Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Diaquabis(1,10-phenanthroline-κ^2N,N')-nickel(II) diperchlorate 0.4-hydrate

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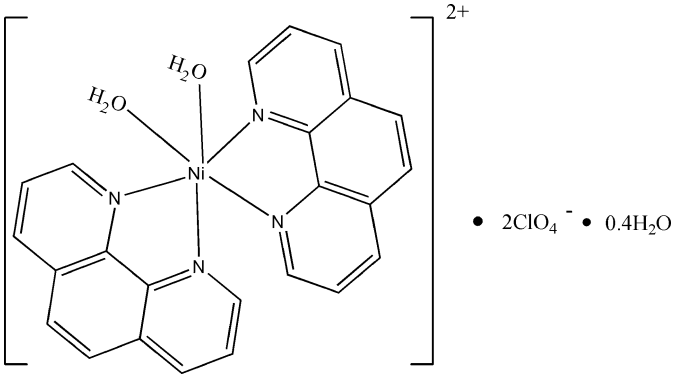
Received 5 August 2007; accepted 5 September 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.012 Å; H-atom completeness 97%; disorder in solvent or counterion; R factor = 0.071; wR factor = 0.262; data-to-parameter ratio = 14.5.

The title complex, $[Ni(C_{12}H_8N_2)_2(H_2O)_2](ClO_4)_2\cdot 0.4H_2O$, possesses crystallographically imposed C_2 symmetry. The Ni^{II} atom is coordinated by four N atoms from two 1,10-phenanthroline ligands and two water molecules in a distorted octahedral coordination geometry. The packing is governed by intermolecular hydrogen bonds and a π–π stacking interaction with a centroid-to-centroid distance of 3.650 (2) Å.

Related literature

For related literature, see: Deisenhofer & Michel (1989); Li *et al.* (2005); Pan & Xu (2004); Wu *et al.* (2003).



Experimental

Crystal data

$[Ni(C_{12}H_8N_2)_2(H_2O)_2](ClO_4)_2\cdot 0.4H_2O$
M_r = 661.26
Monoclinic, $C2/c$
a = 18.2558 (6) Å
b = 15.9362 (6) Å
c = 11.7096 (4) Å
β = 110.591 (2)°
V = 3189.02 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.83 mm^{-1}
T = 293 (2) K
0.26 × 0.20 × 0.18 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.827, T_{max} = 0.867
13780 measured reflections
3488 independent reflections
1861 reflections with $I > 2\sigma(I)$
R_{int} = 0.071

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.262
S = 1.08
3488 reflections
241 parameters
97 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N2	2.068 (5)	Ni1—O1*W*	2.098 (4)
Ni1—N1	2.089 (5)		
N2^i—Ni1—N2	171.9 (3)	N2—Ni1—O1*W*	93.11 (17)
N2^i—Ni1—N1	94.27 (18)	N1^i—Ni1—O1*W*	171.63 (17)
N2—Ni1—N1	80.10 (19)	N1—Ni1—O1*W*	92.70 (18)
N1^i—Ni1—N1	92.5 (3)	O1*W*—Ni1—O1*W*^{i}	83.0 (2)
N2^i—Ni1—O1*W*	92.95 (17)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O1*B*^{ii}	0.82	1.99	2.75 (2)	154
O1*W*—H1*W*···O1*A*^{ii}	0.82	1.97	2.787 (9)	169
O1*W*—H2*W*···O4*A*^{iii}	0.83	1.91	2.733 (8)	174
O1*W*—H2*W*···O4*B*^{iii}	0.83	2.14	2.87 (2)	148

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 1999); 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, 1998); software used to prepare material for publication: *SHELXTL*.

The work was supported by the Natural Science Foundation of Guang Dong Province (grant No. 7005808) and South China Normal University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AV3106).

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 doi:10.1107/S1600536807043565

supplementary materials

Acta Cryst. (2007). E**63**, m2515 [**doi:10.1107/S1600536807043565**]

Diaquabis(1,10-phenanthroline-κ^2N,N')nickel(II) diperchlorate 0.4-hydrate

X.-Y. Tang, Y.-C. Qiu, F. Sun and S.-T. Yue

Comment

We have been recently interested in the nature of π-π stacking as it plays an important role in some biological processes (Deisenhofer & Michel, 1989). A series of metal complexes incorporating different aromatic ligands has been prepared and their crystal structures provide useful information about π-π stacking (Wu *et al.*, 2003; Pan & Xu, 2004; Li *et al.*, 2005). As part of ongoing investigations, the title complex, incorporating 1,10-phenanthroline, (I), has been prepared.

As illustrated in Fig. 1, the Ni^{II} atom lies on a C_2 symmetry position and has a distorted octahedral geometry with six coordinating atoms: four N atoms from two 1,10-phenanthroline ligands, two O from two water molecules (Table 1). A depleted hydration water molecule (occupation: 1/5) completes the structure. Intermolecular O—H···O hydrogen bonding involving the coordinating water molecules as donors and the perchlorate O atoms as acceptors forms chains, which are further assembled *via* π-π stacking interactions between adjacent phen rings, thus forming a supramolecular network structure (Fig. 2; Table 2). The centroid-centroid distance of adjacent phen rings (at $1/2 - x,1/2 - y,1 - z$) is 3.650 (2) Å, indicating a normal π-π interaction.

Experimental

The title complex was prepared by addition of a stoichiometric amount of 1,10-phenanthroline (2 mmol) to warm aqueous solution of nickel perchlorate (2 mmol) (about 333–343 K). The PH was then adjusted from 5.5 to 6.5 with NaOH (10 mmol). The resulting solution was put into a 30 ml stainless steel reaction bottle with the gather four fluorine ethylene inner pad, sealed up completely and stored at 443 K for 144 h. Cyan single crystals were obtained after cooling to room temperature.

Refinement

The occupation factor of a depleted hydration water molecule (O2W) was refined in the initial stages, and kept fixed at the latest cycles of refinement; the corresponding H atoms were disregarded from the model. The disorder of perchlorate unit was refined and split into two positions with an occupancy ratio of (0.721 (1):0.279 (1)). The Cl—O distances were restrained to be 1.44 Å, both within a standard deviation of 0.01 Å. Carbon-bound H atoms were placed at calculated positions and were treated as riding on the parent C atoms with C—H = 0.93 Å and with U_{iso}(H) = 1.2 U_{eq}(C). Water H atoms were tentatively located in difference Fourier maps and were refined with distance restraints of O–H = 0.82 Å and H···H = 1.29 Å, each within a standard deviation of 0.01 Å.

Figures

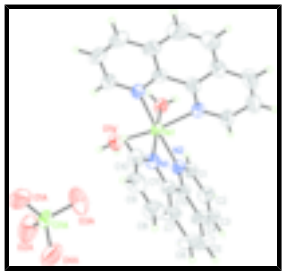

Fig. 1. The structure of (I), showing the atomic numbering scheme. Non-H atoms are shown as 30% probability displacement ellipsoids. The disordered perchlorate ions were omitted for clarity. Symmetry code: as in Table 1.

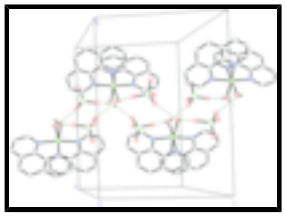

Fig. 2. A packing view of (I), showing the intermolecular hydrogen bonds and the π-π interaction as broken lines. For clarity, H atoms and disordered perchlorate ions are not shown.

Diaquabis(1,10-phenanthroline-κ2 N,N')nickel(II) diperchlorate 0.4-hydrate

Crystal data

$[Ni(C_{12}H_8N_2)_2(H_2O)_2](ClO_4)_2·0.4H_2O$	F_{000} = 1352
M_r = 661.26	D_x = 1.377 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 1167 reflections
a = 18.2558 (6) Å	θ = 1.4–28º
b = 15.9362 (6) Å	μ = 0.83 mm^{-1}
c = 11.7096 (4) Å	*T* = 293 (2) K
β = 110.591 (2)º	Block, green
V = 3189.02 (19) Å^3	0.26 × 0.20 × 0.18 mm
Z = 4	

Data collection

Bruker APEX II area-detector diffractometer	3488 independent reflections
Radiation source: fine-focus sealed tube	1861 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.071
T = 293(2) K	θ_{max} = 27.0º
φ and ω scan	θ_{min} = 2.2º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	*h* = −23→23
T_{min} = 0.827, T_{max} = 0.867	*k* = −20→16
13780 measured reflections	*l* = −14→14

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.071$	H-atom parameters constrained
$wR(F^2) = 0.262$	$w = 1/[\sigma^2(F_o^2) + (0.144P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
3488 reflections	$\Delta\rho_{max} = 0.64$ e Å^{-3}
241 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
97 restraints	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}	Occ. (<1)
Ni1	0.5000	0.33437 (6)	0.7500	0.0538 (4)	
O1W	0.5725 (2)	0.4330 (3)	0.7362 (4)	0.0714 (11)	
H1W	0.6100	0.4324	0.7126	0.107*	
H2W	0.5883	0.4636	0.7969	0.107*	
N1	0.5844 (3)	0.2437 (3)	0.7589 (4)	0.0625 (12)	
N2	0.5543 (3)	0.3252 (3)	0.9371 (4)	0.0601 (12)	
C1	0.5407 (4)	0.3668 (4)	1.0251 (6)	0.0703 (16)	
H1	0.5059	0.4117	1.0042	0.084*	
C2	0.5761 (5)	0.3464 (5)	1.1478 (7)	0.089 (2)	
H2	0.5646	0.3770	1.2070	0.107*	
C3	0.6264 (5)	0.2828 (6)	1.1799 (6)	0.095 (2)	
H3	0.6495	0.2685	1.2618	0.114*	
C4	0.6447 (4)	0.2375 (5)	1.0923 (6)	0.083 (2)	
C5	0.6995 (6)	0.1692 (6)	1.1172 (10)	0.120 (3)	
H5	0.7241	0.1517	1.1973	0.144*	
C6	0.7164 (5)	0.1298 (7)	1.0269 (9)	0.119 (3)	
H6	0.7529	0.0865	1.0463	0.143*	

C7	0.6789 (4)	0.1538 (5)	0.9025 (8)	0.087 (2)	
C8	0.6946 (5)	0.1164 (6)	0.8020 (10)	0.106 (3)	
H8	0.7304	0.0727	0.8154	0.128*	
C9	0.6579 (5)	0.1443 (5)	0.6911 (9)	0.100 (3)	
H9	0.6691	0.1214	0.6260	0.120*	
C10	0.6021 (4)	0.2082 (4)	0.6696 (6)	0.0759 (18)	
H10	0.5765	0.2264	0.5900	0.091*	
C11	0.6231 (3)	0.2178 (4)	0.8737 (6)	0.0674 (16)	
C12	0.6059 (3)	0.2614 (4)	0.9702 (5)	0.0634 (15)	
O2W	0.501 (2)	0.023 (2)	0.449 (3)	0.134 (11)	0.20
Cl1A	0.8269 (3)	0.0925 (3)	0.4969 (4)	0.0610 (12)	0.720 (11)
O1A	0.8132 (5)	0.0811 (7)	0.3699 (6)	0.109 (3)	0.720 (11)
O2A	0.8634 (8)	0.1706 (5)	0.5390 (10)	0.124 (4)	0.720 (11)
O3A	0.7595 (5)	0.0778 (7)	0.5247 (11)	0.131 (4)	0.720 (11)
O4A	0.8859 (5)	0.0327 (6)	0.5610 (8)	0.132 (3)	0.720 (11)
Cl1B	0.8131 (10)	0.0938 (11)	0.4849 (14)	0.103 (6)	0.280 (11)
O1B	0.8366 (14)	0.0403 (15)	0.405 (2)	0.113 (7)	0.280 (11)
O2B	0.8446 (18)	0.1755 (13)	0.485 (3)	0.136 (9)	0.280 (11)
O3B	0.7289 (9)	0.1023 (18)	0.432 (2)	0.140 (8)	0.280 (11)
O4B	0.8293 (15)	0.0550 (14)	0.6000 (14)	0.116 (8)	0.280 (11)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0576 (6)	0.0605 (7)	0.0444 (7)	0.000	0.0195 (4)	0.000
O1W	0.078 (3)	0.074 (3)	0.070 (3)	−0.018 (2)	0.036 (2)	−0.013 (2)
N1	0.065 (3)	0.071 (3)	0.056 (3)	0.003 (2)	0.026 (2)	−0.008 (2)
N2	0.062 (3)	0.071 (3)	0.049 (3)	0.001 (2)	0.022 (2)	0.000 (2)
C1	0.078 (4)	0.081 (4)	0.053 (4)	0.000 (3)	0.025 (3)	−0.007 (3)
C2	0.104 (5)	0.107 (6)	0.057 (4)	−0.012 (5)	0.028 (4)	−0.019 (4)
C3	0.107 (6)	0.124 (7)	0.043 (4)	0.006 (5)	0.013 (4)	0.009 (4)
C4	0.086 (4)	0.093 (5)	0.054 (4)	0.004 (4)	0.006 (3)	0.007 (4)
C5	0.126 (7)	0.120 (7)	0.084 (6)	0.039 (6)	0.000 (5)	0.032 (5)
C6	0.111 (7)	0.118 (7)	0.103 (8)	0.054 (6)	0.007 (5)	0.016 (6)
C7	0.081 (4)	0.083 (5)	0.093 (6)	0.026 (4)	0.025 (4)	0.002 (4)
C8	0.100 (6)	0.097 (6)	0.127 (8)	0.037 (5)	0.045 (5)	0.002 (6)
C9	0.098 (6)	0.101 (6)	0.115 (8)	0.015 (5)	0.054 (5)	−0.015 (5)
C10	0.082 (4)	0.080 (4)	0.075 (5)	0.005 (4)	0.040 (3)	−0.009 (4)
C11	0.067 (4)	0.071 (4)	0.065 (4)	0.007 (3)	0.024 (3)	0.006 (3)
C12	0.058 (3)	0.074 (4)	0.051 (3)	0.000 (3)	0.010 (2)	−0.002 (3)
O2W	0.124 (13)	0.130 (14)	0.135 (14)	−0.002 (10)	0.030 (9)	−0.020 (10)
Cl1A	0.0745 (18)	0.069 (2)	0.048 (2)	0.0005 (14)	0.0329 (15)	0.0057 (15)
O1A	0.103 (6)	0.175 (9)	0.048 (4)	0.019 (6)	0.024 (3)	−0.002 (4)
O2A	0.191 (10)	0.104 (5)	0.091 (7)	−0.044 (5)	0.068 (7)	−0.018 (5)
O3A	0.118 (6)	0.160 (8)	0.158 (9)	−0.008 (6)	0.102 (7)	−0.009 (7)
O4A	0.144 (7)	0.154 (7)	0.115 (6)	0.063 (6)	0.065 (5)	0.075 (6)
Cl1B	0.110 (8)	0.119 (9)	0.077 (8)	−0.008 (7)	0.027 (6)	0.004 (6)
O1B	0.130 (14)	0.132 (14)	0.098 (13)	−0.020 (12)	0.066 (11)	−0.009 (11)

O2B	0.183 (16)	0.108 (12)	0.104 (17)	−0.019 (12)	0.036 (15)	0.005 (10)
O3B	0.108 (10)	0.210 (18)	0.096 (14)	0.022 (11)	0.029 (10)	0.019 (14)
O4B	0.152 (16)	0.128 (14)	0.057 (9)	−0.010 (13)	0.023 (9)	0.004 (9)

Geometric parameters (Å, °)

Ni1—N2^{i}	2.068 (5)	C5—H5	0.9300
Ni1—N2	2.068 (5)	C6—C7	1.427 (11)
Ni1—N1^{i}	2.089 (5)	C6—H6	0.9300
Ni1—N1	2.089 (5)	C7—C11	1.397 (9)
Ni1—O1W	2.098 (4)	C7—C8	1.434 (12)
Ni1—O1W^{i}	2.098 (4)	C8—C9	1.312 (12)
O1W—H1W	0.8234	C8—H8	0.9300
O1W—H2W	0.8268	C9—C10	1.400 (10)
N1—C10	1.323 (7)	C9—H9	0.9300
N1—C11	1.345 (7)	C10—H10	0.9300
N2—C1	1.320 (7)	C11—C12	1.453 (9)
N2—C12	1.346 (7)	O2W—O2W^{ii}	1.41 (6)
C1—C2	1.391 (9)	Cl1A—O3A	1.398 (6)
C1—H1	0.9300	Cl1A—O2A	1.416 (7)
C2—C3	1.331 (10)	Cl1A—O1A	1.431 (6)
C2—H2	0.9300	Cl1A—O4A	1.435 (7)
C3—C4	1.387 (11)	Cl1B—O4B	1.416 (9)
C3—H3	0.9300	Cl1B—O2B	1.423 (10)
C4—C12	1.407 (8)	Cl1B—O1B	1.441 (10)
C4—C5	1.437 (11)	Cl1B—O3B	1.449 (10)
C5—C6	1.355 (13)		
N2^{i}—Ni1—N2	171.9 (3)	C6—C5—C4	121.8 (8)
N2^{i}—Ni1—N1^{i}	80.10 (19)	C6—C5—H5	119.1
N2—Ni1—N1^{i}	94.27 (18)	C4—C5—H5	119.1
N2^{i}—Ni1—N1	94.27 (18)	C5—C6—C7	120.9 (8)
N2—Ni1—N1	80.10 (19)	C5—C6—H6	119.6
N1^{i}—Ni1—N1	92.5 (3)	C7—C6—H6	119.6
N2^{i}—Ni1—O1W	92.95 (17)	C11—C7—C6	119.3 (8)
N2—Ni1—O1W	93.11 (17)	C11—C7—C8	116.4 (7)
N1^{i}—Ni1—O1W	171.63 (17)	C6—C7—C8	124.3 (7)
N1—Ni1—O1W	92.70 (18)	C9—C8—C7	119.5 (7)
N2^{i}—Ni1—O1W^{i}	93.11 (17)	C9—C8—H8	120.3
N2—Ni1—O1W^{i}	92.95 (17)	C7—C8—H8	120.3
N1^{i}—Ni1—O1W^{i}	92.70 (18)	C8—C9—C10	120.7 (8)
N1—Ni1—O1W^{i}	171.63 (17)	C8—C9—H9	119.7
O1W—Ni1—O1W^{i}	83.0 (2)	C10—C9—H9	119.7
Ni1—O1W—H1W	129.8	N1—C10—C9	122.2 (7)
Ni1—O1W—H2W	114.4	N1—C10—H10	118.9
H1W—O1W—H2W	102.5	C9—C10—H10	118.9
C10—N1—C11	118.1 (6)	N1—C11—C7	123.2 (6)

C10—N1—Ni1	129.5 (5)	N1—C11—C12	116.7 (5)
C11—N1—Ni1	112.4 (4)	C7—C11—C12	120.1 (6)
C1—N2—C12	117.3 (5)	N2—C12—C4	123.2 (6)
C1—N2—Ni1	129.8 (4)	N2—C12—C11	117.3 (5)
C12—N2—Ni1	112.6 (4)	C4—C12—C11	119.4 (6)
N2—C1—C2	122.9 (7)	O3A—Cl1A—O2A	114.2 (7)
N2—C1—H1	118.6	O3A—Cl1A—O1A	111.9 (7)
C2—C1—H1	118.6	O2A—Cl1A—O1A	111.3 (6)
C3—C2—C1	119.6 (7)	O3A—Cl1A—O4A	109.1 (6)
C3—C2—H2	120.2	O2A—Cl1A—O4A	103.2 (7)
C1—C2—H2	120.2	O1A—Cl1A—O4A	106.5 (6)
C2—C3—C4	120.7 (7)	O4B—Cl1B—O2B	116.6 (13)
C2—C3—H3	119.7	O4B—Cl1B—O1B	110.6 (13)
C4—C3—H3	119.7	O2B—Cl1B—O1B	109.4 (13)
C3—C4—C12	116.3 (7)	O4B—Cl1B—O3B	106.3 (12)
C3—C4—C5	125.2 (8)	O2B—Cl1B—O3B	106.4 (13)
C12—C4—C5	118.5 (7)	O1B—Cl1B—O3B	107.0 (13)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1W···O1B^{iii}	0.82	1.99	2.75 (2)	154
O1W—H1W···O1A^{iii}	0.82	1.97	2.787 (9)	169
O1W—H2W···O4A^{iv}	0.83	1.91	2.733 (8)	174
O1W—H2W···O4B^{iv}	0.83	2.14	2.87 (2)	148

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

Fig. 1

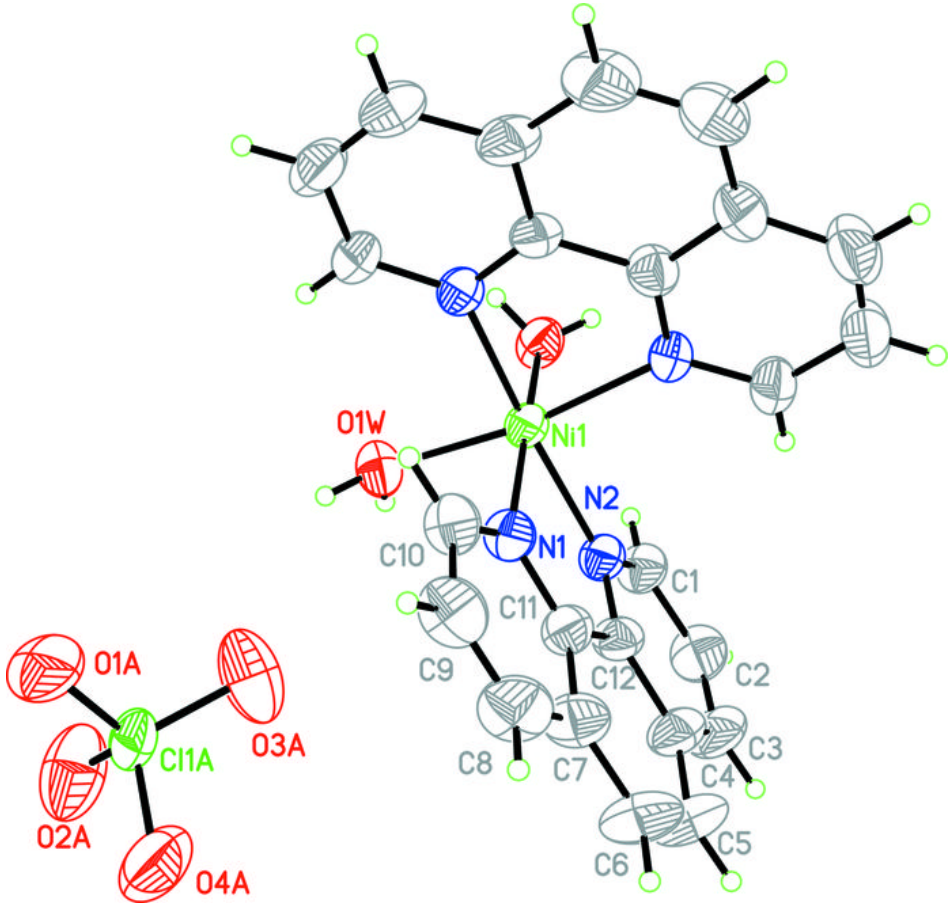
O1W
Ni1
N2
N1
C10
C1
C11
C9
C12
C2
C8
C7
C3
C4
C5
C6
O1A
O3A
Cl1A
O2A
O4A

Fig. 2