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The crystal structure of a new polymorph of hexaaquanickel(II) bis(6-oxo-1,6-dihydropyridine-3-carboxylate)

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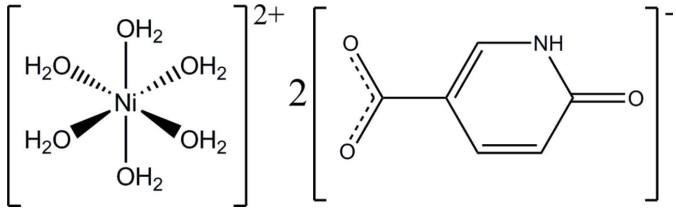
In a new polymorph of the title salt, $[Ni(H_2O)_6](C_6H_4NO_3)_2$, the metal atom of the cationic complex lies on a symmetry centre and is coordinated by six water molecules to provide a quite regular octahedral coordination environment. These cations interact with 6-oxo-1,6-dihydropyridine-3-carboxylate anions through electrostatic interactions and by means of O—H···O and N—H···O hydrogen bonds involving the carboxylate, keto and protonated imine groups of the anion, and the coordinating water molecules from the cationic complex entity to generate a supramolecular three-dimensional architecture. The previously reported polymorph of this compound presents a network of hydrogen bonds, in which the organic anions establish mutual hydrogen-bonding interactions involving their keto and protonated imine groups.

Keywords: crystal structure; polymorph; 6-oxo-1,6-dihydropyridine-3-carboxylate anion; hydrogen bonding,.

CCDC reference: 1438522

1. Related literature

The zinc and cobalt analogues (Zhang *et al.*, 2005; Song *et al.*, 2005; Zhang & Ng, 2005*a*) of the title salt are isostructural with the previously reported polymorph of $[Ni(H_2O)_6](C_6H_4NO_3)_2$ (Zhang & Ng, 2005*b*). It is worth mentioning that although the authors claimed a lactim tautomer of the organic anion to be present in all these structures, the C—O bond length seems to indicate of a lactam tautomer as in the case of the title compound. For additional examples of coordination complexes with 6-oxo-1,6-dihydropyridine-3-carboxylate anions and copper(II), see: Zeng *et al.* (2007).



2. Experimental

2.1. Crystal data

$[Ni(H_2O)_6](C_6H_4NO_3)_2$
M_r = 443.01
Triclinic, $P\overline{1}$
a = 6.2620 (5) Å
b = 7.1053 (7) Å
c = 10.7101 (10) Å
α = 102.461 (8)°
β = 96.754 (7)°
γ = 114.823 (8)°
V = 410.49 (7) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.26 mm^{-1}
T = 100 K
0.08 × 0.07 × 0.06 mm

2.2. Data collection

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2003)
T_{min} = 0.888, T_{max} = 0.936
2781 measured reflections
1801 independent reflections
1654 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.070
S = 1.06
1801 reflections
146 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—O1*W*	2.0184 (16)	Ni1—O2*W*	2.0990 (16)
Ni1—O3*W*	2.0242 (16)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2*W*	0.87 (2)	2.06 (3)	2.906 (2)	167 (2)
O1*W*—H11*W*···O71^{i}	0.77 (3)	1.85 (3)	2.612 (2)	173 (3)
O1*W*—H12*W*···O72^{ii}	0.78 (3)	1.97 (3)	2.748 (2)	173 (3)
O2*W*—H21*W*···O2^{iii}	0.88 (3)	1.90 (3)	2.772 (2)	173 (2)
O2*W*—H22*W*···O2^{iv}	0.77 (3)	1.98 (3)	2.743 (2)	169 (3)
O3*W*—H31*W*···O72^{i}	0.74 (3)	1.92 (3)	2.660 (2)	174 (3)
O3*W*—H32*W*···O2^{v}	0.81 (3)	2.01 (3)	2.813 (2)	172 (3)

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

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics:

ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5241).

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supporting information

Acta Cryst. (2015). E**71**, m238–m239 [https://doi.org/10.1107/S2056989015022422]

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S1. Experimental

6-Oxo-1,6-dihydropyridine-3-carboxylic acid (0.8 mmol) and $Ni(NO_3)_2{\cdot}6H_2O$ (0.4 mmol) were dissolved in 40 ml of distilled water. After stirring for half an hour, the solution was left evaporating at room temperature. Two weeks later light green crystals of the title compound were obtained.

S2. Refinement

H atoms bonded to N and O atoms were located in a difference map and were refined with U_{iso}(H) = 1.2U_{eq}(N) and U_{iso}(H) = 1.5U_{eq}(O). Other H atoms were positioned geometrically and refined using a riding model with C—H = 0.93 Å and with U_{iso}(H) = 1.2U_{eq}(C).

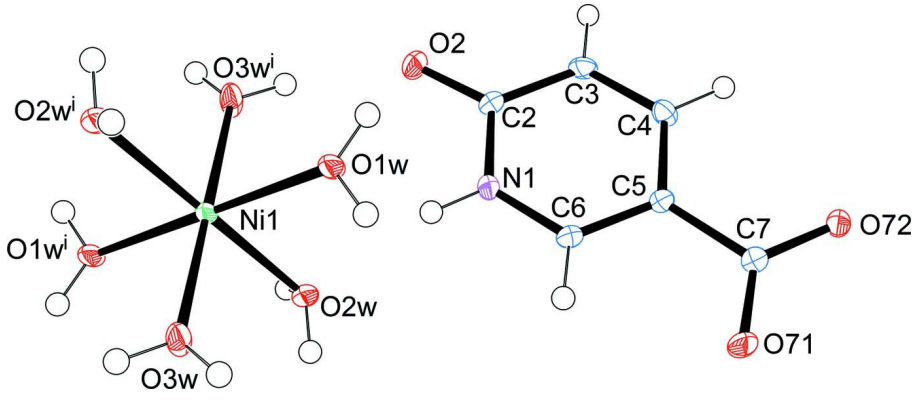

Figure 1

The structures of the molecular entities in (I), drawn with displacement ellipsoids at the 50% probability level. [Symmetry code: -*x*+1, -*y*, -*z*+1.]

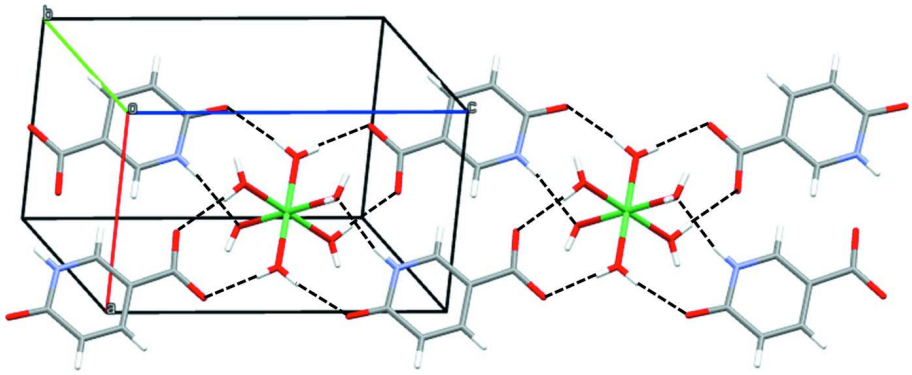

Figure 2

Hydrogen-bonding interactions (dashed lines) taking place between the $[Ni(H_2O)_6]^{2+}$ complex cations and the 6-oxo-1,6-dihydropyridine-3-carboxylate anions.

Hexaaquanickel(II) bis(6-oxo-1,6-dihydropyridine-3-carboxylate)

Crystal data

$[Ni(H_2O)_6](C_6H_4NO_3)_2$
$M_r = 443.01$
Triclinic, $P\overline{1}$
$a = 6.2620$ (5) Å
$b = 7.1053$ (7) Å
$c = 10.7101$ (10) Å
$\alpha = 102.461$ (8)°
$\beta = 96.754$ (7)°
$\gamma = 114.823$ (8)°
$V = 410.49$ (7) Å^3
$Z = 1$
$F(000) = 230$
$D_x = 1.792$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2781 reflections
$\theta = 2.0$–$28.2°$
$\mu = 1.26$ mm^{-1}
$T = 100$ K
Block, light green
0.08 × 0.07 × 0.06 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 8.192 pixels mm^{-1}
thin–slice ω scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2003)
$T_{min} = 0.888$, $T_{max} = 0.936$
2781 measured reflections
1801 independent reflections
1654 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 28.2°$, $\theta_{min} = 2.0°$
$h = -5 \rightarrow 8$
$k = -9 \rightarrow 5$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.070$
$S = 1.06$
1801 reflections
146 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0191P)^2 + 0.3293P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Special details

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.5000	0.0000	0.5000	0.01281 (12)
O1W	0.7185 (3)	0.1609 (3)	0.68193 (15)	0.0168 (3)
O71	0.5271 (3)	−0.1565 (3)	1.13681 (15)	0.0202 (4)
O2W	0.3038 (3)	−0.2654 (3)	0.56622 (15)	0.0154 (3)
O3W	0.2933 (3)	0.1461 (3)	0.55076 (17)	0.0231 (4)
O2	0.8636 (3)	−0.3362 (3)	0.62046 (14)	0.0176 (3)
O72	0.8231 (3)	−0.2245 (3)	1.21937 (15)	0.0202 (4)
N1	0.6616 (3)	−0.2558 (3)	0.76999 (18)	0.0162 (4)
C2	0.8355 (4)	−0.3128 (4)	0.7379 (2)	0.0141 (4)
C4	0.9331 (4)	−0.3021 (3)	0.9661 (2)	0.0140 (4)
H4	1.0278	−0.3170	1.0333	0.017*
C3	0.9726 (4)	−0.3378 (4)	0.8423 (2)	0.0148 (4)
H3	1.0917	−0.3793	0.8264	0.018*
C5	0.7512 (4)	−0.2432 (3)	0.9937 (2)	0.0130 (4)
C7	0.6965 (4)	−0.2048 (3)	1.1271 (2)	0.0144 (4)
C6	0.6196 (4)	−0.2203 (4)	0.8921 (2)	0.0154 (4)
H6	0.4995	−0.1797	0.9070	0.018*
H1	0.574 (4)	−0.240 (4)	0.708 (3)	0.018*
H31W	0.266 (5)	0.177 (4)	0.615 (3)	0.023*
H21W	0.262 (5)	−0.387 (5)	0.505 (3)	0.023*
H22W	0.189 (5)	−0.270 (4)	0.588 (3)	0.023*
H11W	0.650 (5)	0.171 (4)	0.736 (3)	0.023*
H12W	0.844 (5)	0.170 (4)	0.712 (3)	0.023*
H32W	0.236 (5)	0.196 (5)	0.503 (3)	0.038 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0108 (2)	0.0231 (2)	0.0093 (2)	0.01104 (17)	0.00397 (15)	0.00593 (16)
O1W	0.0119 (8)	0.0321 (10)	0.0095 (8)	0.0130 (7)	0.0037 (6)	0.0053 (7)
O71	0.0201 (8)	0.0353 (10)	0.0169 (8)	0.0204 (8)	0.0102 (7)	0.0109 (7)
O2W	0.0127 (8)	0.0239 (9)	0.0126 (8)	0.0102 (7)	0.0056 (6)	0.0058 (7)
O3W	0.0303 (10)	0.0467 (12)	0.0121 (8)	0.0320 (9)	0.0110 (7)	0.0135 (8)
O2	0.0198 (8)	0.0248 (9)	0.0126 (8)	0.0127 (7)	0.0073 (6)	0.0067 (7)
O72	0.0180 (8)	0.0384 (10)	0.0112 (8)	0.0187 (8)	0.0048 (6)	0.0079 (7)
N1	0.0152 (9)	0.0275 (11)	0.0121 (9)	0.0135 (8)	0.0047 (8)	0.0094 (8)
C2	0.0133 (10)	0.0176 (11)	0.0130 (10)	0.0074 (9)	0.0061 (8)	0.0054 (9)
C4	0.0132 (10)	0.0156 (11)	0.0138 (10)	0.0084 (9)	0.0010 (8)	0.0033 (9)
C3	0.0118 (10)	0.0190 (11)	0.0170 (11)	0.0102 (9)	0.0053 (8)	0.0042 (9)

C5	0.0113 (10)	0.0159 (11)	0.0115 (10)	0.0058 (8)	0.0038 (8)	0.0038 (8)
C7	0.0127 (10)	0.0169 (11)	0.0133 (11)	0.0062 (9)	0.0039 (8)	0.0047 (9)
C6	0.0130 (10)	0.0233 (12)	0.0145 (11)	0.0107 (9)	0.0066 (9)	0.0075 (9)

Geometric parameters (Å, º)

Ni1—O1W	2.0184 (16)	O2—C2	1.275 (2)
Ni1—O1W^{i}	2.0184 (16)	O72—C7	1.262 (3)
Ni1—O3W^{i}	2.0242 (16)	N1—C6	1.356 (3)
Ni1—O3W	2.0242 (16)	N1—C2	1.366 (3)
Ni1—O2W^{i}	2.0990 (16)	N1—H1	0.87 (2)
Ni1—O2W	2.0990 (16)	C2—C3	1.417 (3)
O1W—H11W	0.77 (3)	C4—C3	1.367 (3)
O1W—H12W	0.78 (3)	C4—C5	1.409 (3)
O71—C7	1.253 (2)	C4—H4	0.9300
O2W—H21W	0.88 (3)	C3—H3	0.9300
O2W—H22W	0.77 (3)	C5—C6	1.366 (3)
O3W—H31W	0.74 (3)	C5—C7	1.503 (3)
O3W—H32W	0.81 (3)	C6—H6	0.9300
O1W—Ni1—O1W^{i}	180.0	H31W—O3W—H32W	106 (3)
O1W—Ni1—O2W	89.95 (6)	C6—N1—C2	124.28 (18)
O1W—Ni1—O2W^{i}	90.05 (6)	C6—N1—H1	118.1 (16)
O1W—Ni1—O3W	88.06 (7)	C2—N1—H1	117.6 (16)
O1W—Ni1—O3W^{i}	91.94 (7)	O2—C2—N1	118.94 (19)
O2W—Ni1—O3W	92.99 (7)	O2—C2—C3	125.81 (19)
O2W—Ni1—O3W^{i}	87.01 (7)	N1—C2—C3	115.24 (18)
O1W^{i}—Ni1—O3W^{i}	88.06 (7)	C3—C4—C5	121.08 (19)
O1W^{i}—Ni1—O3W	91.94 (7)	C3—C4—H4	119.5
O3W^{i}—Ni1—O3W	180.0	C5—C4—H4	119.5
O1W^{i}—Ni1—O2W^{i}	89.95 (6)	C4—C3—C2	121.22 (19)
O3W^{i}—Ni1—O2W^{i}	92.99 (7)	C4—C3—H3	119.4
O1W^{i}—Ni1—O2W	90.05 (6)	C2—C3—H3	119.4
O3W^{i}—Ni1—O2W	87.01 (7)	C6—C5—C4	117.18 (19)
O2W^{i}—Ni1—O2W	180.0	C6—C5—C7	119.20 (18)
Ni1—O1W—H11W	114 (2)	C4—C5—C7	123.62 (18)
Ni1—O1W—H12W	130 (2)	O71—C7—O72	125.51 (19)
H11W—O1W—H12W	110 (3)	O71—C7—C5	116.72 (18)
Ni1—O2W—H21W	110.1 (17)	O72—C7—C5	117.77 (18)
Ni1—O2W—H22W	116 (2)	N1—C6—C5	120.98 (19)
H21W—O2W—H22W	108 (3)	N1—C6—H6	119.5
Ni1—O3W—H31W	129 (2)	C5—C6—H6	119.5
Ni1—O3W—H32W	124 (2)		
C6—N1—C2—O2	−178.1 (2)	C6—C5—C7—O71	1.2 (3)
C6—N1—C2—C3	1.1 (3)	C4—C5—C7—O71	−178.9 (2)
C5—C4—C3—C2	1.2 (3)	C6—C5—C7—O72	−179.1 (2)
O2—C2—C3—C4	177.9 (2)	C4—C5—C7—O72	0.8 (3)

N1—C2—C3—C4	−1.2 (3)	C2—N1—C6—C5	−1.0 (3)
C3—C4—C5—C6	−1.0 (3)	C4—C5—C6—N1	0.8 (3)
C3—C4—C5—C7	179.1 (2)	C7—C5—C6—N1	−179.3 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2*W*	0.87 (2)	2.06 (3)	2.906 (2)	167 (2)
O1*W*—H11*W*···O71^{ii}	0.77 (3)	1.85 (3)	2.612 (2)	173 (3)
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O2*W*—H21*W*···O2^{iv}	0.88 (3)	1.90 (3)	2.772 (2)	173 (2)
O2*W*—H22*W*···O2^{v}	0.77 (3)	1.98 (3)	2.743 (2)	169 (3)
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