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Diaqua(benzoato-κ^2O,O')(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')nickel(II) nitrate dihydrate

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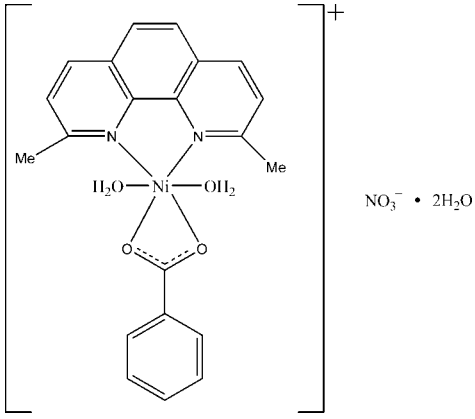
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.004 Å; R factor = 0.034; wR factor = 0.098; data-to-parameter ratio = 13.5.

The title compound, $[Ni(C_7H_5O_2)(C_{14}H_{12}N_2)(H_2O)_2]NO_3\cdot 2H_2O$, consists of one Ni^{II} complex cation, two solvent water molecules and one non-coordinated nitrate anion. The Ni^{II} ion has a slightly distorted octahedral coordination geometry, bonded to two N atoms from one 2,9-dimethyl-1,10-phenanthroline (dmphen) ligand, two O atoms from one benzoate anion and two water molecules. Both the cation and anion lie on a twofold rotation axis. O—H···O hydrogen bonds involving the water molecules as donors and π–π stacking interactions between the dmphen ligands of symmetry-related cations, with a distance between their ring planes of 3.2197 Å, seem to determine the crystal packing.

Related literature

Structurally related Cu^{II} and Mn^{II} complexes have been characterized by Xuan *et al.* (2007) and Zhao *et al.* (2007), respectively.



Experimental

Crystal data

$[Ni(C_7H_5O_2)(C_{14}H_{12}N_2)(H_2O)_2]NO_3\cdot 2H_2O$
M_r = 522.15
Orthorhombic, *Pbcn*
a = 10.4453 (9) Å
b = 22.2586 (19) Å
c = 9.9660 (9) Å
V = 2317.1 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.89 mm^{-1}
T = 291 (2) K
0.37 × 0.30 × 0.23 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.732, T_{max} = 0.817
9175 measured reflections
2129 independent reflections
1723 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.098
S = 1.05
2129 reflections
158 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1W···O1	0.83	2.07	2.883 (2)	167
O2—H2W···O3^{i}	0.82	2.08	2.903 (3)	174
O5—H3W···O2^{ii}	0.83	1.88	2.707 (2)	174
O5—H4W···O4^{iii}	0.82	2.16	2.860 (3)	143

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); 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: BH2128).

References

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supplementary materials

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Diaqua(benzoato-κ^2O,O')(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')nickel(II) nitrate dihydrate

X.-P. Xuan, P.-Z. Zhao and Q.-H. Tang

Comment

The formula unit of (I, Fig. 1) comprises a mononuclear $[Ni(dmphen)(benzoate)(H_2O)_2]^+$ cation, two uncoordinated water molecules, and a nitrate anion (dmphen is 2,9-dimethyl-1,10-phenanthroline). The Ni^{II} ion is in a distorted octahedral NiN_2O_4 geometry, being coordinated by two N atoms of the dmphen ligand, two O atoms of the benzoate anion and two O atoms of two water molecules. The coordination bond lengths and angles are given in Table 1. Both cation and anion have a crystallographic twofold symmetry, passing through the metal atom, dmphen molecule, benzoate anion, and nitrate anion. The non-coordinated nitrate anion is almost perpendicular to the phenyl ring of benzoate anion, with a dihedral angle of 83.05° between mean planes. In the crystal structure, one-dimensional chains along [100] are formed by intermolecular O_{water}—H···$O_{nitrate}$ and O_{water}—H···O_{water} hydrogen bonds (Fig. 2 and Table 2). The crystal packing is also stabilized by π–π interactions between the dmphen rings of neighboring molecules (Fig. 2), with a distance between their ring planes of 3.220 Å.

Experimental

To a solution of dmphen hemihydrate ($C_{14}H_{12}N_2$.0.5 H_2O, 0.1089 g, 0.5 mmol) and sodium benzoate (0.072 g, 0.5 mmol) in ethanol (10 ml) was added a solution of $Ni(NO_3)_2{\cdot}6H_2O$ (0.1455 g, 0.5 mmol) in distilled water (10 ml). The resulting solution was refluxed for 5 h at 333 K and filtrated. Green single crystals of (I) were obtained after 4 d. by slow evaporation of the filtrate.

Refinement

H atoms bonded to C atoms were placed in calculated positions (C—H = 0.93 Å for aromatic CH; 0.96 Å for methyl CH_3), and were included in the refinement in the riding model approximation, with U_{iso}(H) = 1.2U_{eq}(carrier C) (aromatic CH) or U_{iso}(H) = 1.5U_{eq}(carrier C) (methyl CH_3). The water H atoms were located in a difference map and were refined as riding to their O atoms, with O—H bonds fixed to 0.82 Å and U_{iso}(H) = 1.5 U_{eq}(carrier O).

Figures

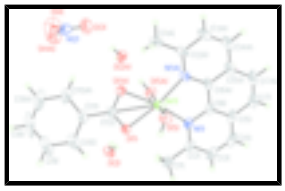

Fig. 1. The structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms. Symmetry code: (A) 1 − *x*, *y*, 3/2 − *z* for cation; 1 − *x*, *y*, 1/2 − *z* for anion.

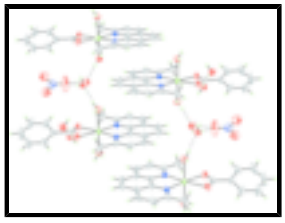

Fig. 2. Part of the crystal structure of (I), showing the formation of hydrogen-bonds (dashed lines) and π–π stacking interactions between dmphen ligands.

Diaqua(benzoato-κ^2*O*,*O*')(2,9-dimethyl-1,10-phenanthroline-κ^2*N*,*N*')nickel(II) nitrate dihydrate

Crystal data

$[Ni(C_7H_5O_2)(C_{14}H_{12}N_2)(H_2O)_2]NO_3{\cdot}2H_2O$	F_{000} = 1088
M_r = 522.15	D_x = 1.497 Mg m^{-3}
Orthorhombic, *Pbcn*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2n 2ab	Cell parameters from 3407 reflections
a = 10.4453 (9) Å	θ = 2.7–26.8º
b = 22.2586 (19) Å	μ = 0.89 mm^{-1}
c = 9.9660 (9) Å	*T* = 291 (2) K
V = 2317.1 (4) Å^3	Block, green
Z = 4	0.37 × 0.30 × 0.23 mm

Data collection

Bruker SMART CCD diffractometer	2129 independent reflections
Radiation source: fine-focus sealed tube	1723 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.019
T = 291(2) K	θ_{max} = 25.5º
φ and ω scans	θ_{min} = 2.7º
Absorption correction: multi-scan (SADABS; Bruker, 1997)	*h* = −12→12
T_{min} = 0.732, T_{max} = 0.817	*k* = −26→26
9175 measured reflections	*l* = −10→12

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.034	H-atom parameters constrained
$wR(F^2)$ = 0.098	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 1.0711P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max}$ = 0.002
2129 reflections	$\Delta\rho_{max}$ = 0.59 e Å^{-3}
158 parameters	$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.5000	0.661272 (16)	0.7500	0.03514 (16)
O1	0.43542 (16)	0.74343 (7)	0.83637 (16)	0.0478 (4)
O2	0.17794 (17)	0.78534 (8)	0.88233 (18)	0.0643 (5)
H1W	0.2518	0.7770	0.8587	0.096*
H2W	0.1234	0.7638	0.8475	0.096*
O3	0.5000	0.7955 (2)	0.2500	0.170 (3)
O4	0.5989 (3)	0.87694 (15)	0.2690 (3)	0.1113 (9)
O5	0.65977 (15)	0.66105 (7)	0.87457 (17)	0.0528 (4)
H4W	0.7245	0.6661	0.8294	0.079*
H3W	0.6625	0.6795	0.9468	0.079*
N1	0.41788 (16)	0.59084 (8)	0.85549 (19)	0.0407 (4)
N2	0.5000	0.84737 (19)	0.2500	0.0668 (10)
C1	0.2989 (3)	0.65071 (12)	1.0176 (3)	0.0645 (8)
H1A	0.3704	0.6778	1.0139	0.097*
H1B	0.2736	0.6451	1.1094	0.097*
H1C	0.2286	0.6673	0.9677	0.097*
C2	0.3362 (2)	0.59182 (11)	0.9585 (3)	0.0492 (6)
C3	0.2870 (2)	0.53789 (13)	1.0127 (3)	0.0627 (7)
H3	0.2291	0.5394	1.0835	0.075*
C4	0.3234 (3)	0.48420 (13)	0.9627 (3)	0.0667 (8)
H4A	0.2910	0.4489	0.9994	0.080*
C5	0.4098 (2)	0.48161 (11)	0.8558 (3)	0.0568 (7)
C6	0.4548 (2)	0.53665 (9)	0.8044 (3)	0.0437 (5)
C7	0.4568 (3)	0.42671 (12)	0.7992 (3)	0.0718 (9)
H7	0.4265	0.3903	0.8319	0.086*
C8	0.5000	0.9625 (2)	0.7500	0.125 (3)
H8	0.5000	1.0043	0.7500	0.150*
C9	0.4668 (3)	0.93192 (15)	0.8644 (6)	0.1001 (15)
H9	0.4455	0.9531	0.9417	0.120*
C10	0.4648 (2)	0.86985 (13)	0.8653 (4)	0.0662 (8)
H10	0.4402	0.8491	0.9422	0.079*
C11	0.5000	0.83864 (14)	0.7500	0.0491 (9)
C12	0.5000	0.77188 (15)	0.7500	0.0410 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0321 (2)	0.0313 (2)	0.0420 (3)	0.000	0.00452 (16)	0.000
O1	0.0499 (10)	0.0394 (9)	0.0541 (10)	0.0009 (7)	0.0145 (8)	0.0002 (7)
O2	0.0565 (11)	0.0593 (11)	0.0772 (13)	0.0097 (9)	0.0016 (9)	−0.0154 (9)
O3	0.220 (6)	0.066 (3)	0.224 (6)	0.000	0.142 (5)	0.000
O4	0.0621 (15)	0.122 (2)	0.150 (3)	−0.0057 (16)	−0.0105 (15)	0.0139 (18)
O5	0.0382 (9)	0.0668 (11)	0.0533 (10)	−0.0016 (7)	−0.0021 (8)	−0.0098 (8)

N1	0.0330 (9)	0.0399 (10)	0.0491 (11)	−0.0007 (8)	−0.0024 (8)	0.0093 (8)
N2	0.048 (2)	0.084 (3)	0.069 (2)	0.000	0.0137 (16)	0.000
C1	0.0607 (17)	0.0714 (18)	0.0614 (17)	0.0167 (14)	0.0241 (14)	0.0206 (14)
C2	0.0338 (11)	0.0587 (15)	0.0551 (14)	0.0011 (10)	0.0013 (11)	0.0180 (11)
C3	0.0396 (12)	0.0765 (19)	0.0719 (18)	−0.0099 (13)	−0.0005 (13)	0.0316 (15)
C4	0.0518 (15)	0.0595 (17)	0.089 (2)	−0.0187 (13)	−0.0211 (15)	0.0331 (15)
C5	0.0528 (14)	0.0438 (14)	0.0737 (17)	−0.0105 (11)	−0.0276 (14)	0.0145 (12)
C6	0.0386 (11)	0.0337 (12)	0.0589 (14)	−0.0037 (9)	−0.0149 (10)	0.0057 (10)
C7	0.087 (2)	0.0361 (13)	0.093 (2)	−0.0081 (13)	−0.0394 (18)	0.0078 (13)
C8	0.050 (3)	0.031 (3)	0.293 (11)	0.000	−0.042 (4)	0.000
C9	0.0472 (16)	0.0515 (19)	0.202 (5)	0.0043 (14)	−0.019 (2)	−0.050 (2)
C10	0.0400 (13)	0.0536 (16)	0.105 (2)	0.0019 (12)	−0.0031 (14)	−0.0244 (16)
C11	0.0326 (16)	0.0364 (18)	0.078 (3)	0.000	0.0001 (16)	0.000
C12	0.0357 (16)	0.0364 (17)	0.0510 (19)	0.000	0.0030 (14)	0.000

Geometric parameters (Å, °)

Ni1—N1	2.0734 (18)	C2—C3	1.413 (3)
Ni1—N1^{i}	2.0734 (18)	C3—C4	1.349 (4)
Ni1—O5	2.0800 (16)	C3—H3	0.9300
Ni1—O5^{i}	2.0800 (16)	C4—C5	1.398 (4)
Ni1—O1^{i}	2.1307 (15)	C4—H4A	0.9300
Ni1—O1	2.1308 (15)	C5—C6	1.409 (3)
Ni1—C12	2.462 (3)	C5—C7	1.433 (4)
O1—C12	1.264 (2)	C6—C6^{i}	1.438 (5)
O2—H1W	0.8271	C7—C7^{i}	1.332 (7)
O2—H2W	0.8214	C7—H7	0.9300
O3—N2	1.155 (5)	C8—C9	1.373 (5)
O4—N2	1.239 (3)	C8—C9^{i}	1.373 (5)
O5—H4W	0.8200	C8—H8	0.9300
O5—H3W	0.8291	C9—C10	1.382 (5)
N1—C2	1.335 (3)	C9—H9	0.9300
N1—C6	1.365 (3)	C10—C11	1.393 (3)
N2—O4^{ii}	1.239 (3)	C10—H10	0.9300
C1—C2	1.489 (4)	C11—C10^{i}	1.392 (3)
C1—H1A	0.9600	C11—C12	1.486 (5)
C1—H1B	0.9600	C12—O1^{i}	1.264 (2)
C1—H1C	0.9600		
N1—Ni1—N1^{i}	81.75 (10)	H1B—C1—H1C	109.5
N1—Ni1—O5	91.57 (7)	N1—C2—C3	120.8 (2)
N1^{i}—Ni1—O5	88.22 (7)	N1—C2—C1	119.1 (2)
N1—Ni1—O5^{i}	88.22 (7)	C3—C2—C1	120.1 (2)
N1^{i}—Ni1—O5^{i}	91.57 (7)	C4—C3—C2	120.6 (3)
O5—Ni1—O5^{i}	179.72 (9)	C4—C3—H3	119.7
N1—Ni1—O1^{i}	169.99 (7)	C2—C3—H3	119.7
N1^{i}—Ni1—O1^{i}	108.25 (7)	C3—C4—C5	120.0 (2)

O5—Ni1—O1^{i}	89.38 (7)	C3—C4—H4A	120.0
O5^{i}—Ni1—O1^{i}	90.86 (7)	C5—C4—H4A	120.0
N1—Ni1—O1	108.25 (7)	C4—C5—C6	117.2 (2)
N1^{i}—Ni1—O1	169.99 (7)	C4—C5—C7	123.8 (2)
O5—Ni1—O1	90.86 (7)	C6—C5—C7	119.0 (3)
O5^{i}—Ni1—O1	89.38 (7)	N1—C6—C5	122.6 (2)
O1^{i}—Ni1—O1	61.76 (8)	N1—C6—C6^{i}	117.83 (13)
N1—Ni1—C12	139.13 (5)	C5—C6—C6^{i}	119.55 (17)
N1^{i}—Ni1—C12	139.13 (5)	C7^{i}—C7—C5	121.46 (17)
O5—Ni1—C12	90.14 (5)	C7^{i}—C7—H7	119.3
O5^{i}—Ni1—C12	90.14 (5)	C5—C7—H7	119.3
O1^{i}—Ni1—C12	30.88 (4)	C9—C8—C9^{i}	120.5 (5)
O1—Ni1—C12	30.88 (4)	C9—C8—H8	119.7
C12—O1—Ni1	89.19 (15)	C9^{i}—C8—H8	119.7
H1W—O2—H2W	113.3	C8—C9—C10	120.3 (4)
Ni1—O5—H4W	109.5	C8—C9—H9	119.8
Ni1—O5—H3W	123.0	C10—C9—H9	119.8
H4W—O5—H3W	112.4	C9—C10—C11	119.3 (4)
C2—N1—C6	118.81 (19)	C9—C10—H10	120.3
C2—N1—Ni1	129.93 (16)	C11—C10—H10	120.3
C6—N1—Ni1	111.24 (15)	C10^{i}—C11—C10	120.1 (4)
O3—N2—O4^{ii}	122.1 (2)	C10^{i}—C11—C12	119.93 (18)
O3—N2—O4	122.1 (2)	C10—C11—C12	119.93 (18)
O4^{ii}—N2—O4	115.8 (5)	O1—C12—O1^{i}	119.8 (3)
C2—C1—H1A	109.5	O1—C12—C11	120.07 (15)
C2—C1—H1B	109.5	O1^{i}—C12—C11	120.08 (15)
H1A—C1—H1B	109.5	O1—C12—Ni1	59.93 (15)
C2—C1—H1C	109.5	O1^{i}—C12—Ni1	59.92 (15)
H1A—C1—H1C	109.5	C11—C12—Ni1	180.0
N1—Ni1—O1—C12	−179.22 (8)	C2—N1—C6—C6^{i}	−178.6 (2)
N1^{i}—Ni1—O1—C12	4.2 (4)	Ni1—N1—C6—C6^{i}	2.9 (3)
O5—Ni1—O1—C12	88.84 (9)	C4—C5—C6—N1	0.4 (3)
O5^{i}—Ni1—O1—C12	−91.31 (9)	C7—C5—C6—N1	−177.9 (2)
O1^{i}—Ni1—O1—C12	0.0	C4—C5—C6—C6^{i}	179.2 (3)
N1^{i}—Ni1—N1—C2	−179.3 (2)	C7—C5—C6—C6^{i}	0.9 (4)
O5—Ni1—N1—C2	92.7 (2)	C4—C5—C7—C7^{i}	−177.3 (3)
O5^{i}—Ni1—N1—C2	−87.5 (2)	C6—C5—C7—C7^{i}	0.9 (5)
O1^{i}—Ni1—N1—C2	−2.7 (5)	C9^{i}—C8—C9—C10	−0.8 (2)
O1—Ni1—N1—C2	1.3 (2)	C8—C9—C10—C11	1.6 (4)
C12—Ni1—N1—C2	0.7 (2)	C9—C10—C11—C10^{i}	−0.8 (2)
N1^{i}—Ni1—N1—C6	−1.03 (11)	C9—C10—C11—C12	179.2 (2)
O5—Ni1—N1—C6	−89.00 (15)	Ni1—O1—C12—O1^{i}	0.000 (1)
O5^{i}—Ni1—N1—C6	90.82 (15)	Ni1—O1—C12—C11	180.0

O1^{i}—Ni1—N1—C6	175.6 (3)	C10^{i}—C11—C12—O1	−159.65 (15)
O1—Ni1—N1—C6	179.58 (14)	C10—C11—C12—O1	20.35 (15)
C12—Ni1—N1—C6	178.97 (11)	C10^{i}—C11—C12—O1^{i}	20.35 (15)
C6—N1—C2—C3	−1.0 (3)	C10—C11—C12—O1^{i}	−159.65 (15)
Ni1—N1—C2—C3	177.21 (17)	N1^{i}—Ni1—C12—O1	−178.88 (12)
C6—N1—C2—C1	178.0 (2)	O5—Ni1—C12—O1	−91.44 (11)
Ni1—N1—C2—C1	−3.8 (3)	O5^{i}—Ni1—C12—O1	88.56 (11)
N1—C2—C3—C4	1.1 (4)	O1^{i}—Ni1—C12—O1	180.0
C1—C2—C3—C4	−177.9 (3)	N1—Ni1—C12—O1^{i}	−178.87 (12)
C2—C3—C4—C5	−0.4 (4)	N1^{i}—Ni1—C12—O1^{i}	1.12 (12)
C3—C4—C5—C6	−0.3 (4)	O5—Ni1—C12—O1^{i}	88.56 (11)
C3—C4—C5—C7	177.9 (3)	O5^{i}—Ni1—C12—O1^{i}	−91.44 (11)
C2—N1—C6—C5	0.2 (3)	O1—Ni1—C12—O1^{i}	180.000 (1)
Ni1—N1—C6—C5	−178.29 (18)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1W···O1	0.83	2.07	2.883 (2)	167
O2—H2W···O3^{iii}	0.82	2.08	2.903 (3)	174
O5—H3W···O2^{iv}	0.83	1.88	2.707 (2)	174
O5—H4W···O4^{v}	0.82	2.16	2.860 (3)	143

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

Fig. 1

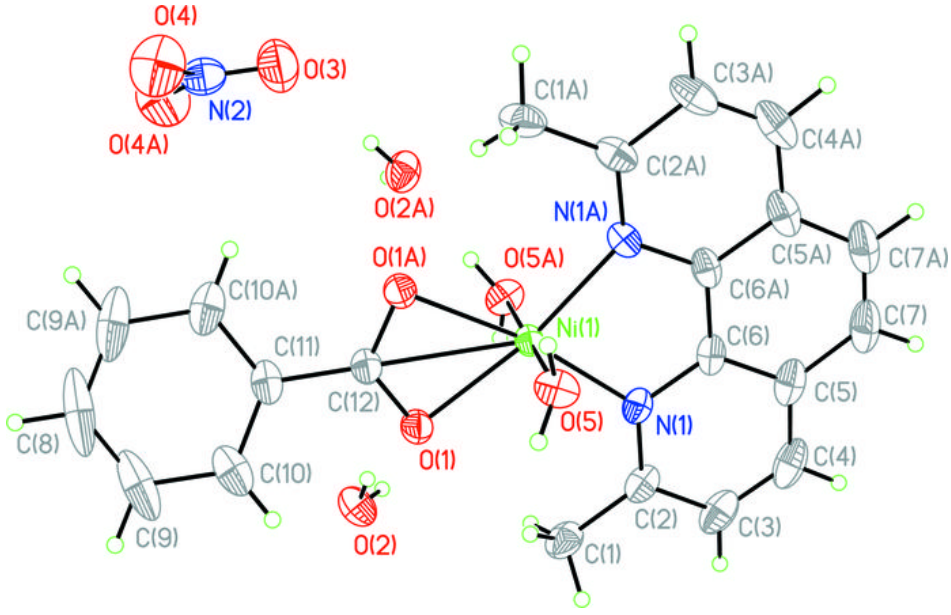
O(4)
O(3)
N(2)
O(4A)
O(2A)
C(1A)
C(3A)
C(4A)
C(2A)
N(1A)
C(5A)
C(7A)
C(6A)
C(7)
O(1A)
O(5A)
C(10A)
C(9A)
Ni(1)
C(6)
C(11)
C(12)
C(5)
O(5)
N(1)
O(1)
C(8)
C(10)
C(4)
C(2)
C(3)
C(9)
O(2)
C(1)

Fig. 2