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Poly[[tetraaquabis[μ_3-1-ethyl-6-fluoro-4-oxo-7-(piperazinium-1-yl)-1*H*-quinoline-3-carboxylato]dinickel(II)] hydroxide nitrate]

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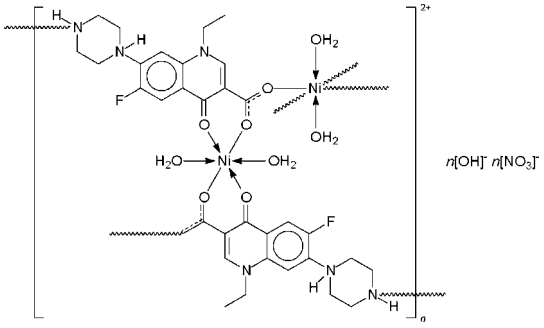
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.008 Å; disorder in solvent or counterion; R factor = 0.069; wR factor = 0.219; data-to-parameter ratio = 15.4.

In the title compound, $[Ni_2(C_{16}H_{18}FN_3O_3)_2(H_2O)_4](OH)(NO_3)$, the cationic $[Ni_2(C_{16}H_{18}FN_3O_3)_2(H_2O)_4]^{2+}$ building units are linked through Ni–$O_{carboxylate}$ and Ni—N_{amino} bridges into a layer structure. The two independent nickel atoms lie on inversion centres: one adopts an NiO_6 octahedral geometry, the other a *trans*-NiN_2O_4 octahedral arrangement. The charge-balancing hydroxide and nitrate ions are of half site occupancy each. A network of O—H···O and N—H···O hydrogen bonds helps to establish the packing.

Related literature

For related structures, see Barbas *et al.* (2007); Florence *et al.* (2000). For medical background on norfloxacin, see Goldstein (1987).



Experimental

Crystal data

$[Ni_2(C_{16}H_{18}FN_3O_3)_2(H_2O)_4](NO_3)(OH)$
M_r = 907.17
Triclinic, $P\overline{1}$
a = 8.9633 (2) Å
b = 9.8121 (2) Å
c = 13.2119 (3) Å
α = 101.504 (2)°
β = 106.301 (2)°
γ = 113.528 (2)°
V = 956.34 (4) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.07 mm^{-1}
T = 295 (2) K
0.18 × 0.16 × 0.15 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.686, T_{max} = 0.856
11320 measured reflections
4304 independent reflections
2869 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.219
S = 1.03
4304 reflections
280 parameters
34 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—O1	2.022 (3)	Ni2—O2	1.979 (4)
Ni1—O1*w*	2.103 (4)	Ni2—O3	2.021 (3)
Ni1—N3^{i}	2.157 (5)	Ni2—O3*w*	2.108 (6)

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2008).

We thank Guangdong Ocean University and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2663).

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supplementary materials

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Poly[[tetraaquabis[μ_3-1-ethyl-6-fluoro-4-oxo-7-(piperazinium-1-yl)-1*H*-quinoline-3-carboxylato]dinickel(II)] hydroxide nitrate]

W.-D. Song, Y.-L. Wan, P.-Z. Hong and S. W. Ng

Comment

The drug norfloxacin has been used in the synthesis of metal complexes as it is a carboxylic acid. There are many crystal structure reports of transition metal derivatives (Cambridge Structural Database Version 5.28, Nov. 2006) but all these have the compound in the mono-deprotonated form, in which the piperazinyl group is a neutral substitutent. In the title compound (I), the substituent is protonated (Fig. 1). There are two nickel ions in the asymmetric unit of (I), both with site symmety $\bar{1}$. One adopts an NiO_6 geometry, the other a *trans*-NiN_2O_4 arrangement (Table 1). A network of O—H···O and N—H···O hydrogen bonds (Table 2) helps to establish the packing.

For related structures, see Barbas *et al.* (2007) and Florence *et al.* (2000). For medical background on norfloxacin, see Goldstein (1987).

Experimental

Nickel nitrate (1.0 mmol), 2,2'-bipyridine (1.0 mmol), norfloxacin (1 mmol) and water (10 ml) were hydrothermally treated in a Parr bomb at K22 K for 48 h. The bomb was cooled (5 K h^{-1}) to room temperature to furnish blue blocks of (I).

Refinement

The divalent cation in (I) requires two negative charges for charge balance. As the hydroxide $[OH]^-$ group lies near a special position, the occupancy of the O2*w* atom (arbitrarily labeled with a *w*) should be only half. Consequently, the nitrate $[NO_3]^-$ group occupancy should also be half. Attempts to refine this group with full occupancy led to high displacement factors. The group was refined with a distance restraint of N–O 1.24±0.01 Å; the four atoms were restrained to lie on a plane. The U^{ij} values of the four atoms as well as those of the O2*w* atom were restrained to be nearly isotropic.

The carbon- and nitrogen-bound H atoms were placed at calculated positions (C—H = 0.93–0.97 Å, N—H = 0.86 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(carrier). The hydroxy and water H atoms were placed in chemically reasonable positions with O—H = 0.85Å and refined as riding with U_{iso}(H) = 1.5U_{eq}(O).

The final difference Fourier map had two large peaks in the vicinity of the diordered groups.

Figures

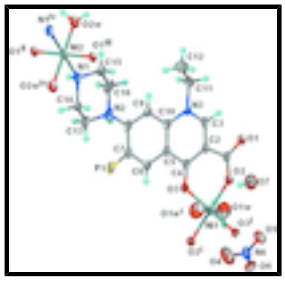


Fig. 1. View of a fragment of the polymeric structure of (I). Displacement ellipsoids are drawn at the 30% probability level, and hydrogen atoms as sphere of arbitrary radius. Symmetry codes: (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) *x*, *y*, 1 + *z*; (iii) 1 - *x*, 1 - *y*, -*z*; (iv) 2 - *x*, 2 - *y*, 1 - *z*.

Poly[[tetraaquabis[μ$_3$-1-ethyl-6-fluoro-4-oxo-7-(piperazinium-1-yl)- 1*H*-quinoline-3-carboxylato]dinickel(II)] hydroxide nitrate]

Crystal data

$[Ni_2(C_{16}H_{18}FN_3O_3)_2(H_2O)_4](NO_3)(OH)$	$Z = 1$
$M_r = 907.17$	$F(000) = 472$
Triclinic, $P\overline{1}$	$D_x = 1.575$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.9633$ (2) Å	Cell parameters from 2076 reflections
$b = 9.8121$ (2) Å	$\theta = 2.6$–$28.0°$
$c = 13.2119$ (3) Å	$\mu = 1.07$ mm^{-1}
$\alpha = 101.504$ (2)°	$T = 295$ K
$\beta = 106.301$ (2)°	Block, blue
$\gamma = 113.528$ (2)°	0.18 × 0.16 × 0.15 mm
$V = 956.34$ (4) Å^3	

Data collection

Bruker APEXII diffractometer	4304 independent reflections
Radiation source: medium-focus sealed tube	2869 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.051$
φ and ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -11 \rightarrow 11$
$T_{min} = 0.686$, $T_{max} = 0.856$	$k = -12 \rightarrow 12$
11320 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.069$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.219$	H-atom parameters constrained

S = 1.03	$w = 1/[\sigma^2(F_o^2) + (0.1076P)^2 + 1.3612P]$ where $P = (F_o^2 + 2F_c^2)/3$
4304 reflections	$(\Delta/\sigma)_{max} = 0.001$
280 parameters	$\Delta\rho_{max} = 1.65$ e Å^{-3}
34 restraints	$\Delta\rho_{min} = -0.59$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.5000	0.5000	0.5000	0.0328 (3)	
Ni2	1.0000	1.0000	0.5000	0.0362 (3)	
F1	0.8924 (5)	1.1417 (4)	0.0053 (3)	0.0597 (10)	
O1	0.5117 (4)	0.6049 (4)	0.3832 (3)	0.0403 (9)	
O2	0.7870 (5)	0.8001 (5)	0.4694 (3)	0.0522 (11)	
O3	0.9054 (5)	0.9832 (5)	0.3374 (3)	0.0450 (10)	
O1w	0.7762 (5)	0.5892 (5)	0.5746 (3)	0.0516 (10)	
H1w1	0.8119	0.6231	0.6459	0.077*	
H1w2	0.8280	0.6650	0.5537	0.077*	
O2w	1.4635 (5)	0.9364 (5)	0.4764 (3)	0.079 (3)	0.50
H2w	1.4173	0.8742	0.4083	0.118*	0.50
O3w	1.1392 (8)	0.8776 (7)	0.4696 (5)	0.0892 (17)	
H3w1	1.2209	0.9326	0.4513	0.134*	
H3w2	1.0678	0.7887	0.4163	0.134*	
N1	0.4068 (5)	0.6750 (5)	0.0911 (3)	0.0353 (9)	
N2	0.5693 (6)	0.9176 (6)	−0.1764 (3)	0.0445 (11)	
H2n	0.5624	1.0037	−0.1616	0.053*	
N3	0.5140 (6)	0.7018 (5)	−0.3881 (4)	0.0399 (10)	
H3n	0.4886	0.7535	−0.4294	0.048*	
C1	0.6428 (6)	0.7216 (6)	0.3853 (4)	0.0355 (11)	
C2	0.6166 (6)	0.7618 (6)	0.2808 (4)	0.0343 (11)	
C3	0.4548 (7)	0.6655 (6)	0.1942 (4)	0.0372 (11)	
H3	0.3704	0.5865	0.2075	0.045*	
C4	0.7510 (6)	0.8857 (6)	0.2651 (4)	0.0330 (10)	
C5	0.6994 (6)	0.8949 (6)	0.1519 (4)	0.0324 (10)	
C6	0.8197 (7)	1.0130 (6)	0.1263 (4)	0.0378 (11)	
H6	0.9307	1.0882	0.1824	0.045*	
C7	0.7757 (7)	1.0182 (6)	0.0216 (4)	0.0400 (12)	
C8	0.6112 (7)	0.9076 (6)	−0.0698 (4)	0.0367 (11)	
C9	0.4899 (7)	0.7932 (6)	−0.0432 (4)	0.0360 (11)	
H9	0.3790	0.7186	−0.0996	0.043*	
C10	0.5301 (6)	0.7878 (6)	0.0651 (4)	0.0328 (10)	
C11	0.2248 (7)	0.5575 (7)	0.0058 (5)	0.0445 (13)	
H11A	0.1846	0.6056	−0.0457	0.053*	
H11B	0.1444	0.5287	0.0434	0.053*	
C12	0.2190 (9)	0.4110 (8)	−0.0597 (6)	0.0684 (19)	
H12A	0.0997	0.3378	−0.1137	0.103*	
H12B	0.2569	0.3622	−0.0091	0.103*	
H12C	0.2965	0.4389	−0.0984	0.103*	

C13	0.6999 (9)	0.9619 (7)	−0.2271 (5)	0.0551 (16)	
H13A	0.8181	1.0297	−0.1679	0.066*	
H13B	0.6758	1.0214	−0.2739	0.066*	
C14	0.6927 (7)	0.8160 (7)	−0.2977 (4)	0.0481 (14)	
H14A	0.7776	0.8489	−0.3319	0.058*	
H14B	0.7280	0.7627	−0.2490	0.058*	
C15	0.3826 (7)	0.6632 (7)	−0.3352 (4)	0.0431 (12)	
H15A	0.4053	0.6045	−0.2873	0.052*	
H15B	0.2638	0.5959	−0.3938	0.052*	
C16	0.3921 (8)	0.8111 (8)	−0.2659 (5)	0.0489 (14)	
H16A	0.3623	0.8665	−0.3147	0.059*	
H16B	0.3056	0.7812	−0.2327	0.059*	
O4	0.9439 (11)	0.5634 (8)	0.7796 (6)	0.0490 (19)	0.50
O5	1.0325 (17)	0.4310 (17)	0.6823 (12)	0.126 (5)	0.50
O6	0.8282 (11)	0.3095 (10)	0.7300 (8)	0.063 (2)	0.50
N4	0.9354 (9)	0.4383 (9)	0.7316 (5)	0.046 (2)	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0328 (5)	0.0316 (5)	0.0269 (5)	0.0082 (4)	0.0117 (4)	0.0128 (4)
Ni2	0.0337 (5)	0.0332 (5)	0.0259 (5)	0.0042 (4)	0.0075 (4)	0.0122 (4)
F1	0.074 (2)	0.0439 (19)	0.0362 (17)	0.0039 (17)	0.0227 (16)	0.0180 (15)
O1	0.0361 (19)	0.040 (2)	0.0340 (18)	0.0079 (16)	0.0113 (15)	0.0198 (16)
O2	0.044 (2)	0.050 (2)	0.0309 (19)	−0.0013 (18)	0.0047 (16)	0.0212 (18)
O3	0.0351 (19)	0.045 (2)	0.0303 (18)	0.0017 (17)	0.0050 (15)	0.0163 (17)
O1w	0.041 (2)	0.051 (2)	0.053 (2)	0.0136 (19)	0.0144 (18)	0.024 (2)
O2w	0.069 (7)	0.093 (9)	0.067 (7)	0.037 (7)	0.024 (6)	0.024 (7)
O3w	0.084 (4)	0.093 (4)	0.094 (4)	0.050 (3)	0.034 (3)	0.028 (3)
N1	0.029 (2)	0.041 (2)	0.029 (2)	0.0115 (18)	0.0106 (16)	0.0132 (18)
N2	0.064 (3)	0.041 (3)	0.028 (2)	0.024 (2)	0.018 (2)	0.015 (2)
N3	0.046 (3)	0.035 (2)	0.034 (2)	0.013 (2)	0.0175 (19)	0.0142 (19)
C1	0.037 (3)	0.037 (3)	0.028 (2)	0.013 (2)	0.013 (2)	0.014 (2)
C2	0.035 (3)	0.035 (3)	0.027 (2)	0.012 (2)	0.0110 (19)	0.013 (2)
C3	0.037 (3)	0.040 (3)	0.037 (3)	0.015 (2)	0.019 (2)	0.020 (2)
C4	0.036 (3)	0.033 (3)	0.029 (2)	0.015 (2)	0.013 (2)	0.014 (2)
C5	0.035 (2)	0.033 (3)	0.027 (2)	0.013 (2)	0.0120 (19)	0.013 (2)
C6	0.035 (3)	0.035 (3)	0.031 (2)	0.009 (2)	0.012 (2)	0.009 (2)
C7	0.048 (3)	0.033 (3)	0.034 (3)	0.012 (2)	0.018 (2)	0.015 (2)
C8	0.048 (3)	0.039 (3)	0.031 (2)	0.025 (2)	0.017 (2)	0.017 (2)
C9	0.037 (3)	0.035 (3)	0.027 (2)	0.014 (2)	0.0076 (19)	0.010 (2)
C10	0.036 (3)	0.034 (3)	0.029 (2)	0.017 (2)	0.0125 (19)	0.012 (2)
C11	0.029 (3)	0.056 (3)	0.037 (3)	0.014 (2)	0.007 (2)	0.017 (3)
C12	0.056 (4)	0.046 (4)	0.069 (5)	0.011 (3)	0.009 (3)	0.004 (3)
C13	0.072 (4)	0.039 (3)	0.031 (3)	0.006 (3)	0.022 (3)	0.012 (2)
C14	0.045 (3)	0.044 (3)	0.033 (3)	0.002 (3)	0.019 (2)	0.007 (2)
C15	0.044 (3)	0.047 (3)	0.033 (3)	0.020 (3)	0.015 (2)	0.009 (2)
C16	0.062 (4)	0.067 (4)	0.032 (3)	0.043 (3)	0.017 (3)	0.021 (3)

O4	0.062 (5)	0.030 (4)	0.038 (4)	0.019 (3)	0.006 (3)	0.005 (3)
O5	0.126 (8)	0.116 (8)	0.138 (8)	0.022 (5)	0.098 (7)	0.060 (7)
O6	0.057 (5)	0.046 (5)	0.080 (6)	0.016 (4)	0.029 (4)	0.026 (4)
N4	0.044 (5)	0.058 (5)	0.048 (5)	0.026 (4)	0.018 (4)	0.037 (4)

Geometric parameters (Å, °)

Ni1—O1	2.022 (3)	C1—C2	1.492 (6)
Ni1—O1^{i}	2.022 (3)	C2—C3	1.359 (7)
Ni1—O1w	2.103 (4)	C2—C4	1.430 (6)
Ni1—O1w^{i}	2.103 (4)	C3—H3	0.9300
Ni1—N3^{ii}	2.157 (5)	C4—C5	1.468 (6)
Ni1—N3^{iii}	2.157 (5)	C5—C6	1.408 (6)
Ni2—O2	1.979 (4)	C5—C10	1.411 (7)
Ni2—O2^{iv}	1.979 (4)	C6—C7	1.345 (7)
Ni2—O3^{iv}	2.021 (3)	C6—H6	0.9300
Ni2—O3	2.021 (3)	C7—C8	1.418 (7)
Ni2—O3w^{iv}	2.108 (6)	C8—C9	1.401 (7)
Ni2—O3w	2.108 (6)	C9—C10	1.390 (6)
F1—C7	1.352 (6)	C9—H9	0.9300
O1—C1	1.260 (6)	C11—C12	1.496 (10)
O2—C1	1.247 (6)	C11—H11A	0.9700
O3—C4	1.256 (6)	C11—H11B	0.9700
O1w—H1w1	0.8501	C12—H12A	0.9600
O1w—H1w2	0.8500	C12—H12B	0.9600
O2w—O2w^{v}	1.088 (8)	C12—H12C	0.9600
O2w—H2w	0.8500	C13—C14	1.511 (9)
O3w—H3w1	0.8501	C13—H13A	0.9700
O3w—H3w2	0.8501	C13—H13B	0.9700
N1—C3	1.343 (6)	C14—H14A	0.9700
N1—C10	1.398 (6)	C14—H14B	0.9700
N1—C11	1.486 (6)	C15—C16	1.509 (8)
N2—C8	1.387 (6)	C15—H15A	0.9700
N2—C16	1.463 (7)	C15—H15B	0.9700
N2—C13	1.469 (7)	C16—H16A	0.9700
N2—H2n	0.8600	C16—H16B	0.9700
N3—C14	1.485 (7)	O4—N4	1.225 (8)
N3—C15	1.493 (7)	O5—N4	1.241 (9)
N3—Ni1^{vi}	2.157 (5)	O6—N4	1.237 (8)
N3—H3n	0.8600		
O1—Ni1—O1^{i}	180.000 (1)	N1—C3—H3	117.3
O1—Ni1—O1w	94.08 (14)	C2—C3—H3	117.3
O1^{i}—Ni1—O1w	85.92 (14)	O3—C4—C2	126.4 (4)
O1—Ni1—O1w^{i}	85.92 (14)	O3—C4—C5	118.6 (4)
O1^{i}—Ni1—O1w^{i}	94.08 (14)	C2—C4—C5	115.0 (4)
O1w—Ni1—O1w^{i}	180.0	C6—C5—C10	117.4 (4)

O1—Ni1—N3^{iii}	89.36 (15)	C6—C5—C4	120.4 (4)
O1^{i}—Ni1—N3^{iii}	90.64 (15)	C10—C5—C4	122.2 (4)
O1w—Ni1—N3^{iii}	87.36 (16)	C7—C6—C5	120.7 (5)
O1w^{i}—Ni1—N3^{iii}	92.64 (16)	C7—C6—H6	119.7
O1—Ni1—N3^{ii}	90.64 (15)	C5—C6—H6	119.7
O1^{i}—Ni1—N3^{ii}	89.36 (15)	C6—C7—F1	117.3 (5)
O1w—Ni1—N3^{ii}	92.64 (16)	C6—C7—C8	123.8 (4)
O1w^{i}—Ni1—N3^{ii}	87.36 (16)	F1—C7—C8	118.8 (4)
N3^{iii}—Ni1—N3^{ii}	180.0 (2)	N2—C8—C9	122.3 (5)
O2^{iv}—Ni2—O2	180.0	N2—C8—C7	122.3 (4)
O2^{iv}—Ni2—O3^{iv}	91.12 (14)	C9—C8—C7	115.3 (4)
O2—Ni2—O3^{iv}	88.88 (14)	C10—C9—C8	122.0 (5)
O2^{iv}—Ni2—O3	88.88 (14)	C10—C9—H9	119.0
O2—Ni2—O3	91.12 (14)	C8—C9—H9	119.0
O3^{iv}—Ni2—O3	180.000 (1)	C9—C10—N1	121.5 (4)
O2^{iv}—Ni2—O3w^{iv}	91.8 (2)	C9—C10—C5	120.7 (4)
O2—Ni2—O3w^{iv}	88.2 (2)	N1—C10—C5	117.8 (4)
O3^{iv}—Ni2—O3w^{iv}	92.6 (2)	N1—C11—C12	111.7 (5)
O3—Ni2—O3w^{iv}	87.4 (2)	N1—C11—H11A	109.3
O2^{iv}—Ni2—O3w	88.2 (2)	C12—C11—H11A	109.3
O2—Ni2—O3w	91.8 (2)	N1—C11—H11B	109.3
O3^{iv}—Ni2—O3w	87.4 (2)	C12—C11—H11B	109.3
O3—Ni2—O3w	92.6 (2)	H11A—C11—H11B	107.9
O3w^{iv}—Ni2—O3w	180.000 (3)	C11—C12—H12A	109.5
C1—O1—Ni1	128.4 (3)	C11—C12—H12B	109.5
C1—O2—Ni2	130.1 (3)	H12A—C12—H12B	109.5
C4—O3—Ni2	125.3 (3)	C11—C12—H12C	109.5
Ni1—O1w—H1w1	109.5	H12A—C12—H12C	109.5
Ni1—O1w—H1w2	109.5	H12B—C12—H12C	109.5
H1w1—O1w—H1w2	109.5	N2—C13—C14	110.9 (4)
O2w^{v}—O2w—H2w	138.4	N2—C13—H13A	109.5
Ni2—O3w—H3w1	109.5	C14—C13—H13A	109.5
Ni2—O3w—H3w2	109.4	N2—C13—H13B	109.5
H3w1—O3w—H3w2	109.5	C14—C13—H13B	109.5
C3—N1—C10	119.8 (4)	H13A—C13—H13B	108.0
C3—N1—C11	118.1 (4)	N3—C14—C13	113.3 (5)
C10—N1—C11	122.0 (4)	N3—C14—H14A	108.9
C8—N2—C16	120.9 (4)	C13—C14—H14A	108.9
C8—N2—C13	122.5 (5)	N3—C14—H14B	108.9
C16—N2—C13	109.1 (4)	C13—C14—H14B	108.9
C8—N2—H2n	99.1	H14A—C14—H14B	107.7
C16—N2—H2n	99.1	N3—C15—C16	111.8 (5)
C13—N2—H2n	99.1	N3—C15—H15A	109.2
C14—N3—C15	108.2 (4)	C16—C15—H15A	109.2

C14—N3—Ni1^{vi}	115.0 (4)	N3—C15—H15B	109.2
C15—N3—Ni1^{vi}	115.5 (3)	C16—C15—H15B	109.2
C14—N3—H3n	105.7	H15A—C15—H15B	107.9
C15—N3—H3n	105.7	N2—C16—C15	111.5 (5)
Ni1^{vi}—N3—H3n	105.7	N2—C16—H16A	109.3
O2—C1—O1	122.5 (4)	C15—C16—H16A	109.3
O2—C1—C2	121.2 (4)	N2—C16—H16B	109.3
O1—C1—C2	116.2 (4)	C15—C16—H16B	109.3
C3—C2—C4	119.6 (4)	H16A—C16—H16B	108.0
C3—C2—C1	115.7 (4)	O4—N4—O6	121.5 (9)
C4—C2—C1	124.6 (4)	O4—N4—O5	123.2 (10)
N1—C3—C2	125.4 (4)	O6—N4—O5	115.3 (10)
O1w—Ni1—O1—C1	−20.5 (5)	C4—C5—C6—C7	177.4 (5)
O1w^{i}—Ni1—O1—C1	159.5 (5)	C5—C6—C7—F1	175.2 (5)
N3^{iii}—Ni1—O1—C1	−107.8 (5)	C5—C6—C7—C8	−1.0 (9)
N3^{ii}—Ni1—O1—C1	72.2 (5)	C16—N2—C8—C9	2.1 (8)
O3^{iv}—Ni2—O2—C1	168.0 (5)	C13—N2—C8—C9	−144.4 (5)
O3—Ni2—O2—C1	−12.0 (5)	C16—N2—C8—C7	−174.0 (5)
O3w^{iv}—Ni2—O2—C1	75.3 (6)	C13—N2—C8—C7	39.5 (8)
O3w—Ni2—O2—C1	−104.7 (6)	C6—C7—C8—N2	179.2 (5)
O2^{iv}—Ni2—O3—C4	−170.1 (5)	F1—C7—C8—N2	3.0 (8)
O2—Ni2—O3—C4	9.9 (5)	C6—C7—C8—C9	2.9 (8)
O3w^{iv}—Ni2—O3—C4	−78.3 (5)	F1—C7—C8—C9	−173.3 (5)
O3w—Ni2—O3—C4	101.7 (5)	N2—C8—C9—C10	−177.4 (5)
Ni2—O2—C1—O1	−172.1 (4)	C7—C8—C9—C10	−1.0 (8)
Ni2—O2—C1—C2	7.9 (8)	C8—C9—C10—N1	178.8 (5)
Ni1—O1—C1—O2	−6.5 (8)	C8—C9—C10—C5	−2.6 (8)
Ni1—O1—C1—C2	173.5 (3)	C3—N1—C10—C9	174.9 (5)
O2—C1—C2—C3	178.7 (5)	C11—N1—C10—C9	−1.6 (8)
O1—C1—C2—C3	−1.2 (7)	C3—N1—C10—C5	−3.7 (7)
O2—C1—C2—C4	2.5 (8)	C11—N1—C10—C5	179.7 (5)
O1—C1—C2—C4	−177.5 (5)	C6—C5—C10—C9	4.4 (7)
C10—N1—C3—C2	2.2 (8)	C4—C5—C10—C9	−175.7 (5)
C11—N1—C3—C2	178.9 (5)	C6—C5—C10—N1	−177.0 (5)
C4—C2—C3—N1	0.3 (9)	C4—C5—C10—N1	3.0 (7)
C1—C2—C3—N1	−176.1 (5)	C3—N1—C11—C12	−89.1 (6)
Ni2—O3—C4—C2	−4.4 (8)	C10—N1—C11—C12	87.5 (6)
Ni2—O3—C4—C5	176.5 (3)	C8—N2—C13—C14	92.7 (6)
C3—C2—C4—O3	179.8 (5)	C16—N2—C13—C14	−57.2 (6)
C1—C2—C4—O3	−4.1 (9)	C15—N3—C14—C13	−53.8 (5)
C3—C2—C4—C5	−1.0 (7)	Ni1^{vi}—N3—C14—C13	175.4 (3)
C1—C2—C4—C5	175.1 (5)	N2—C13—C14—N3	56.8 (6)
O3—C4—C5—C6	−1.4 (8)	C14—N3—C15—C16	54.0 (6)
C2—C4—C5—C6	179.3 (5)	Ni1^{vi}—N3—C15—C16	−175.4 (3)
O3—C4—C5—C10	178.6 (5)	C8—N2—C16—C15	−91.7 (6)
C2—C4—C5—C10	−0.7 (7)	C13—N2—C16—C15	58.7 (6)

C10—C5—C6—C7	−2.6 (8)	N3—C15—C16—N2	−58.6 (6)

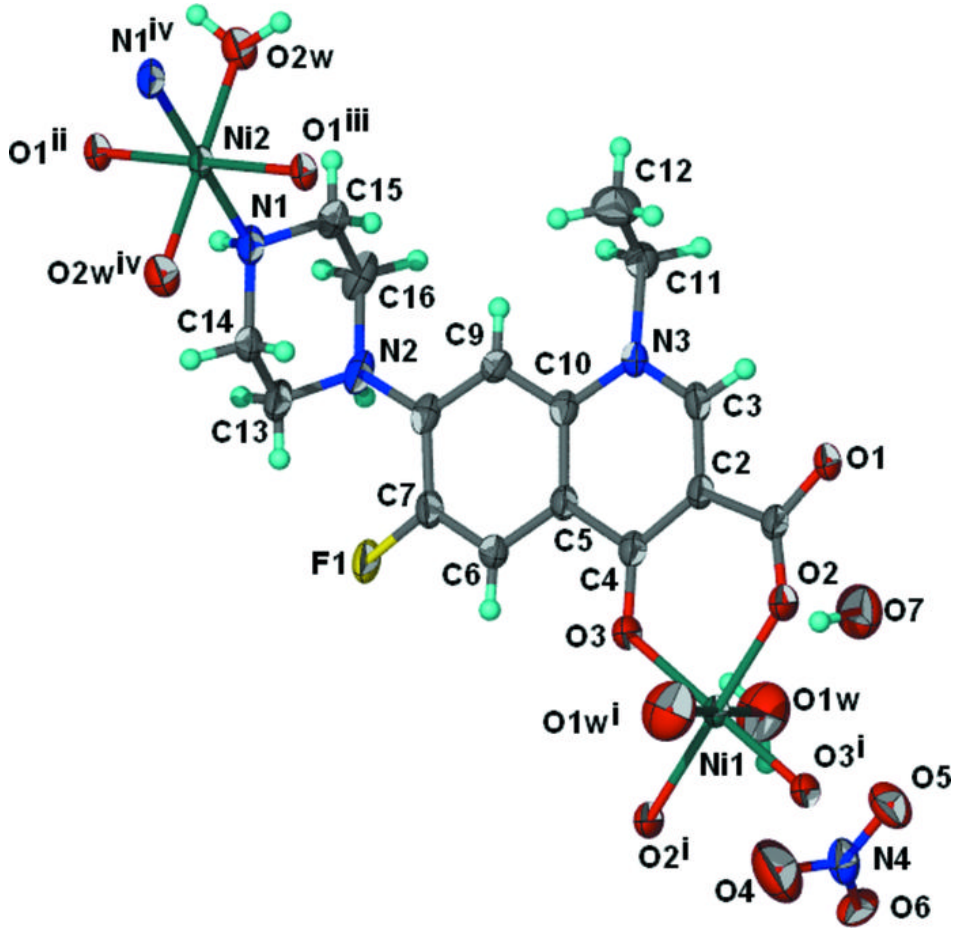
Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*, *y*, *z*+1; (iii) −*x*+1, −*y*+1, −*z*; (iv) −*x*+2, −*y*+2, −*z*+1; (v) −*x*+3, −*y*+2, −*z*+1; (vi) *x*, *y*, *z*−1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1w—H1w1···O4	0.85	2.16	2.820 (8)	135
O1w—H1w2···O2	0.85	1.97	2.700 (5)	143
O2w—H2w···O6^{vii}	0.85	2.17	2.90 (1)	145
O3w—H3w1···O2w	0.85	2.09	2.699 (7)	128
O3w—H3w2···O5^{vii}	0.85	1.96	2.77 (2)	161
N3—H3n···O2w^{viii}	0.86	2.43	3.277 (6)	171

Symmetry codes: (vii) −*x*+2, −*y*+1, −*z*+1; (viii) *x*−1, *y*, *z*−1.

Fig. 1


N1iv
O2w
O1ii
Ni2
O1iii
C15
N1
O2wiv
C16
C14
N2
C9
C10
N3
C12
C11
C3
C13
C2
O1
C7
C5
F1
C6
C4
O2
O7
O3
O1w
O1wi
Ni1
O3i
O5
N4
O2i
O4
O6