

Bis(2-pyridinecarboxylato *N*-oxide- κ^2O,O')nickel(II)

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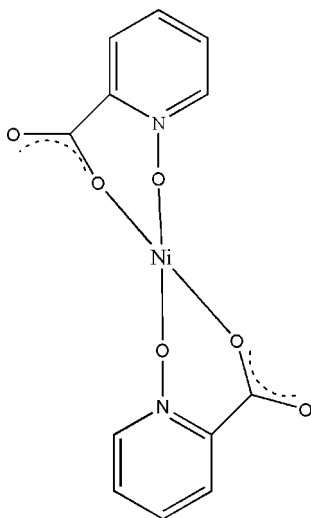
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.020; wR factor = 0.051; data-to-parameter ratio = 9.4.

In the title complex, $[Ni(C_6H_4NO_3)_2]$ or $[Ni(L)_2]$ ($L = 2$ -pyridinecarboxylic acid *N*-oxide), the Ni atom occupies a crystallographic inversion center and is coordinated by four O atoms of two ligands L , giving a square-planar geometry. The O atom of the *N*-oxide is also engaged in a weak interaction with symmetry-related complexes $[2.58(3)$ Å] to form long Ni—O—Ni bridges, which extend parallel to the a axis. The stacking of the square-planar complexes is further stabilized by a slipped π – π interaction between the pyridine rings of adjacent molecules with a centroid-to-centroid distance of $3.3900(7)$ Å and an interplanar distance of $3.099(2)$ Å, resulting in an offset angle of 24° .

Related literature

For related literature, see: Blay *et al.* (2001); Knuuttila (1982); Lassahn *et al.* (2004); Liu & Xu (2005).



Experimental

Crystal data

$[Ni(C_6H_4NO_3)_2]$
 $M_r = 334.91$
 Monoclinic, $P2_1/c$
 $a = 3.3900(7)$ Å
 $b = 12.590(3)$ Å
 $c = 12.170(2)$ Å
 $\beta = 94.18(3)^\circ$

$V = 518.04(18)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.91$ mm⁻¹
 $T = 298(2)$ K
 $0.29 \times 0.21 \times 0.18$ mm

Data collection

Bruker APEXII area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
 $T_{min} = 0.607$, $T_{max} = 0.725$

3157 measured reflections
 915 independent reflections
 839 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.051$
 $S = 1.12$
 915 reflections

97 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.17$ e Å⁻³
 $\Delta\rho_{min} = -0.24$ e Å⁻³

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPIII (Burnett & Johnson, 1996), ORTEP-3 for Windows (Farrugia, 1997) and Mercury (Version 1.4; Macrae *et al.*, 2006); 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: DN2274).

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supplementary materials

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Bis(2-pyridinecarboxylato *N*-oxide- κ^2O,O')nickel(II)

W. Liang-Gui

Comment

Metalcarboxylates with a high stability are efficient catalysts in a vast range of chemical and biochemical processes (Blay *et al.*, 2001; Lassahn *et al.*, 2004). Although a great number of metal carboxylate have been obtained to date, the rational design and synthesis of novel metal carboxylates by employing new synthetic tools or by varying the natures of the reactants and synthetic conditions are currently under active investigation (Liu & Xu, 2005) In this context, 2-pyridine carboxylic acid *N*-oxide, which can exhibit a variety of coordination abilities and has a tendency to form architectures with multi-dimensional frameworks. In this paper, we report the synthesis and crystal structure of the title complex,(I).

In the title complex(I), [Ni(C₁₂H₈N₂O₆)₂] or [Ni(L)₂] (L=2-pyridine carboxylic acid *N*-oxide), the Ni atom occupies a crystallographic inversion center and is coordinated by four oxygen atoms from the carboxylate groups of the ligand L, giving a square planar geometry (Fig. 1). The square planar geometry is very similar to the previously reported structure in which the apical position were occupied by water molecules (at 2.09Å from the Ni) (Knuuttila, 1982).

The oxygen of the *N*-oxide is also engaged in a weak interaction with symmetry related molecules to form long Ni—O—Ni bridges which extend parallel to the *a* axis (Fig. 2). The stacking of the square planar complexes is further stabilized by slipped π - π interaction between the pyridine rings of adjacent molecules with a centroid-to-centroid distance of 3.3900 (7)Å and an interplanar distance of 3.099 (2)Å resulting in an offset angle of 24° (Fig. 2).

Experimental

L(0.026 g, 0.013 mmol), NiCl₂ (0.16 g, 0.11 mmol) and NaOH(0.048 mmol,0.12 mmol), were added in a mixed solvent of ethanol, the mixture was heated for three hours under reflux. during the process stirring and influx were required. The resultant was then filtered to give a pure solution which was infiltrated by diethyl ether freely in a closed vessel, a weeks later some single crystals of the size suitable for X-Ray diffraction analysis.

Refinement

All H atoms were placed in calculated positions and treated as riding on their parent C atoms with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

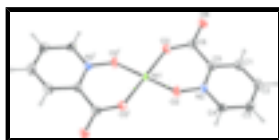


Fig. 1. Molecular view of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. [Symmetry code (i): $-x + 1, -y + 1, -z + 1$]

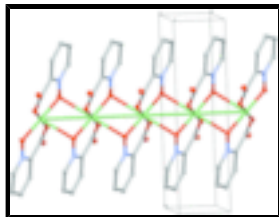


Fig. 2. Partial packing view showing the stacking of the complexes through formation of elongated Ni—O—Ni bridges and slipped π - π interaction.

Bis(*N*-oxido-2-pyridinecarboxylato- κ^2 O,*O'*)nickel(II)

Crystal data

[Ni(C ₆ H ₄ NO ₃) ₂]	$F_{000} = 340$
$M_r = 334.91$	$D_x = 2.147 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P 2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 3.3900 (7) \text{ \AA}$	Cell parameters from 915 reflections
$b = 12.590 (3) \text{ \AA}$	$\theta = 2.3\text{--}25.2^\circ$
$c = 12.170 (2) \text{ \AA}$	$\mu = 1.91 \text{ mm}^{-1}$
$\beta = 94.18 (3)^\circ$	$T = 298 (2) \text{ K}$
$V = 518.04 (18) \text{ \AA}^3$	Block, colourless
$Z = 2$	$0.29 \times 0.21 \times 0.18 \text{ mm}$

Data collection

Bruker APEXII area-detector diffractometer	915 independent reflections
Radiation source: fine-focus sealed tube	839 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.017$
$T = 298(2) \text{ K}$	$\theta_{\text{max}} = 25.2^\circ$
φ and ω scan	$\theta_{\text{min}} = 2.3^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -4 \rightarrow 4$
$T_{\text{min}} = 0.607$, $T_{\text{max}} = 0.725$	$k = -14 \rightarrow 15$
3157 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.020$	H-atom parameters constrained
$wR(F^2) = 0.051$	$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 0.1009P]$
$S = 1.12$	where $P = (F_o^2 + 2F_c^2)/3$
915 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$

97 parameters

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.5000	0.5000	0.02274 (13)
O2	0.8684 (4)	0.39064 (10)	0.52462 (10)	0.0332 (3)
O3	0.4295 (4)	0.46542 (10)	0.34855 (10)	0.0321 (3)
O6	0.5595 (4)	0.38865 (11)	0.19304 (10)	0.0363 (3)
N2	0.8894 (4)	0.30378 (11)	0.46114 (12)	0.0234 (3)
C1	0.8087 (5)	0.20531 (14)	0.29725 (15)	0.0303 (4)
H1	0.7196	0.2011	0.2233	0.036*
C2	0.9798 (6)	0.11894 (15)	0.34717 (18)	0.0354 (5)
H2	1.0072	0.0558	0.3089	0.042*
C3	1.1109 (5)	0.12780 (14)	0.45565 (17)	0.0334 (4)
H3	1.2339	0.0703	0.4918	0.040*
C4	1.0625 (5)	0.22033 (15)	0.51132 (14)	0.0276 (4)
H4	1.1517	0.2252	0.5853	0.033*
C5	0.7630 (5)	0.29947 (13)	0.35319 (14)	0.0239 (4)
C6	0.5738 (5)	0.39276 (13)	0.29371 (14)	0.0253 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0274 (2)	0.02038 (19)	0.01969 (18)	0.00616 (11)	-0.00324 (13)	-0.00257 (11)
O2	0.0392 (8)	0.0295 (7)	0.0294 (7)	0.0109 (6)	-0.0084 (5)	-0.0096 (5)
O3	0.0357 (7)	0.0339 (7)	0.0258 (6)	0.0108 (6)	-0.0044 (5)	-0.0034 (6)
O6	0.0428 (8)	0.0429 (8)	0.0226 (7)	0.0039 (6)	-0.0008 (6)	-0.0025 (6)
N2	0.0215 (7)	0.0223 (8)	0.0267 (7)	-0.0003 (6)	0.0029 (6)	-0.0027 (6)
C1	0.0239 (9)	0.0338 (10)	0.0335 (9)	-0.0038 (7)	0.0033 (7)	-0.0066 (8)
C2	0.0279 (10)	0.0267 (10)	0.0523 (12)	-0.0003 (7)	0.0074 (9)	-0.0095 (9)
C3	0.0250 (10)	0.0256 (10)	0.0499 (12)	0.0011 (7)	0.0050 (9)	0.0036 (8)
C4	0.0231 (9)	0.0286 (10)	0.0310 (9)	0.0024 (7)	0.0012 (7)	0.0051 (7)
C5	0.0198 (9)	0.0263 (9)	0.0258 (8)	-0.0045 (7)	0.0027 (7)	-0.0014 (7)

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C6 0.0231 (9) 0.0265 (9) 0.0259 (9) -0.0042 (7) -0.0009 (7) -0.0030 (7)

Geometric parameters (Å, °)

Ni1—O2	1.8684 (13)	C1—C2	1.355 (3)
Ni1—O2 ⁱ	1.8684 (13)	C1—C5	1.381 (2)
Ni1—O3	1.8920 (13)	C1—H1	0.9300
Ni1—O3 ⁱ	1.8920 (13)	C2—C3	1.367 (3)
O2—N2	1.3437 (18)	C2—H2	0.9300
O3—C6	1.253 (2)	C3—C4	1.364 (3)
O6—C6	1.224 (2)	C3—H3	0.9300
N2—C4	1.330 (2)	C4—H4	0.9300
N2—C5	1.353 (2)	C5—C6	1.499 (2)
O2—Ni1—O2 ⁱ	180.000 (1)	C1—C2—H2	121.1
O2—Ni1—O3	91.27 (6)	C3—C2—H2	121.1
O2 ⁱ —Ni1—O3	88.73 (6)	C4—C3—C2	120.49 (17)
O2—Ni1—O3 ⁱ	88.73 (6)	C4—C3—H3	119.8
O2 ⁱ —Ni1—O3 ⁱ	91.27 (6)	C2—C3—H3	119.8
O3—Ni1—O3 ⁱ	180.000 (1)	N2—C4—C3	120.78 (16)
N2—O2—Ni1	124.77 (10)	N2—C4—H4	119.6
C6—O3—Ni1	131.34 (12)	C3—C4—H4	119.6
C4—N2—O2	114.77 (14)	N2—C5—C1	118.30 (16)
C4—N2—C5	120.80 (15)	N2—C5—C6	122.10 (14)
O2—N2—C5	124.38 (14)	C1—C5—C6	119.59 (16)
C2—C1—C5	121.83 (18)	O6—C6—O3	125.15 (17)
C2—C1—H1	119.1	O6—C6—C5	115.76 (15)
C5—C1—H1	119.1	O3—C6—C5	119.01 (15)
C1—C2—C3	117.77 (18)		

Symmetry codes: (i) $-x+1, -y+1, -z+1$.

Fig. 2

