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Bis(1*H*-imidazole- κ N³)bis(2-oxido-pyridinium-3-carboxylato- κ^2 O²,O³)-nickel(II)

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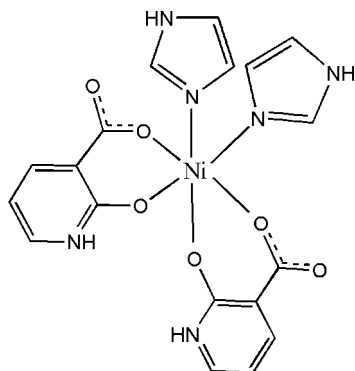
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 Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.025; wR factor = 0.067; data-to-parameter ratio = 13.7.

In the crystal structure of the title Ni^{II} complex, [Ni(C₆H₄NO₃)₂(C₃H₄N₂)₂], the Ni^{II} atom is located on a twofold rotation axis and is chelated by two oxidopyridiniumcarboxylate anions and further *cis*-coordinated by two imidazole ligands in a distorted *cis*-N₂O₄ octahedral geometry. The C—O bond distance of 1.2573 (19) Å found for the non-coordinating O atom of the carboxylate group indicates significant delocalization of π -electron density over this residue. Similarly, the C—O bond distance of 1.260 (2) Å in the heteroaromatic ring indicates delocalization between the deprotonated hydroxy group and the pyridinium ring. The uncoordinated carboxylate O atom links with the imidazole and pyridinium rings of adjacent molecules *via* N—H...O and C—H...O hydrogen bonding, leading to a two-dimensional array parallel to (100).

Related literature

For the nature of π - π stacking, see: Deisenhofer & Michel (1989); Xu *et al.* (2007); Li *et al.* (2005). For the short C—O bond distance between a pyridine ring and hydroxy-O atom in metal complexes of 2-oxidopyridinium-3-carboxylate, see: Yao *et al.* (2004); Yan & Hu (2007*a,b*); Wen & Liu (2007).



Experimental

Crystal data

[Ni(C₆H₄NO₃)₂(C₃H₄N₂)₂]
 $M_r = 471.08$
 Monoclinic, $C2/c$
 $a = 16.5603$ (12) Å
 $b = 9.9687$ (7) Å
 $c = 12.7981$ (9) Å
 $\beta = 111.203$ (2)°

$V = 1969.7$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.04$ mm⁻¹
 $T = 294$ K
 $0.28 \times 0.22 \times 0.18$ mm

Data collection

Rigaku R-Axis RAPID IP diffractometer
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.730$, $T_{\max} = 0.830$

10787 measured reflections
 1934 independent reflections
 1690 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.067$
 $S = 1.09$
 1934 reflections

141 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.26$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O2 ⁱ	0.86	1.93	2.7848 (19)	177
N3—H3 \cdots O2 ⁱⁱ	0.86	2.03	2.796 (2)	148
C3—H3A \cdots O3 ⁱⁱⁱ	0.93	2.41	3.323 (2)	167

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2499).

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supporting information

Acta Cryst. (2009). E65, m977 [doi:10.1107/S1600536809028347]

Bis(1*H*-imidazole- κ N³)bis(2-oxidopyridinium-3-carboxylato- κ^2 O²,O³)nickel(II)

Bing-Yu Zhang, Jing-Jing Nie and Duan-Jun Xu

S1. Comment

As π - π stacking between aromatic rings is correlated with electron transfer process in some biological systems (Deisenhofer & Michel, 1989), metal complexes incorporating aromatic ligands have attracted much attention. As a part of an on-going investigation of π - π stacking (Xu *et al.*, 2007*a, b*; Li *et al.*, 2005), the title complex, (I), has been prepared and its crystal structure reported herein.

The analysis of (I) shows the Ni atom to be located on a 2-fold axis and to be chelated by two oxidopyridinium-carboxylate anions and two *cis*-orientated imidazole ligands to complete a distorted octahedral coordination geometry (Fig. 1). The carboxylate group is twisted with respect to the benzene ring with a dihedral angle of 22.09 (11)°. The C1—O3 bond distance of 1.260 (2) Å is much shorter than a normal single C—O bond, indicating delocalization of π -electron density over the deprotonated hydroxy group and the pyridinium ring, an observation which agrees with similar features found in the other transition metal complexes of oxidopyridinium-carboxylate (Yao *et al.*, 2004; Yan & Hu, 2007*a, b*; Wen & Liu, 2007).

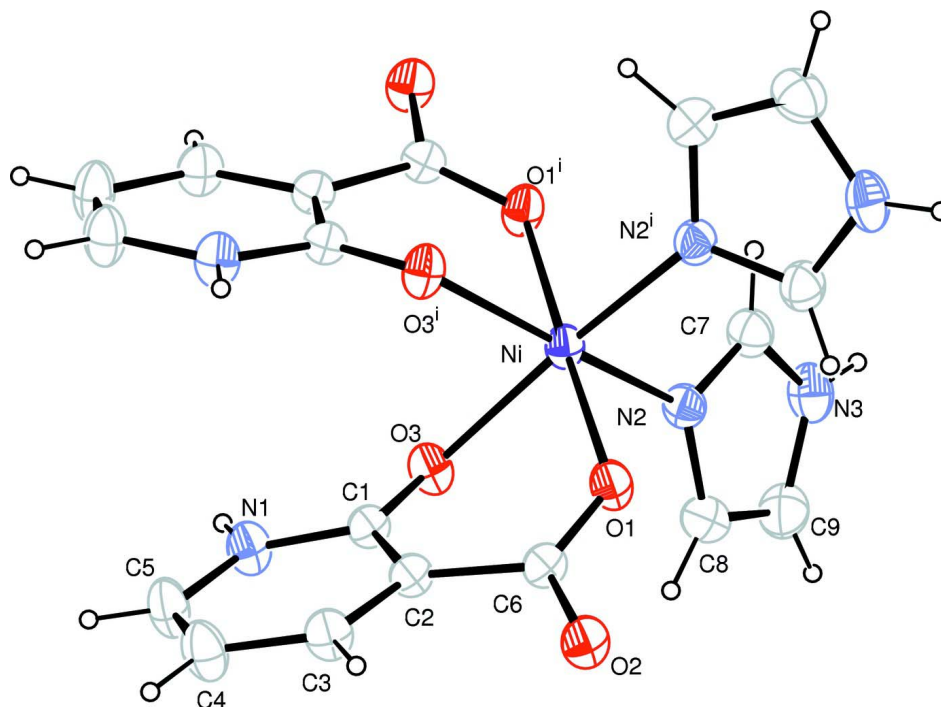
The uncoordinated carboxyl-O atom simultaneously links the imidazole and pyridinium rings *via* N—H \cdots O hydrogen bonding leading to a 2-D array (Table 2). Weak C—H \cdots O hydrogen bonding is also present in the crystal structure but no π - π stacking is evident.

S2. Experimental

2-Hydroxy-pyridine-3-carboxylic acid (0.13 g, 1 mmol), NaOH (0.04 g, 1 mmol), imidazole (0.14 g, 2 mmol) and NiCl₂·6H₂O (0.24 g, 1 mmol) were dissolved in water (15 ml). The solution was refluxed for 4.5 h. After cooling to room temperature, the solution was filtered. Single crystals of (I) were obtained from the filtrate after one week.

S3. Refinement

H atoms were placed in calculated positions with C—H = 0.93 and N—H = 0.86 Å, and refined in riding model approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

**Figure 1**

The molecular structure of (I) showing 40% probability displacement ellipsoids (arbitrary spheres for H atoms) [symmetry code: (i) $1 - x, y, 1/2 - z$].

Bis(1*H*-imidazole- κ N³)bis(2-oxidopyridinium-3-carboxylato- κ^2 O²,O³)nickel(II)

Crystal data

$[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_3)_2(\text{C}_3\text{H}_4\text{N}_2)_2]$

$M_r = 471.08$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 16.5603$ (12) Å

$b = 9.9687$ (7) Å

$c = 12.7981$ (9) Å

$\beta = 111.203$ (2)°

$V = 1969.7$ (2) Å³

$Z = 4$

$F(000) = 968$

$D_x = 1.589$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3268 reflections

$\theta = 2.5\text{--}25.0^\circ$

$\mu = 1.04$ mm⁻¹

$T = 294$ K

Block, green

$0.28 \times 0.22 \times 0.18$ mm

Data collection

Rigaku R-AXIS RAPID IP
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 10.00 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.730$, $T_{\max} = 0.830$

10787 measured reflections

1934 independent reflections

1690 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -20 \rightarrow 20$

$k = -11 \rightarrow 12$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.067$

$S = 1.09$

1934 reflections

141 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

$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 1.5451P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni	0.5000	0.24819 (3)	0.2500	0.02609 (11)
N1	0.61183 (10)	-0.12600 (15)	0.30054 (12)	0.0340 (4)
H1	0.6130	-0.1389	0.2346	0.041*
N2	0.58315 (9)	0.39012 (14)	0.22850 (12)	0.0307 (3)
N3	0.62487 (11)	0.55962 (16)	0.15138 (14)	0.0413 (4)
H3	0.6224	0.6275	0.1088	0.050*
O1	0.55981 (9)	0.25034 (11)	0.42031 (10)	0.0345 (3)
O2	0.62229 (8)	0.17047 (12)	0.59099 (9)	0.0370 (3)
O3	0.58766 (8)	0.09254 (12)	0.25646 (9)	0.0320 (3)
C1	0.59865 (11)	0.00219 (17)	0.32922 (13)	0.0269 (4)
C2	0.60022 (10)	0.01871 (17)	0.44182 (13)	0.0270 (4)
C3	0.61083 (12)	-0.09161 (18)	0.50917 (14)	0.0347 (4)
H3A	0.6108	-0.0806	0.5813	0.042*
C4	0.62173 (15)	-0.22061 (19)	0.47285 (16)	0.0429 (5)
H4	0.6278	-0.2947	0.5192	0.051*
C5	0.62318 (15)	-0.23420 (18)	0.36860 (17)	0.0418 (5)
H5	0.6320	-0.3184	0.3433	0.050*
C6	0.59302 (11)	0.15609 (17)	0.48631 (13)	0.0273 (4)
C7	0.55757 (13)	0.48832 (18)	0.15514 (15)	0.0362 (4)
H7	0.5001	0.5059	0.1115	0.043*
C8	0.67175 (12)	0.4006 (2)	0.27398 (16)	0.0404 (4)
H8	0.7082	0.3442	0.3287	0.049*
C9	0.69804 (13)	0.5053 (2)	0.22712 (18)	0.0456 (5)
H9	0.7547	0.5343	0.2434	0.055*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni	0.03550 (19)	0.02420 (17)	0.01909 (17)	0.000	0.01048 (13)	0.000
N1	0.0520 (9)	0.0317 (8)	0.0228 (7)	0.0040 (7)	0.0192 (7)	-0.0015 (6)
N2	0.0348 (8)	0.0290 (8)	0.0276 (7)	-0.0003 (6)	0.0106 (6)	0.0026 (6)
N3	0.0577 (11)	0.0309 (8)	0.0428 (9)	-0.0040 (7)	0.0272 (8)	0.0049 (7)
O1	0.0514 (8)	0.0281 (6)	0.0213 (6)	0.0057 (5)	0.0098 (6)	0.0002 (5)
O2	0.0551 (8)	0.0371 (7)	0.0175 (6)	0.0040 (6)	0.0117 (5)	-0.0025 (5)
O3	0.0475 (7)	0.0306 (6)	0.0229 (6)	0.0056 (5)	0.0190 (5)	0.0040 (5)
C1	0.0297 (8)	0.0290 (9)	0.0234 (8)	0.0004 (7)	0.0114 (7)	-0.0011 (7)
C2	0.0313 (9)	0.0301 (9)	0.0207 (8)	0.0008 (7)	0.0109 (7)	-0.0010 (7)
C3	0.0479 (11)	0.0357 (10)	0.0230 (9)	0.0020 (8)	0.0156 (8)	0.0016 (7)
C4	0.0682 (14)	0.0303 (10)	0.0339 (10)	0.0057 (9)	0.0229 (10)	0.0069 (8)
C5	0.0647 (14)	0.0268 (10)	0.0370 (11)	0.0057 (9)	0.0222 (10)	-0.0012 (8)
C6	0.0309 (9)	0.0317 (9)	0.0220 (8)	-0.0007 (7)	0.0127 (7)	-0.0021 (7)
C7	0.0415 (10)	0.0335 (10)	0.0335 (10)	-0.0003 (8)	0.0134 (8)	0.0034 (8)
C8	0.0371 (10)	0.0394 (11)	0.0419 (11)	0.0031 (8)	0.0108 (8)	0.0026 (8)
C9	0.0393 (11)	0.0432 (11)	0.0589 (13)	-0.0039 (9)	0.0233 (10)	-0.0059 (10)

Geometric parameters (\AA , $^\circ$)

Ni—O1 ⁱ	2.0422 (12)	O2—C6	1.2573 (19)
Ni—O1	2.0422 (12)	O3—C1	1.260 (2)
Ni—O3 ⁱ	2.1059 (12)	C1—C2	1.441 (2)
Ni—O3	2.1058 (12)	C2—C3	1.369 (2)
Ni—N2	2.0610 (14)	C2—C6	1.504 (2)
Ni—N2 ⁱ	2.0610 (14)	C3—C4	1.401 (3)
N1—C5	1.356 (2)	C3—H3A	0.9300
N1—C1	1.369 (2)	C4—C5	1.350 (3)
N1—H1	0.8600	C4—H4	0.9300
N2—C7	1.316 (2)	C5—H5	0.9300
N2—C8	1.373 (2)	C7—H7	0.9300
N3—C7	1.337 (2)	C8—C9	1.352 (3)
N3—C9	1.361 (3)	C8—H8	0.9300
N3—H3	0.8600	C9—H9	0.9300
O1—C6	1.250 (2)		
O1 ⁱ —Ni—O1	178.80 (6)	O3—C1—C2	127.05 (15)
O1 ⁱ —Ni—N2	86.55 (5)	N1—C1—C2	115.33 (14)
O1—Ni—N2	92.62 (5)	C3—C2—C1	119.31 (15)
O1 ⁱ —Ni—N2 ⁱ	92.62 (5)	C3—C2—C6	120.19 (14)
O1—Ni—N2 ⁱ	86.55 (5)	C1—C2—C6	120.47 (14)
N2—Ni—N2 ⁱ	93.29 (8)	C2—C3—C4	122.08 (16)
O1 ⁱ —Ni—O3 ⁱ	84.52 (5)	C2—C3—H3A	119.0
O1—Ni—O3 ⁱ	96.37 (5)	C4—C3—H3A	119.0
N2—Ni—O3 ⁱ	170.03 (5)	C5—C4—C3	118.07 (17)
N2 ⁱ —Ni—O3 ⁱ	91.53 (5)	C5—C4—H4	121.0

O1 ⁱ —Ni—O3	96.37 (5)	C3—C4—H4	121.0
O1—Ni—O3	84.52 (5)	C4—C5—N1	120.47 (17)
N2—Ni—O3	91.53 (5)	C4—C5—H5	119.8
N2 ⁱ —Ni—O3	170.03 (5)	N1—C5—H5	119.8
O3 ⁱ —Ni—O3	85.08 (7)	O1—C6—O2	122.70 (15)
C5—N1—C1	124.68 (15)	O1—C6—C2	120.28 (14)
C5—N1—H1	117.7	O2—C6—C2	117.02 (15)
C1—N1—H1	117.7	N2—C7—N3	111.32 (17)
C7—N2—C8	105.36 (15)	N2—C7—H7	124.3
C7—N2—Ni	123.21 (12)	N3—C7—H7	124.3
C8—N2—Ni	131.20 (12)	C9—C8—N2	109.68 (17)
C7—N3—C9	107.57 (16)	C9—C8—H8	125.2
C7—N3—H3	126.2	N2—C8—H8	125.2
C9—N3—H3	126.2	C8—C9—N3	106.06 (17)
C6—O1—Ni	129.67 (11)	C8—C9—H9	127.0
C1—O3—Ni	117.96 (10)	N3—C9—H9	127.0
O3—C1—N1	117.62 (14)		

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O2 ⁱⁱ	0.86	1.93	2.7848 (19)	177
N3—H3...O2 ⁱⁱⁱ	0.86	2.03	2.796 (2)	148
C3—H3 <i>A</i> ...O3 ^{iv}	0.93	2.41	3.323 (2)	167

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