16—C17—C22	121.5 (2)		

N1—C1—C2—C3	−0.1 (4)	C18—C19—C23—O8	177.5 (2)
C1—C2—C3—C4	0.9 (4)	C20—C19—C23—O8	0.7 (4)
C2—C3—C4—C5	−0.2 (4)	C18—C19—C23—O7	−0.9 (3)
C2—C3—C4—C12	178.8 (2)	C20—C19—C23—O7	−177.7 (2)
C3—C4—C5—N1	−1.4 (3)	C2—C1—N1—C5	−1.4 (4)
C12—C4—C5—N1	179.49 (19)	C2—C1—N1—Ni1	−177.93 (17)
C3—C4—C5—C6	176.1 (2)	C4—C5—N1—C1	2.2 (3)
C12—C4—C5—C6	−3.1 (3)	C6—C5—N1—C1	−175.4 (2)
N1—C5—C6—N2	1.3 (3)	C4—C5—N1—Ni1	179.18 (17)
C4—C5—C6—N2	−176.32 (19)	C6—C5—N1—Ni1	1.6 (2)
N1—C5—C6—C7	179.14 (19)	O3—Ni1—N1—C1	154.2 (5)

C4—C5—C6—C7	1.6 (3)	N2—Ni1—N1—C1	174.0 (2)
N2—C6—C7—C8	0.9 (3)	O1—Ni1—N1—C1	81.8 (2)
C5—C6—C7—C8	−176.9 (2)	O2—Ni1—N1—C1	−8.6 (2)
N2—C6—C7—C11	178.9 (2)	O4^{i}—Ni1—N1—C1	−96.8 (2)
C5—C6—C7—C11	1.1 (3)	O3—Ni1—N1—C5	−22.5 (7)
C6—C7—C8—C9	0.2 (3)	N2—Ni1—N1—C5	−2.66 (15)
C11—C7—C8—C9	−177.6 (2)	O1—Ni1—N1—C5	−94.83 (16)
C7—C8—C9—C10	−0.4 (4)	O2—Ni1—N1—C5	174.76 (15)
C8—C9—C10—N2	−0.5 (4)	O4^{i}—Ni1—N1—C5	86.53 (15)
C8—C7—C11—C12	175.6 (2)	C9—C10—N2—C6	1.5 (3)
C6—C7—C11—C12	−2.2 (3)	C9—C10—N2—Ni1	−178.89 (16)
C8—C7—C11—N3	−2.5 (4)	C7—C6—N2—C10	−1.7 (3)
C6—C7—C11—N3	179.7 (2)	C5—C6—N2—C10	176.17 (19)
N3—C11—C12—N4	0.7 (3)	C7—C6—N2—Ni1	178.65 (16)
C7—C11—C12—N4	−177.7 (2)	C5—C6—N2—Ni1	−3.5 (2)
N3—C11—C12—C4	179.1 (2)	O3—Ni1—N2—C10	1.62 (19)
C7—C11—C12—C4	0.7 (4)	N1—Ni1—N2—C10	−176.3 (2)
C3—C4—C12—C11	−177.0 (2)	O1—Ni1—N2—C10	−86.85 (19)
C5—C4—C12—C11	2.0 (3)	O2—Ni1—N2—C10	142.9 (9)
C3—C4—C12—N4	0.9 (4)	O4^{i}—Ni1—N2—C10	89.23 (19)
C5—C4—C12—N4	179.9 (2)	O3—Ni1—N2—C6	−178.76 (15)
O3—C14—C15—C16	34.7 (3)	N1—Ni1—N2—C6	3.35 (15)
O4—C14—C15—C16	−146.4 (2)	O1—Ni1—N2—C6	92.77 (15)
O3—C14—C15—C20	−147.8 (2)	O2—Ni1—N2—C6	−37.4 (10)
O4—C14—C15—C20	31.1 (3)	O4^{i}—Ni1—N2—C6	−91.14 (15)
C20—C15—C16—C17	−2.2 (3)	N4—C13—N3—C11	−0.1 (3)
C14—C15—C16—C17	175.4 (2)	C12—C11—N3—C13	−0.4 (3)
C15—C16—C17—C18	2.0 (3)	C7—C11—N3—C13	177.8 (2)
C15—C16—C17—C22	−175.8 (2)	N3—C13—N4—C12	0.5 (3)
C16—C17—C18—C19	0.4 (3)	C11—C12—N4—C13	−0.7 (3)
C22—C17—C18—C19	178.3 (2)	C4—C12—N4—C13	−178.9 (2)
C17—C18—C19—C20	−2.6 (3)	O4—C14—O3—Ni1	−1.4 (3)
C17—C18—C19—C23	−179.4 (2)	C15—C14—O3—Ni1	177.45 (13)
C18—C19—C20—C15	2.3 (3)	N1—Ni1—O3—C14	168.8 (6)
C23—C19—C20—C15	179.2 (2)	N2—Ni1—O3—C14	149.23 (18)
C16—C15—C20—C19	0.0 (3)	O1—Ni1—O3—C14	−118.78 (18)
C14—C15—C20—C19	−177.6 (2)	O2—Ni1—O3—C14	−28.32 (18)
C18—C17—C22—O5	165.0 (2)	O4^{i}—Ni1—O3—C14	59.44 (18)
C16—C17—C22—O5	−17.2 (3)	O3—C14—O4—Ni1^{i}	−101.9 (2)
C18—C17—C22—O6	−16.0 (3)	C15—C14—O4—Ni1^{i}	79.2 (2)
C16—C17—C22—O6	161.7 (2)		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O6^{ii}	0.86	1.93	2.772 (3)	165

O1—H1*WA*···O5^{iii}	0.88	1.82	2.676 (2)	165
O1—H1*WB*···O8^{iv}	0.84	1.94	2.741 (2)	161
O2—H2*WA*···N3^{v}	0.89	1.94	2.798 (3)	160
O2—H2*WB*···O4	0.89	1.86	2.630 (2)	144
O7—H7*O*···O9^{iv}	0.85	1.72	2.558 (2)	166
O9—H9*WA*···O5^{iii}	0.86	1.88	2.684 (2)	153
O9—H9*WB*···O6^{vi}	0.87	1.99	2.813 (3)	159

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