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Poly[bis[μ-1-cyclopropyl-6-fluoro-4-oxido-7-(1-piperazinyl)-1,4-dihydroquinoline-3-carboxylato]nickel(II)]

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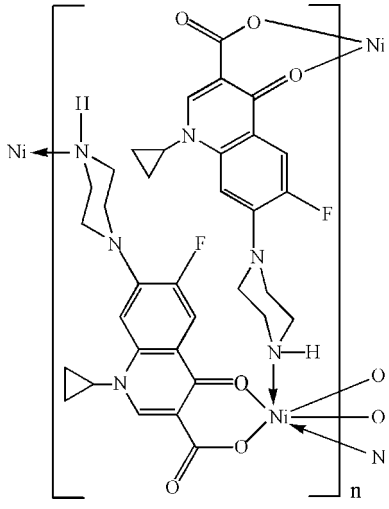
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.006 Å; R factor = 0.057; wR factor = 0.173; data-to-parameter ratio = 12.8.

In the title compound, $[Ni(C_{17}H_{17}FN_3O_3)_2]_n$, the Ni^{II} atom exists in a distorted *trans*-NiN_2O_4 octahedral geometry defined by two monodentate *N*-bonded and two bidentate *O*,*O*-bonded 1-cyclopropyl-6-fluoro-4-oxido-7-(1-piperazinyl)-1,4-dihydroquinoline-3-carboxylate (ciprofloxacinium) monoanions. The extended two-dimensional structure is a square grid. The Ni atom lies on a center of inversion.

Related literature

For the manganese, zinc and copper complexes of the ciprofloxacinium (cf) anion, see: Xiao *et al.* (2005); An *et al.* (2007). For background on the medicinal uses of Hcf, see: Mizuki *et al.* (1996).



Experimental

Crystal data

$[Ni(C_{17}H_{17}FN_3O_3)_2]$
M_r = 719.38
Monoclinic, $P2_1/c$
a = 5.9999 (6) Å
b = 21.437 (2) Å
c = 13.2287 (14) Å
β = 101.886 (2)°
V = 1665.0 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.65 mm^{-1}
T = 295 (2) K
0.34 × 0.26 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.810, T_{max} = 0.892
8098 measured reflections
2890 independent reflections
2466 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.173
S = 1.00
2890 reflections
226 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.92 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
N3—H3N···O2^{i}	0.861 (10)	2.48 (4)	3.184 (4)	139 (5)

Symmetry code: (i) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); 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: CS2060).

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  doi:10.1107/S1600536807065555

supplementary materials

Acta Cryst. (2008). E**64**, m176 [**doi:10.1107/S1600536807065555**]

Poly[bis[μ-1-cyclopropyl-6-fluoro-4-oxido-7-(1-piperazinyl)-1,4-dihydroquinoline-3-carboxylato]nickel(II)]

Z. An, L.-R. Liu and Y.-Q. Liu

Comment

Ciprofloxacin (1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo -7-(1-piperazinyl)-3-quinoline carboxylic acid, H-*cf*) is a member of a class of quinolones that is used to treat infections (Mizuki *et al.*, 1996). Manganese(II), zinc(II) and copper(II) derivatives of H-*cf* have been reported (Xiao *et al.*, 2005; An *et al.*, 2007). The title compound nickel(II) derivative is a two-dimensional coordination polymer in which the anion acts in a bridging mode (Fig. 1).

The Ni(II) atom is coordinated by four oxygen atoms and two N atoms from four *cf* ligands (two monodentate-N and two O,*O*-bidentate) to form a square grid propagating approximately in the *bc* plane (Fig. 2).

Experimental

A mixture of $Ni(NO_3)_2.6H_2O$ (0.07 g, 0.25 mmol), ciprofloxacin hydrochloride (0.19 g, 0.5 mmol), and water (12 ml) was stirred for 30 min in air. The mixture was then transferred to a 23 ml Teflon-lined hydrothermal bomb. The bomb was kept at 433 K for 72 h under autogenous pressure. Green single crystals of the title compound suitable for X-ray analysis were obtained from the reaction mixture after cooling. Green blocks of (I) with a yield of 21%. Anal. Calc. for $C_{34}H_{34}F_2N_6O_6Ni$: C 56.77, H 4.73, N 11.69%, O 13.36; Found: C 56.73, H 4.78, N 11.64%, O 13.40.

Refinement

The carbon-bound H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The N-bound H atom was located in a difference map and refined with a distance restraint of 0.86 (1) Å and the constraint U_{iso}(H) = 1.2U_{eq}(N).

Figures

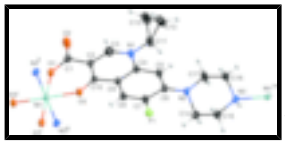

Fig. 1. The asymmetric unit of the title compound, extended to show the Ni coordination, showing 50% displacement ellipsoids and the atom-numbering scheme [symmetry codes: (i)*x*, *y*, *z*; (ii)-*x*, *y* + 1/2, -*z* + 1/2; (iii)-*x*, -*y*, -*z*; (iv)*x*, -*y* - 1/2, *z* - 1/2]

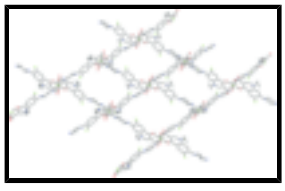

Fig. 2. A view of part of a two-dimensional polymeric sheet in the crystal of the title compound showing the square-grid connectivity.

Poly[bis[μ-1-cyclopropyl-6-fluoro-4-oxido-7-(1-piperazinyl)-1,4-\ dihydroquinoline-3-carboxylato]nickel(II)]

Crystal data

$[Ni(C_{17}H_{17}FN_3O_3)_2]$	F_{000} = 748
M_r = 719.38	D_x = 1.435 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 5.9999 (6) Å	Cell parameters from 2967 reflections
b = 21.437 (2) Å	θ = 2.5–27.3º
c = 13.2287 (14) Å	μ = 0.65 mm^{-1}
β = 101.886 (2)º	T = 295 (2) K
V = 1665.0 (3) Å^3	Block, green
Z = 2	0.34 × 0.26 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer	2890 independent reflections
Radiation source: fine-focus sealed tube	2466 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.030
T = 295(2) K	θ_{max} = 25.1º
ω scans	θ_{min} = 2.5º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −6→7
T_{min} = 0.810, T_{max} = 0.892	k = −25→21
8098 measured reflections	l = −15→15

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.057	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.173	$w = 1/[\sigma^2(F_o^2) + (0.1083P)^2 + 3.3784P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max}$ = 0.008
2890 reflections	$\Delta\rho_{max}$ = 1.92 e Å^{-3}
226 parameters	$\Delta\rho_{min}$ = −0.43 e Å^{-3}
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.0000	0.5000	0.5000	0.0191 (2)
F1	0.7020 (4)	0.74254 (11)	0.67877 (19)	0.0407 (6)
O1	−0.2122 (4)	0.48858 (11)	0.6010 (2)	0.0254 (6)
O2	−0.3432 (6)	0.49499 (14)	0.7453 (3)	0.0489 (9)
O3	0.1687 (4)	0.56702 (11)	0.59535 (18)	0.0246 (5)
N1	0.0052 (5)	0.65173 (14)	0.8485 (2)	0.0275 (7)
N2	0.5762 (5)	0.81201 (14)	0.8367 (2)	0.0266 (7)
N3	0.7552 (5)	0.93356 (13)	0.9140 (2)	0.0244 (6)
C1	−0.2146 (6)	0.51226 (17)	0.6881 (3)	0.0261 (8)
C2	−0.0603 (6)	0.56768 (15)	0.7245 (3)	0.0236 (7)
C3	−0.1042 (6)	0.59953 (17)	0.8074 (3)	0.0274 (8)
H3	−0.2188	0.5841	0.8383	0.033*
C4	0.1761 (6)	0.67679 (16)	0.8044 (3)	0.0242 (7)
C5	0.2833 (6)	0.73317 (17)	0.8400 (3)	0.0264 (8)
H5	0.2370	0.7542	0.8937	0.032*
C6	0.4567 (6)	0.75847 (16)	0.7975 (3)	0.0243 (7)
C7	0.5192 (6)	0.72338 (17)	0.7174 (3)	0.0253 (8)
C8	0.4147 (6)	0.67009 (16)	0.6793 (3)	0.0251 (7)
H8	0.4605	0.6498	0.6249	0.030*
C9	0.2363 (6)	0.64486 (16)	0.7215 (3)	0.0232 (7)
C10	0.1164 (6)	0.58960 (15)	0.6756 (3)	0.0216 (7)
C11	−0.0674 (7)	0.6856 (2)	0.9317 (3)	0.0345 (9)
H11	−0.1386	0.7262	0.9124	0.041*
C12	0.0698 (10)	0.6814 (3)	1.0393 (4)	0.0550 (13)
H12A	0.0834	0.7187	1.0817	0.066*
H12B	0.2035	0.6548	1.0512	0.066*
C13	−0.1585 (10)	0.6507 (3)	1.0120 (4)	0.0632 (16)
H13A	−0.1629	0.6055	1.0075	0.076*
H13B	−0.2829	0.6694	1.0379	0.076*
C14	0.6114 (8)	0.86219 (18)	0.7651 (3)	0.0360 (9)
H14A	0.4703	0.8850	0.7425	0.043*
H14B	0.6543	0.8441	0.7047	0.043*
C15	0.7969 (7)	0.90671 (18)	0.8177 (3)	0.0347 (9)

H15A	0.9409	0.8846	0.8324	0.042*
H15B	0.8105	0.9403	0.7703	0.042*
C16	0.7067 (9)	0.8829 (2)	0.9801 (3)	0.0464 (12)
H16A	0.6634	0.9008	1.0406	0.056*
H16B	0.8452	0.8591	1.0035	0.056*
C17	0.5196 (8)	0.8385 (2)	0.9285 (3)	0.0458 (12)
H17A	0.5018	0.8054	0.9762	0.055*
H17B	0.3764	0.8609	0.9104	0.055*
H3N	0.641 (6)	0.9588 (19)	0.902 (4)	0.055*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0266 (4)	0.0117 (4)	0.0186 (4)	0.0001 (2)	0.0035 (3)	−0.0027 (2)
F1	0.0451 (13)	0.0358 (13)	0.0491 (14)	−0.0169 (10)	0.0284 (11)	−0.0146 (11)
O1	0.0311 (13)	0.0194 (12)	0.0252 (13)	−0.0048 (10)	0.0042 (10)	−0.0037 (10)
O2	0.067 (2)	0.0467 (19)	0.0417 (18)	−0.0339 (15)	0.0306 (17)	−0.0182 (13)
O3	0.0307 (13)	0.0206 (12)	0.0240 (12)	−0.0021 (10)	0.0090 (10)	−0.0075 (10)
N1	0.0331 (16)	0.0258 (16)	0.0263 (16)	−0.0096 (12)	0.0123 (13)	−0.0114 (12)
N2	0.0389 (17)	0.0178 (14)	0.0245 (15)	−0.0098 (12)	0.0101 (13)	−0.0055 (12)
N3	0.0304 (16)	0.0155 (14)	0.0268 (15)	−0.0031 (11)	0.0044 (12)	−0.0007 (12)
C1	0.0301 (19)	0.0209 (17)	0.0271 (19)	−0.0049 (14)	0.0055 (15)	−0.0005 (14)
C2	0.0299 (18)	0.0164 (17)	0.0236 (17)	−0.0038 (13)	0.0040 (14)	−0.0030 (13)
C3	0.0317 (18)	0.0248 (18)	0.0267 (18)	−0.0058 (14)	0.0081 (15)	−0.0016 (15)
C4	0.0285 (18)	0.0204 (17)	0.0246 (18)	−0.0042 (14)	0.0077 (14)	−0.0044 (14)
C5	0.0320 (19)	0.0224 (17)	0.0260 (18)	−0.0060 (15)	0.0088 (15)	−0.0087 (14)
C6	0.0286 (18)	0.0185 (17)	0.0251 (18)	−0.0042 (14)	0.0044 (14)	−0.0041 (14)
C7	0.0291 (18)	0.0239 (18)	0.0253 (18)	−0.0054 (14)	0.0108 (14)	−0.0036 (14)
C8	0.0312 (18)	0.0216 (17)	0.0241 (17)	−0.0019 (14)	0.0092 (14)	−0.0039 (14)
C9	0.0257 (17)	0.0217 (17)	0.0227 (17)	−0.0029 (13)	0.0058 (13)	−0.0039 (13)
C10	0.0261 (17)	0.0156 (16)	0.0221 (17)	0.0016 (13)	0.0024 (13)	−0.0002 (13)
C11	0.040 (2)	0.033 (2)	0.034 (2)	−0.0064 (17)	0.0166 (17)	−0.0116 (17)
C12	0.078 (3)	0.056 (3)	0.030 (2)	−0.009 (3)	0.009 (2)	−0.014 (2)
C13	0.094 (4)	0.063 (3)	0.046 (3)	−0.029 (3)	0.045 (3)	−0.017 (2)
C14	0.058 (3)	0.0240 (19)	0.0253 (19)	−0.0120 (17)	0.0057 (18)	−0.0016 (15)
C15	0.050 (2)	0.029 (2)	0.029 (2)	−0.0149 (17)	0.0159 (17)	−0.0059 (16)
C16	0.074 (3)	0.039 (2)	0.029 (2)	−0.035 (2)	0.018 (2)	−0.0119 (18)
C17	0.064 (3)	0.041 (2)	0.040 (2)	−0.032 (2)	0.028 (2)	−0.0232 (19)

Geometric parameters (Å, °)

Ni1—O3	2.038 (2)	C5—C6	1.391 (5)
Ni1—O3^{i}	2.038 (2)	C5—H5	0.9300
Ni1—O1^{i}	2.041 (3)	C6—C7	1.411 (5)
Ni1—O1	2.041 (3)	C7—C8	1.350 (5)
Ni1—N3^{ii}	2.189 (3)	C8—C9	1.412 (5)
Ni1—N3^{iii}	2.189 (3)	C8—H8	0.9300
F1—C7	1.365 (4)	C9—C10	1.453 (5)

O1—C1	1.261 (5)	C11—C13	1.491 (6)
O2—C1	1.243 (5)	C11—C12	1.492 (7)
O3—C10	1.264 (4)	C11—H11	0.9800
N1—C3	1.353 (5)	C12—C13	1.495 (7)
N1—C4	1.387 (5)	C12—H12A	0.9700
N1—C11	1.459 (5)	C12—H12B	0.9700
N2—C6	1.396 (4)	C13—H13A	0.9700
N2—C17	1.443 (5)	C13—H13B	0.9700
N2—C14	1.476 (5)	C14—C15	1.521 (5)
N3—C16	1.461 (5)	C14—H14A	0.9700
N3—C15	1.466 (5)	C14—H14B	0.9700
N3—Ni1^{iv}	2.189 (3)	C15—H15A	0.9700
N3—H3N	0.861 (10)	C15—H15B	0.9700
C1—C2	1.522 (5)	C16—C17	1.521 (6)
C2—C3	1.363 (5)	C16—H16A	0.9700
C2—C10	1.430 (5)	C16—H16B	0.9700
C3—H3	0.9300	C17—H17A	0.9700
C4—C5	1.404 (5)	C17—H17B	0.9700
C4—C9	1.402 (5)		
O3—Ni1—O3^{i}	180.00 (9)	C7—C8—H8	119.7
O3—Ni1—O1^{i}	91.34 (10)	C9—C8—H8	119.7
O3^{i}—Ni1—O1^{i}	88.66 (10)	C4—C9—C8	117.4 (3)
O3—Ni1—O1	88.66 (10)	C4—C9—C10	122.7 (3)
O3^{i}—Ni1—O1	91.34 (10)	C8—C9—C10	119.8 (3)
O1^{i}—Ni1—O1	180.000 (1)	O3—C10—C2	126.1 (3)
O3—Ni1—N3^{ii}	93.30 (11)	O3—C10—C9	118.4 (3)
O3^{i}—Ni1—N3^{ii}	86.70 (11)	C2—C10—C9	115.4 (3)
O1^{i}—Ni1—N3^{ii}	91.38 (11)	N1—C11—C13	119.9 (4)
O1—Ni1—N3^{ii}	88.62 (11)	N1—C11—C12	119.9 (4)
O3—Ni1—N3^{iii}	86.70 (11)	C13—C11—C12	60.2 (3)
O3^{i}—Ni1—N3^{iii}	93.30 (11)	N1—C11—H11	115.3
O1^{i}—Ni1—N3^{iii}	88.62 (11)	C13—C11—H11	115.3
O1—Ni1—N3^{iii}	91.38 (11)	C12—C11—H11	115.3
N3^{ii}—Ni1—N3^{iii}	180.000 (1)	C11—C12—C13	59.9 (3)
C1—O1—Ni1	132.5 (2)	C11—C12—H12A	117.8
C10—O3—Ni1	127.7 (2)	C13—C12—H12A	117.8
C3—N1—C4	119.4 (3)	C11—C12—H12B	117.8
C3—N1—C11	121.3 (3)	C13—C12—H12B	117.8
C4—N1—C11	119.1 (3)	H12A—C12—H12B	114.9
C6—N2—C17	116.4 (3)	C11—C13—C12	60.0 (3)
C6—N2—C14	119.4 (3)	C11—C13—H13A	117.8
C17—N2—C14	110.0 (3)	C12—C13—H13A	117.8
C16—N3—C15	108.6 (3)	C11—C13—H13B	117.8
C16—N3—Ni1^{iv}	111.6 (2)	C12—C13—H13B	117.8
C15—N3—Ni1^{iv}	119.4 (2)	H13A—C13—H13B	114.9

C16—N3—H3N	109 (4)	N2—C14—C15	110.6 (3)
C15—N3—H3N	111 (4)	N2—C14—H14A	109.5
Ni1^{iv}—N3—H3N	96 (4)	C15—C14—H14A	109.5
O2—C1—O1	124.1 (3)	N2—C14—H14B	109.5
O2—C1—C2	116.9 (3)	C15—C14—H14B	109.5
O1—C1—C2	118.9 (3)	H14A—C14—H14B	108.1
C3—C2—C10	118.9 (3)	N3—C15—C14	113.8 (3)
C3—C2—C1	116.1 (3)	N3—C15—H15A	108.8
C10—C2—C1	124.9 (3)	C14—C15—H15A	108.8
N1—C3—C2	125.4 (3)	N3—C15—H15B	108.8
N1—C3—H3	117.3	C14—C15—H15B	108.8
C2—C3—H3	117.3	H15A—C15—H15B	107.7
N1—C4—C5	121.3 (3)	N3—C16—C17	114.6 (4)
N1—C4—C9	118.1 (3)	N3—C16—H16A	108.6
C5—C4—C9	120.6 (3)	C17—C16—H16A	108.6
C6—C5—C4	121.9 (3)	N3—C16—H16B	108.6
C6—C5—H5	119.0	C17—C16—H16B	108.6
C4—C5—H5	119.0	H16A—C16—H16B	107.6
C5—C6—N2	122.7 (3)	N2—C17—C16	110.1 (3)
C5—C6—C7	115.6 (3)	N2—C17—H17A	109.6
N2—C6—C7	121.4 (3)	C16—C17—H17A	109.6
C8—C7—F1	117.5 (3)	N2—C17—H17B	109.6
C8—C7—C6	123.8 (3)	C16—C17—H17B	109.6
F1—C7—C6	118.6 (3)	H17A—C17—H17B	108.2
C7—C8—C9	120.5 (3)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3N···O2^{v}	0.861 (10)	2.48 (4)	3.184 (4)	139 (5)

Symmetry codes: (v) −*x*, *y*+1/2, −*z*+3/2.

Fig. 1

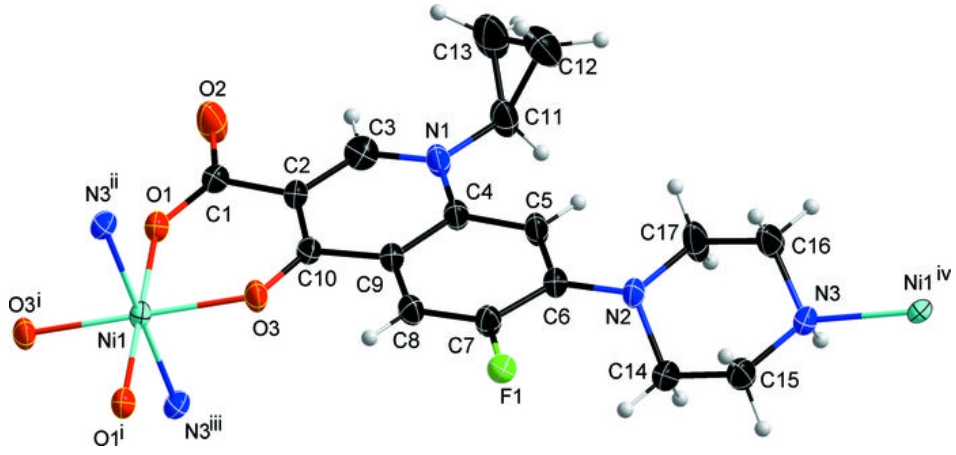
C13
C12
O2
C3
N1
C11
N3ii
O1
C1
C2
C4
C5
C17
C16
O3i
C10
C9
N3
Ni1iv
Ni1
O3
C8
C7
C6
N2
C14
C15
F1
O1i
N3iii

Fig. 2