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Diaqua(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')(3-hydroxybenzoato-κ^2O,O')-nickel(II) nitrate

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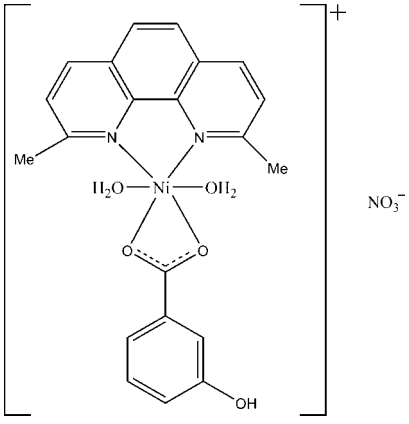
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.033; wR factor = 0.084; data-to-parameter ratio = 12.7.

The asymmetric unit of the title compound, $[Ni(C_7H_5O_3)(C_{14}H_{12}N_2)(H_2O)_2]NO_3$, comprises one half of the Ni^{II} complex cation and one half of the non-coordinated nitrate anion, as both the Ni atom and the N and one O atoms of the anion lie on twofold rotation axes. The Ni^{2+} cation is coordinated by a bidentate 2,9-dimethyl-1,10-phenanthroline (dmphen) ligand, two water molecules and a bidentate 3-hydroxybenzoate anion in a distorted octahedral environment. The OH group of the benzoate is disordered over two positions with equal occupancy. An extensive series of O—H···O hydrogen bonds leads to a supramolecular network structure.

Related literature

For the structure of a closely related complex, see: Xuan *et al.* (2007).



Experimental

Crystal data

$[Ni(C_7H_5O_3)(C_{14}H_{12}N_2)(H_2O)_2]NO_3$
M_r = 501.11
Monoclinic, $C2/c$
a = 10.9278 (15) Å
b = 28.509 (4) Å
c = 7.9738 (11) Å
β = 119.311 (1)°
V = 2166.2 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.95 mm^{-1}
T = 293 (2) K
0.39 × 0.18 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.708, T_{max} = 0.950
8026 measured reflections
2025 independent reflections
1688 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.085
S = 0.99
2025 reflections
159 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H2W···O1^{i}	0.83	1.96	2.784 (2)	173
O3—H1W···O4	0.83	1.97	2.7746 (19)	166
O2—H2···O5^{i}	0.82	2.01	2.692 (4)	140

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

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: SJ2386).

References

Bruker (1997). *SMART*, *SAINT*, *SADABS* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Xuan, X.-P., Zhao, P.-Z. & Tang, Q.-H. (2007). *Acta Cryst.* E**63**, m2405.

  doi:10.1107/S1600536807052944

supplementary materials

Acta Cryst. (2007). E**63**, m2856 [**doi:10.1107/S1600536807052944**]

Diaqua(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')(3-hydroxybenzoato-κ^2O,O')nickel(II) nitrate

X. Xuan and P. Zhao

Comment

The crystal structure of a compound containing the $[Ni(dmphen)(benzoate]^{2+}$ fragment has been reported (Xuan *et al.* 2007)(dmphen is 2,9-dimethyl-1,10-phenanthroline) and we report here the structure of a closely related Ni^{II} complex, (I), Fig. 1.

The Ni^{II} atom is located on a twofold symmetry axis and is six-coordinated by two N atoms from the dmphen ligand, O atoms from two water molecules and is also chelated by two O atoms from carboxyl group of the 3-hydroxy-benzoate anion. The NiO_4N_2unit is in a a distorted octahedral geometry, with the O atoms of two water molecules occupying axial positions with a Ni1—O3 distance of 2.0393 (15) Å. The equatorial planes are defined by the N atoms of dmphen and the carboxyl O atoms of the 3-hydroxy-benzoate anion. The OH group on phenyl ring of the benzoato ligand is disordered over two positions with site occupancy factors of 0.5.

In the crystal structure, the uncoordinated nitrate anion, lying on twofold axis, links to the Ni^{II} complex cation *via* O—H···O hydrogen bonds (Table 1 and Figure 2). In the crystal molecules are linked into a supramolecular network structure by O_{water}—*H*···$O_{carbonyl}$ and O_{water}—H···$O_{nitrate}$ hydrogen bonding.

Experimental

To a solution of 2,9-dimethyl-1,10-phenanthroline ($C_{14}H_{12}N_2{\cdot}0.5H_2O$, 0.1089 g, 0.5 mmol), 3-hydroxy-benzoate (0.0696 g, 0.5 mmol) and sodium hydroxide (0.01859 g, 0.5 mmol) in ethanol/water (*v*:*v*=1:1, 20 ml) was added a solution of $Ni(NO_3)_2{\cdot}6H_2O$ (0.1460 g, 0.5 mmol) in distilled water (5 ml). The resulting solution was stirred for 4 h at 323 K and then a pale green precipitate was filtered. Blue single crystals of (I) were obtained by slow evaporation of the filtrate over 90 days.

Refinement

The OH group of the benzoate anion is disordered over two symmetry-related positions with site occupancy factors of 0.5. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with d(C—H) = 0.93 Å, U_{iso}=1.2U_{eq} (C) for aromatic and 0.96 Å, U_{iso} = 1.5U_{eq} (C) for CH_3 atoms. The hydroxyl H atoms were placed in calculated positions (O—H =0.82 Å) and refined with free torsion angles to fit the electron density, with U_{iso}(H) = 1.5 U_{eq}(O).

Figures

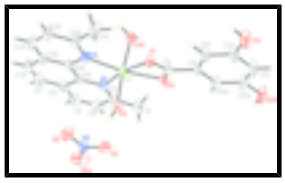

Fig. 1. The structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms. Symmetry code: (A) 1 − *x*, *y*, 3/2 − *z* for the cation; 1 − *x*, *y*, 1/2 − *z* for the anion.

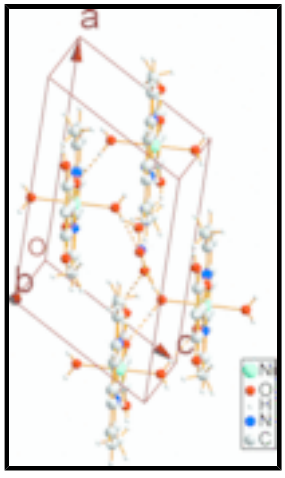

Fig. 2. Part of the crystal packing of (I), showing the formation of hydrogen-bonds drawn as dashed lines.

Diaqua(2,9-dimethyl-1,10-phenanthroline-κ^2*N*,*N*')(3-hydroxybenzoato-\ κ^2*O*,*O*')nickel(II) nitrate

Crystal data

$[Ni(C_7H_5O_3)(C_{14}H_{12}N_2)(H_2O)_2]NO_3$	F_{000} = 1036
M_r = 501.11	D_x = 1.537 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 2940 reflections
a = 10.9278 (15) Å	θ = 2.7–25.6º
b = 28.509 (4) Å	μ = 0.95 mm^{-1}
c = 7.9738 (11) Å	*T* = 293 (2) K
β = 119.311 (1)º	Block, blue
V = 2166.2 (5) Å^3	0.39 × 0.18 × 0.05 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	2025 independent reflections
Radiation source: fine-focus sealed tube	1688 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.055
T = 293(2) K	θ_{max} = 25.5º
φ and ω scans	θ_{min} = 2.7º
Absorption correction: multi-scan (SADABS; Bruker, 1997)	*h* = −13→13

T_{min} = 0.708, T_{max} = 0.950	k = −34→34
8026 measured reflections	l = −9→9

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.033	H-atom parameters constrained
$wR(F^2)$ = 0.085	$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.99	$(\Delta/\sigma)_{max}$ = 0.001
2025 reflections	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
159 parameters	$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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}	Occ. (<1)
Ni1	0.5000	0.294675 (12)	0.7500	0.03422 (15)	
O1	0.39684 (13)	0.22911 (5)	0.7403 (2)	0.0397 (4)	
O2	0.3150 (4)	0.05478 (12)	0.7986 (8)	0.0832 (14)	0.50

H2	0.2666	0.0711	0.8279	0.125*	0.50
O3	0.38872 (15)	0.29142 (5)	0.4572 (2)	0.0448 (4)	
H1W	0.4134	0.3082	0.3948	0.067*	
H2W	0.3025	0.2877	0.3996	0.067*	
O4	0.5000	0.33471 (10)	0.2500	0.0957 (11)	
O5	0.4233 (3)	0.39816 (10)	0.2940 (3)	0.1127 (9)	
N1	0.61633 (17)	0.35019 (6)	0.7301 (3)	0.0410 (4)	
N2	0.5000	0.37810 (10)	0.2500	0.0479 (6)	
C1	0.7845 (3)	0.30371 (9)	0.6822 (5)	0.0729 (9)	
H1A	0.8548	0.2926	0.8059	0.109*	
H1B	0.8252	0.3077	0.6003	0.109*	
H1C	0.7094	0.2813	0.6256	0.109*	
C2	0.7287 (2)	0.34941 (9)	0.7052 (4)	0.0514 (6)	
C3	0.7936 (3)	0.39192 (10)	0.6978 (4)	0.0702 (8)	
H3A	0.8727	0.3910	0.6827	0.084*	
C4	0.7417 (3)	0.43345 (11)	0.7125 (4)	0.0780 (9)	
H4	0.7856	0.4611	0.7086	0.094*	
C5	0.6220 (3)	0.43551 (9)	0.7335 (4)	0.0629 (7)	
C6	0.5625 (2)	0.39226 (7)	0.7414 (3)	0.0457 (6)	
C7	0.5579 (4)	0.47808 (9)	0.7422 (5)	0.0859 (11)	
H7	0.5977	0.5065	0.7369	0.103*	
C8	0.5000	0.20663 (10)	0.7500	0.0362 (7)	
C9	0.5000	0.15418 (10)	0.7500	0.0408 (7)	
C10	0.3994 (2)	0.12960 (8)	0.7713 (4)	0.0521 (6)	
H10	0.3314	0.1458	0.7859	0.063*	
C11	0.3989 (3)	0.08092 (9)	0.7711 (5)	0.0688 (8)	
C12	0.5000	0.05679 (12)	0.7500	0.0792 (13)	
H12	0.5000	0.0242	0.7500	0.095*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0248 (2)	0.0285 (2)	0.0475 (3)	0.000	0.01626 (18)	0.000
O1	0.0278 (7)	0.0326 (8)	0.0590 (10)	0.0008 (6)	0.0215 (7)	−0.0001 (7)
O2	0.075 (3)	0.0368 (19)	0.171 (4)	−0.0047 (18)	0.086 (3)	0.007 (2)
O3	0.0337 (8)	0.0483 (9)	0.0480 (9)	−0.0074 (6)	0.0167 (7)	0.0026 (7)
O4	0.179 (4)	0.0497 (16)	0.092 (2)	0.000	0.092 (2)	0.000
O5	0.1028 (18)	0.151 (2)	0.0926 (17)	0.0680 (17)	0.0541 (15)	0.0065 (15)
N1	0.0319 (9)	0.0374 (10)	0.0459 (11)	−0.0045 (8)	0.0130 (8)	0.0029 (8)
N2	0.0437 (15)	0.0499 (17)	0.0535 (17)	0.000	0.0266 (14)	0.000
C1	0.0514 (16)	0.0655 (18)	0.122 (3)	0.0110 (13)	0.0580 (18)	0.0287 (17)
C2	0.0347 (12)	0.0551 (15)	0.0592 (15)	−0.0078 (10)	0.0190 (11)	0.0095 (12)
C3	0.0497 (16)	0.074 (2)	0.086 (2)	−0.0219 (14)	0.0321 (15)	0.0072 (16)
C4	0.084 (2)	0.0551 (18)	0.092 (2)	−0.0329 (16)	0.0408 (19)	−0.0012 (16)
C5	0.0782 (19)	0.0424 (14)	0.0647 (17)	−0.0178 (13)	0.0324 (15)	−0.0047 (12)
C6	0.0495 (14)	0.0340 (12)	0.0448 (13)	−0.0057 (10)	0.0161 (11)	−0.0012 (9)
C7	0.130 (3)	0.0309 (13)	0.106 (2)	−0.0159 (15)	0.065 (3)	−0.0031 (15)
C8	0.0290 (15)	0.0322 (15)	0.0431 (17)	0.000	0.0142 (13)	0.000

C9	0.0350 (16)	0.0311 (16)	0.0521 (19)	0.000	0.0180 (15)	0.000
C10	0.0434 (13)	0.0370 (12)	0.0794 (18)	0.0008 (10)	0.0327 (13)	0.0045 (12)
C11	0.0608 (17)	0.0374 (13)	0.114 (2)	−0.0041 (12)	0.0470 (17)	0.0067 (14)
C12	0.080 (3)	0.0290 (18)	0.139 (4)	0.000	0.062 (3)	0.000

Geometric parameters (Å, °)

Ni1—O3^{i}	2.0393 (15)	C2—C3	1.420 (3)
Ni1—O3	2.0393 (15)	C3—C4	1.342 (4)
Ni1—N1^{i}	2.0839 (17)	C3—H3A	0.9300
Ni1—N1	2.0840 (17)	C4—C5	1.398 (4)
Ni1—O1^{i}	2.1645 (14)	C4—H4	0.9300
Ni1—O1	2.1647 (14)	C5—C6	1.410 (3)
O1—C8	1.2658 (19)	C5—C7	1.420 (4)
O2—C11	1.281 (4)	C6—C6^{i}	1.437 (5)
O2—H2	0.8200	C7—C7^{i}	1.332 (7)
O3—H1W	0.8251	C7—H7	0.9300
O3—H2W	0.8281	C8—O1^{i}	1.2659 (19)
O4—N2	1.237 (4)	C8—C9	1.495 (4)
O5—N2	1.200 (2)	C9—C10^{i}	1.382 (3)
N1—C2	1.337 (3)	C9—C10	1.382 (3)
N1—C6	1.358 (3)	C10—C11	1.388 (3)
N2—O5^{ii}	1.200 (2)	C10—H10	0.9300
C1—C2	1.487 (3)	C11—C12	1.380 (3)
C1—H1A	0.9600	C12—C11^{i}	1.380 (3)
C1—H1B	0.9600	C12—H12	0.9300
C1—H1C	0.9600		
O3^{i}—Ni1—O3	174.80 (8)	N1—C2—C1	119.6 (2)
O3^{i}—Ni1—N1^{i}	89.51 (6)	C3—C2—C1	120.0 (2)
O3—Ni1—N1^{i}	94.45 (6)	C4—C3—C2	120.6 (3)
O3^{i}—Ni1—N1	94.44 (6)	C4—C3—H3A	119.7
O3—Ni1—N1	89.51 (6)	C2—C3—H3A	119.7
N1^{i}—Ni1—N1	81.18 (10)	C3—C4—C5	120.5 (2)
O3^{i}—Ni1—O1^{i}	84.94 (6)	C3—C4—H4	119.8
O3—Ni1—O1^{i}	90.56 (6)	C5—C4—H4	119.8
N1^{i}—Ni1—O1^{i}	168.37 (6)	C4—C5—C6	116.6 (3)
N1—Ni1—O1^{i}	109.39 (6)	C4—C5—C7	123.7 (2)
O3^{i}—Ni1—O1	90.57 (6)	C6—C5—C7	119.7 (3)
O3—Ni1—O1	84.93 (6)	N1—C6—C5	123.0 (2)
N1^{i}—Ni1—O1	109.40 (6)	N1—C6—C6^{i}	117.96 (12)
N1—Ni1—O1	168.37 (6)	C5—C6—C6^{i}	119.02 (16)
O1^{i}—Ni1—O1	60.57 (7)	C7^{i}—C7—C5	121.26 (16)
C8—O1—Ni1	90.13 (13)	C7^{i}—C7—H7	119.4
C11—O2—H2	109.5	C5—C7—H7	119.4

Ni1—O3—H1W	118.5	O1—C8—O1^{i}	119.2 (3)
Ni1—O3—H2W	121.3	O1—C8—C9	120.42 (13)
H1W—O3—H2W	111.0	O1^{i}—C8—C9	120.42 (13)
C2—N1—C6	118.93 (19)	C10^{i}—C9—C10	119.1 (3)
C2—N1—Ni1	129.63 (16)	C10^{i}—C9—C8	120.46 (15)
C6—N1—Ni1	111.43 (14)	C10—C9—C8	120.47 (15)
O5—N2—O5^{ii}	123.1 (4)	C9—C10—C11	120.7 (2)
O5—N2—O4	118.5 (2)	C9—C10—H10	119.7
O5^{ii}—N2—O4	118.5 (2)	C11—C10—H10	119.7
C2—C1—H1A	109.5	O2—C11—C12	114.4 (3)
C2—C1—H1B	109.5	O2—C11—C10	125.8 (3)
H1A—C1—H1B	109.5	C12—C11—C10	119.7 (3)
C2—C1—H1C	109.5	C11—C12—C11^{i}	120.2 (3)
H1A—C1—H1C	109.5	C11—C12—H12	119.9
H1B—C1—H1C	109.5	C11^{i}—C12—H12	119.9
N1—C2—C3	120.4 (2)		
O3^{i}—Ni1—O1—C8	−83.86 (8)	C3—C4—C5—C7	−177.4 (3)
O3—Ni1—O1—C8	93.52 (8)	C2—N1—C6—C5	−1.8 (3)
N1^{i}—Ni1—O1—C8	−173.54 (7)	Ni1—N1—C6—C5	179.46 (19)
N1—Ni1—O1—C8	31.8 (3)	C2—N1—C6—C6^{i}	176.9 (2)
O1^{i}—Ni1—O1—C8	0.0	Ni1—N1—C6—C6^{i}	−1.8 (3)
O3^{i}—Ni1—N1—C2	93.27 (19)	C4—C5—C6—N1	0.1 (4)
O3—Ni1—N1—C2	−83.34 (19)	C7—C5—C6—N1	178.7 (2)
N1^{i}—Ni1—N1—C2	−177.9 (2)	C4—C5—C6—C6^{i}	−178.6 (3)
O1^{i}—Ni1—N1—C2	7.1 (2)	C7—C5—C6—C6^{i}	−0.1 (4)
O1—Ni1—N1—C2	−22.0 (4)	C4—C5—C7—C7^{i}	178.4 (4)
O3^{i}—Ni1—N1—C6	−88.19 (15)	C6—C5—C7—C7^{i}	0.0 (6)
O3—Ni1—N1—C6	95.20 (15)	Ni1—O1—C8—O1^{i}	0.000 (1)
N1^{i}—Ni1—N1—C6	0.62 (11)	Ni1—O1—C8—C9	180.0
O1^{i}—Ni1—N1—C6	−174.37 (13)	O1—C8—C9—C10^{i}	169.33 (14)
O1—Ni1—N1—C6	156.5 (2)	O1^{i}—C8—C9—C10^{i}	−10.67 (14)
C6—N1—C2—C3	2.3 (3)	O1—C8—C9—C10	−10.67 (14)
Ni1—N1—C2—C3	−179.25 (18)	O1^{i}—C8—C9—C10	169.33 (14)
C6—N1—C2—C1	−176.8 (2)	C10^{i}—C9—C10—C11	−0.10 (19)
Ni1—N1—C2—C1	1.6 (3)	C8—C9—C10—C11	179.90 (19)
N1—C2—C3—C4	−1.1 (4)	C9—C10—C11—O2	176.5 (4)
C1—C2—C3—C4	178.0 (3)	C9—C10—C11—C12	0.2 (4)
C2—C3—C4—C5	−0.6 (5)	O2—C11—C12—C11^{i}	−176.8 (4)
C3—C4—C5—C6	1.1 (4)	C10—C11—C12—C11^{i}	−0.10 (19)

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*

O3—H2W···O1^{iii}	0.83	1.96	2.784 (2)	173
O3—H1W···O4	0.83	1.97	2.7746 (19)	166
O2—H2···O5^{iii}	0.82	2.01	2.692 (4)	140

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

Fig. 1

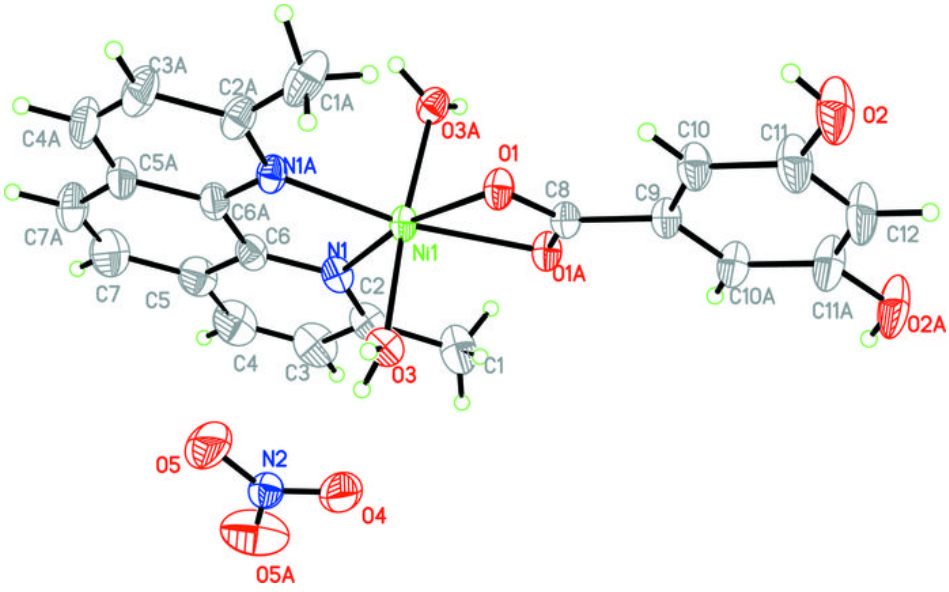
C3A
C2A
C1A
C4A
C5A
N1A
C6A
C7A
C6
N1
C7
C5
C2
C4
C3
O3
C1
O3A
O1
C8
Ni1
O1A
C9
C10
C11
O2
C12
C10A
C11A
O2A
O5
N2
O4
O5A

Fig. 2