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Tetraaquabis(6-chloropyridine-3-carboxylato-κO)nickel(II) tetrahydrate

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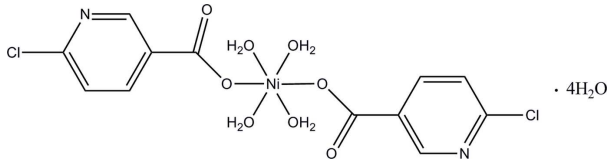
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.028; wR factor = 0.076; data-to-parameter ratio = 17.7.

In the title compound, $[Ni(C_6H_3ClNO_2)_2(H_2O)_4]\cdot 4H_2O$, the Ni^{II} ion is located on an inversion centre and is octahedrally coordinated by four O atoms from four water molecules in the equatorial plane and two O atoms of two 6-chloro-3-carboxylate ligands in axial positions. There are also four lattice water molecules present. The organic ligands are bound to the Ni^{II} ion in a monodentate manner through a carboxylate O atom. There is one strong intramolecular O—H···O hydrogen bond and six intermolecular O—H···O and O—H···N hydrogen-bonding interactions in the packing, resulting in a complex three-dimensional network structure.

Related literature

For background to complexes based on 6-chloronicotinic acid, see: Long *et al.* (2007); Li *et al.* (2006).



Experimental

Crystal data

$[Ni(C_6H_3ClNO_2)_2(H_2O)_4]\cdot 4H_2O$
M_r = 515.91
Triclinic, $P\overline{1}$
a = 7.0245 (14) Å
b = 7.3436 (15) Å
c = 11.547 (2) Å
α = 86.35 (3)°
β = 77.78 (3)°
γ = 64.55 (3)°
V = 525.4 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.24 mm^{-1}
T = 293 K
0.39 × 0.29 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.754, T_{max} = 0.862
5167 measured reflections
2371 independent reflections
2170 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.076
S = 1.06
2371 reflections
134 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
OW2—H2WA···O2^{i}	0.83	1.83	2.6401 (18)	167
OW1—H1WB···OW3^{ii}	0.81	2.07	2.869 (2)	167
OW1—H1WA···OW4^{iii}	0.82	1.97	2.7915 (19)	179
OW4—H4WA···N^{iv}	0.81	2.14	2.850 (2)	147
OW3—H3WB···OW4^{v}	0.80	1.99	2.763 (2)	163
OW3—H3WA···OW2^{vi}	0.81	2.21	2.933 (2)	149
OW2—H2WB···OW3	0.84	1.98	2.819 (2)	177
OW4—H4WB···O2	0.82	1.97	2.764 (2)	162

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2376).

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supporting information

Acta Cryst. (2012). E**68**, m1393 [doi:10.1107/S160053681204322X]

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S1. Comment

The asymmetric unit of the title complex, contains a half of Ni^{II} ion lying on a crystallographic inversion center, 6-chloropyridine-3-carboxylate anion, two coordinated water molecules and two lattice water molecules (Fig. 1). The Ni^{II} ion is six-coordinated within a octahedral, NiO_6 coordination geometry. Six coordination arises from two 6-chloropyridine-3-carboxylate ligands in the apical positions [Ni—O = 2.0335 (12) Å] and four water molecules in the equatorial plane [Ni—O = 2.0742 (16) Å and 2.0814 (12) Å]. The bond angles around the Ni center lie within the range 88.8–91.2° for the formally *cis* pairs of ligating atoms. The 6-chloropyridine-3-carboxylate carboxylate ligands are bound to the Ni^{II} ion in a monodentate mode through a carboxylate O atom. There is one strong intramolecular hydrogen bond of type O—H···O, formed by coordinated water atom OW2 and uncoordinated carboxylate atom O2, as well as six strong intermolecular hydrogen bonds of O—H···O type and one of O—H···N type in the packing of the title compound forming a three-dimensional supramolecular structure (Fig.2).

S2. Experimental

All commercially obtained reagent grade chemicals were used without further purification. A mixture of nickelous sulfate hexahydrate (0.5698 g) and 6-chloronicotinic acid (0.1701 g) were added into 20 ml water and with 20 drops of 0.1 mol/*L* sodium hydroxide solution, and then stirred for 1 h. Finally, 10 ml 95% ethanol carefully layered above-mentioned solution in glass tube. After 1 days, green crystals of the title complex were collected.

S3. Refinement

H atoms bonded to C atoms were introduced in calculated positions and refined using a riding model [C—H = 0.93 Å and U_{iso}(H) = 1.2Ueq(C) for aromatic H atoms. H atoms belonging to water molecules were found in difference Fourier maps.

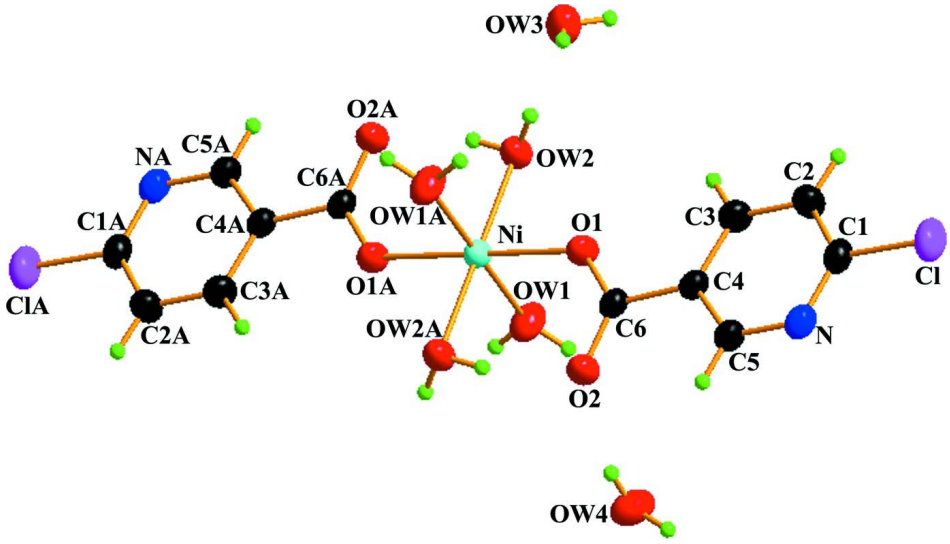

Figure 1

The molecular structure of the title complex, with 50% probability displacement ellipsoids for non-H atoms. Symmetry codes: (A) -*x*, -*y*, 1 - *z*.

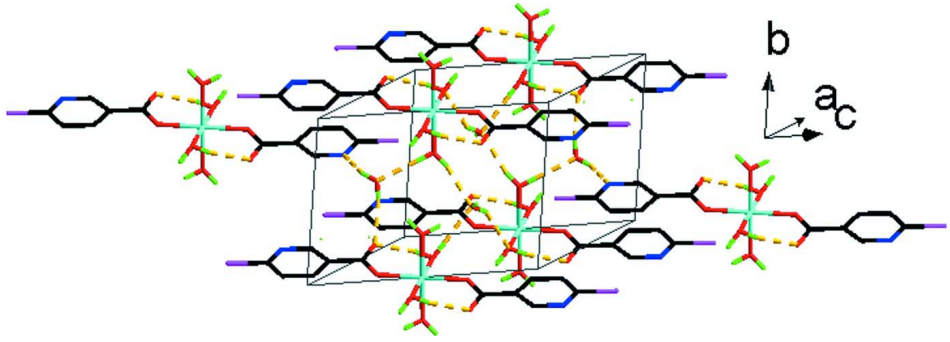

Figure 2

Crystal packing diagram for the title compound. All atoms are shown as isotropic spheres of arbitrary size. H atoms bonded to C atoms are omitted for clarity. The H-bonding interactions are shown as yellow dashed lines.

Tetraaquabis(6-chloropyridine-3-carboxylato-*κO*)nickel(II) tetrahydrate

Crystal data

$[Ni(C_6H_3ClNO_2)_2(H_2O)_4]\cdot 4H_2O$
$M_r = 515.91$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.0245\ (14)$ Å
$b = 7.3436\ (15)$ Å
$c = 11.547\ (2)$ Å
$\alpha = 86.35\ (3)°$
$\beta = 77.78\ (3)°$
$\gamma = 64.55\ (3)°$
$V = 525.4\ (2)$ Å^3
$Z = 1$
$F(000) = 266$
$D_x = 1.630$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4651 reflections
$\theta = 3.1–27.5°$
$\mu = 1.24$ mm^{-1}
$T = 293$ K
Block, green
0.39 × 0.29 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.754, T_{max} = 0.862
5167 measured reflections
2371 independent reflections
2170 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 27.5°, θ_{min} = 3.1°
h = −8→9
k = −9→9
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.076
S = 1.06
2371 reflections
134 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 0.1122P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.115 (6)

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}
Cl	0.49297 (8)	−0.29064 (8)	1.14788 (4)	0.04615 (15)
Ni	0.0000	0.0000	0.5000	0.02619 (12)
O1	0.1088 (2)	−0.0624 (2)	0.65419 (10)	0.0345 (3)
O2	−0.1079 (2)	−0.1909 (2)	0.76064 (10)	0.0369 (3)
OW1	0.1737 (2)	−0.2994 (2)	0.44232 (11)	0.0438 (3)
H1WB	0.2196	−0.3961	0.4838	0.066*
H1WA	0.1310	−0.3310	0.3897	0.066*
OW2	0.27477 (19)	0.0432 (2)	0.42777 (10)	0.0354 (3)
H2WB	0.2884	0.1261	0.4680	0.053*
H2WA	0.2366	0.0978	0.3668	0.053*
OW3	0.3330 (2)	0.3218 (2)	0.55701 (12)	0.0476 (3)
H3WB	0.2430	0.3539	0.6168	0.071*
H3WA	0.4486	0.2539	0.5747	0.071*
OW4	−0.0265 (2)	−0.5912 (2)	0.73619 (11)	0.0475 (3)
H4WB	−0.0788	−0.4682	0.7463	0.071*

H4WA	−0.0208	−0.6457	0.7992	0.071*
N	0.1923 (2)	−0.2769 (2)	1.04439 (11)	0.0334 (3)
C1	0.3679 (3)	−0.2457 (3)	1.02767 (14)	0.0316 (3)
C2	0.4551 (3)	−0.1812 (3)	0.92311 (15)	0.0362 (4)
H2A	0.5800	−0.1626	0.9159	0.043*
C3	0.3501 (3)	−0.1457 (3)	0.83059 (14)	0.0347 (4)
H3A	0.4023	−0.1003	0.7593	0.042*
C4	0.1653 (2)	−0.1777 (2)	0.84378 (13)	0.0273 (3)
C5	0.0943 (3)	−0.2442 (3)	0.95247 (13)	0.0312 (3)
H5A	−0.0282	−0.2673	0.9620	0.037*
C6	0.0457 (2)	−0.1415 (2)	0.74546 (13)	0.0270 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0594 (3)	0.0454 (3)	0.0361 (2)	−0.0180 (2)	−0.0256 (2)	0.00447 (19)
Ni	0.03131 (17)	0.03082 (19)	0.02103 (16)	−0.01728 (13)	−0.00745 (11)	0.00611 (10)
O1	0.0433 (6)	0.0454 (8)	0.0255 (5)	−0.0280 (6)	−0.0117 (5)	0.0114 (5)
O2	0.0415 (6)	0.0468 (8)	0.0335 (6)	−0.0283 (6)	−0.0127 (5)	0.0120 (5)
OW1	0.0630 (8)	0.0321 (7)	0.0362 (6)	−0.0166 (6)	−0.0186 (6)	0.0031 (5)
OW2	0.0389 (6)	0.0457 (8)	0.0303 (5)	−0.0251 (6)	−0.0116 (5)	0.0085 (5)
OW3	0.0432 (7)	0.0526 (9)	0.0462 (7)	−0.0186 (7)	−0.0140 (6)	0.0092 (6)
OW4	0.0700 (9)	0.0437 (9)	0.0328 (6)	−0.0308 (7)	−0.0047 (6)	0.0033 (6)
N	0.0412 (8)	0.0352 (9)	0.0235 (6)	−0.0162 (6)	−0.0076 (6)	0.0065 (5)
C1	0.0383 (8)	0.0279 (9)	0.0266 (7)	−0.0102 (7)	−0.0114 (6)	0.0018 (6)
C2	0.0357 (8)	0.0462 (11)	0.0326 (8)	−0.0224 (8)	−0.0093 (7)	0.0054 (7)
C3	0.0387 (9)	0.0428 (11)	0.0264 (7)	−0.0224 (8)	−0.0052 (7)	0.0061 (7)
C4	0.0313 (7)	0.0262 (8)	0.0241 (7)	−0.0125 (6)	−0.0053 (6)	0.0036 (6)
C5	0.0347 (8)	0.0342 (10)	0.0263 (7)	−0.0166 (7)	−0.0067 (6)	0.0062 (6)
C6	0.0330 (8)	0.0245 (8)	0.0232 (7)	−0.0119 (6)	−0.0066 (6)	0.0037 (6)

Geometric parameters (Å, º)

Cl—C1	1.7369 (16)	OW1—H1WB	0.8140
Ni—O1^{i}	2.0335 (12)	OW1—H1WA	0.8174
Ni—O1	2.0335 (12)	C4—C5	1.389 (2)
Ni—OW1	2.0742 (16)	C4—C3	1.392 (2)
Ni—OW1^{i}	2.0742 (16)	C2—C3	1.374 (2)
Ni—OW2	2.0814 (12)	C2—H2A	0.9300
Ni—OW2^{i}	2.0814 (12)	N—C5	1.339 (2)
O1—C6	1.2607 (18)	C5—H5A	0.9300
C6—O2	1.2550 (19)	C3—H3A	0.9300
C6—C4	1.496 (2)	OW4—H4WB	0.8210
C1—N	1.321 (2)	OW4—H4WA	0.8080
C1—C2	1.386 (2)	OW3—H3WB	0.8000
OW2—H2WB	0.8378	OW3—H3WA	0.8121
OW2—H2WA	0.8252		

O1^{i}—Ni—O1	180.00 (2)	Ni—OW2—H2WB	112.2
O1^{i}—Ni—OW1	88.84 (6)	Ni—OW2—H2WA	97.3
O1—Ni—OW1	91.16 (6)	H2WB—OW2—H2WA	108.5
O1^{i}—Ni—OW1^{i}	91.16 (6)	Ni—OW1—H1WB	126.3
O1—Ni—OW1^{i}	88.84 (6)	Ni—OW1—H1WA	114.0
OW1—Ni—OW1^{i}	180.0	H1WB—OW1—H1WA	108.8
O1^{i}—Ni—OW2	93.00 (5)	C5—C4—C3	117.46 (14)
O1—Ni—OW2	87.00 (5)	C5—C4—C6	120.79 (14)
OW1—Ni—OW2	87.71 (6)	C3—C4—C6	121.74 (14)
OW1^{i}—Ni—OW2	92.29 (6)	C3—C2—C1	117.44 (15)
O1^{i}—Ni—OW2^{i}	87.00 (5)	C3—C2—H2A	121.3
O1—Ni—OW2^{i}	93.00 (5)	C1—C2—H2A	121.3
OW1—Ni—OW2^{i}	92.29 (6)	C1—N—C5	116.77 (14)
OW1^{i}—Ni—OW2^{i}	87.71 (6)	N—C5—C4	123.71 (15)
OW2—Ni—OW2^{i}	180.00 (3)	N—C5—H5A	118.1
C6—O1—Ni	128.83 (10)	C4—C5—H5A	118.1
O2—C6—O1	125.72 (14)	C2—C3—C4	119.83 (15)
O2—C6—C4	117.79 (14)	C2—C3—H3A	120.1
O1—C6—C4	116.49 (13)	C4—C3—H3A	120.1
N—C1—C2	124.78 (14)	H4WB—OW4—H4WA	110.3
N—C1—Cl	115.91 (13)	H3WB—OW3—H3WA	107.9
C2—C1—Cl	119.31 (13)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*2—H2*WA*···O2^{i}	0.83	1.83	2.6401 (18)	167
O*W*1—H1*WB*···O*W*3^{ii}	0.81	2.07	2.869 (2)	167
O*W*1—H1*WA*···O*W*4^{iii}	0.82	1.97	2.7915 (19)	179
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O*W*2—H2*WB*···O*W*3	0.84	1.98	2.819 (2)	177
O*W*4—H4*WB*···O2	0.82	1.97	2.764 (2)	162

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