

Monoclinic and triclinic forms of bis[2-hydroxy-2,2-bis(2-pyridyl)-ethanoato-*O*¹,*N,N'*]nickel(II)

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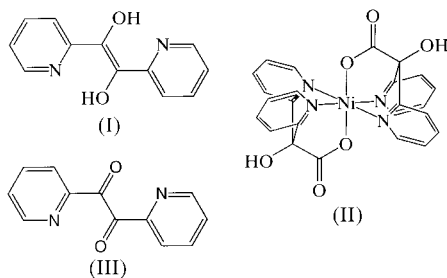
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Reaction of pyridoin with nickel nitrate in methanol in air gives crystals of two forms of the title compound, $[\text{Ni}(\text{C}_{12}\text{H}_9\text{N}_2\text{O}_3)_2]$; a triclinic form with the Ni atom on an inversion centre and a monoclinic form with one molecule in a general position in the asymmetric unit. Both forms show an octahedral nickel centre coordinated by two facial tridentate ligands with their O-atom donors *trans*.

Comment

As part of a broad study to examine relatively simple chelating ligands which have the potential to bridge metal centres, the reaction between 2,2'-pyridoin, (I), and nickel nitrate in the presence of base was investigated. From the initial reaction mixture pale-mauve triclinic centrosymmetric crystals of bis(pyridilato)nickel(II), (II), were obtained. This complex, which has been reported previously (Black, 1967; Black & Srivastava, 1969) but was not crystallographically characterized, can be obtained by the metal-promoted rearrangement of 2,2'-pyridil, (III), in basic solution. The reaction is analogous to the benzilic acid rearrangement which applies broadly to aromatic α -diketones (Selman & Eastman, 1960). We propose that oxidation of (I) to (III) occurs in our mixture and this is followed by the rearrangement reported by Black.



Analysis of the geometry of the bonds in the complex suggests very little strain. From a consideration of bond angles

at donor atoms, it appears that non-bonded electron pairs are oriented directly towards the octahedral nickel centre. The complementary relationship between the geometry of the tridentate ligand and the octahedral metal centre suggests that this monoanion and substituted derivatives have potential as blocking ligands when three vacant facial sites on an octahedral metal centre are required.

Further attempts at the above reaction yielded monoclinic crystals with systematic absences consistent with the space groups $P2_1$ and $P2_1/m$. Despite a thorough investigation, a solution could only be obtained in the space group $P2_1$. The monoclinic form shows the absence of crystallographic symmetry within the complex leading to an asymmetric unit twice the size of the triclinic form.

Experimental

Both types of crystals were obtained by the following procedure: 50 mg of pyridoin was dissolved in 15 ml of methanol by gentle heating followed by the addition of an excess of tetramethylammonium hydroxide. A 5 ml methanolic solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (45 mg) was then added. Crystals were grown directly from this solution.

Triclinic (II)

Crystal data

$[\text{Ni}(\text{C}_{12}\text{H}_9\text{N}_2\text{O}_3)_2]$
 $M_r = 517.13$
Triclinic, $P\bar{1}$
 $a = 7.6800$ (11) Å
 $b = 8.576$ (2) Å
 $c = 8.889$ (2) Å
 $\alpha = 88.29$ (2)°
 $\beta = 78.46$ (2)°
 $\gamma = 67.29$ (2)°
 $V = 528.40$ (18) Å³

$Z = 1$
 $D_x = 1.625$ Mg m⁻³
Cu $K\alpha$ radiation
Cell parameters from 24 reflections
 $\theta = 10.6\text{--}34.6^\circ$
 $\mu = 1.788$ mm⁻¹
 $T = 293$ (2) K
Parallelepiped, pale purple
0.17 × 0.11 × 0.08 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω - 2θ scans
Absorption correction: numerical (*SHELXL76*; Sheldrick, 1976)
 $T_{\text{min}} = 0.755$, $T_{\text{max}} = 0.875$
2619 measured reflections
2168 independent reflections
1844 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$
 $\theta_{\text{max}} = 74.70^\circ$
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -11 \rightarrow 1$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.131$
 $S = 1.071$
2168 reflections
162 parameters
Only H-atom U 's refined

$w = 1/[\sigma^2(F_o^2) + (0.0796P)^2 + 0.1640P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.67$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for triclinic (II).

Ni1—O1	2.0445 (18)	O1—C12	1.261 (3)
Ni1—N2	2.073 (2)	O2—C12	1.233 (3)
Ni1—N1	2.079 (2)	O3—C6	1.404 (3)

O1—Ni1—N2	86.87 (8)	C12—O1—Ni1	121.67 (17)	O4—Ni1—O1	177.53 (17)	N1—Ni1—N4	95.73 (19)
O1—Ni1—N2 ⁱ	93.13 (8)	C1—N1—Ni1	119.03 (17)	O4—Ni1—N2	90.52 (17)	C12—O1—Ni1	121.9 (4)
O1—Ni1—N1	87.04 (8)	C5—N1—Ni1	122.39 (19)	O1—Ni1—N2	87.83 (19)	C24—O4—Ni1	122.0 (4)
N2—Ni1—N1	84.90 (9)	C7—N2—Ni1	119.36 (17)	O4—Ni1—N3	87.50 (18)	C1—N1—Ni1	118.8 (4)
O1—Ni1—N1 ⁱ	92.96 (8)	C11—N2—Ni1	122.06 (18)	O1—Ni1—N3	94.42 (18)	C5—N1—Ni1	122.3 (4)
N2—Ni1—N1 ⁱ	95.10 (9)	O2—C12—O1	127.1 (3)	N2—Ni1—N3	93.30 (18)	C11—N2—Ni1	122.4 (4)
				O4—Ni1—N1	92.50 (18)	C7—N2—Ni1	119.1 (3)
				O1—Ni1—N1	85.56 (17)	C17—N3—Ni1	121.7 (4)
				N2—Ni1—N1	86.27 (18)	C13—N3—Ni1	119.2 (4)
				N3—Ni1—N1	179.6 (2)	C19—N4—Ni1	119.9 (4)
				O4—Ni1—N4	86.37 (19)	C23—N4—Ni1	122.0 (4)
				O1—Ni1—N4	95.33 (18)	O2—C12—O1	128.5 (6)
				N2—Ni1—N4	176.4 (2)	O5—C24—O4	126.5 (6)
				N3—Ni1—N4	84.70 (18)		

Symmetry code: (i) $-x, -y, -z$.

Monoclinic (II)

Crystal data

[Ni(C₁₂H₉N₂O₃)₂]

$M_r = 517.13$

Monoclinic, $P2_1$

$a = 7.7763$ (8) Å

$b = 15.736$ (2) Å

$c = 8.8390$ (14) Å

$\beta = 96.560$ (11)°

$V = 1074.5$ (2) Å³

$Z = 2$

$D_x = 1.598$ Mg m⁻³

Cu $K\alpha$ radiation

Cell parameters from 25

reflections

$\theta = 11.7$ – 37.6°

$\mu = 1.758$ mm⁻¹

$T = 293$ (2) K

Parallelepiped, pale purple

$0.11 \times 0.10 \times 0.07$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer

ω – 2θ scans

Absorption correction: numerical

(*SHELXL76*; Sheldrick, 1976)

$T_{\min} = 0.776$, $T_{\max} = 0.905$

2922 measured reflections

2445 independent reflections

2102 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\text{max}} = 74.60^\circ$

$h = -9 \rightarrow 9$

$k = -19 \rightarrow 1$

$l = -1 \rightarrow 11$

3 standard reflections

frequency: 120 min

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.116$

$S = 1.054$

2445 reflections

321 parameters

Only H-atom U 's refined

$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.3968P]$

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

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

$\Delta\rho_{\text{max}} = 0.43$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.56$ e Å⁻³

Absolute structure: Flack (1983)

Flack parameter = 0.48 (10)

Table 2

Selected geometric parameters (Å, °) for monoclinic (II).

Ni1—O4	2.037 (4)	O1—C12	1.249 (7)
Ni1—O1	2.042 (4)	O2—C12	1.232 (7)
Ni1—N2	2.069 (4)	O3—C6	1.405 (6)
Ni1—N3	2.075 (4)	O4—C24	1.269 (7)
Ni1—N1	2.077 (4)	O5—C24	1.218 (7)
Ni1—N4	2.082 (5)	O6—C18	1.416 (7)

Given that the Ni atom in the triclinic crystal is situated on a centre of symmetry, the decision to opt for the non-centrosymmetric space group $P2_1$ over $P2_1/m$ for the monoclinic form was made after careful examination of the data, the Patterson map and the refined structure. Furthermore, the absence of a mirror plane normal to the b axis as required for the space group $P2_1/m$ is apparent in a unit-cell diagram. The Flack test result is ambiguous indicating that the absolute configuration could not be reliably determined. It was not possible to unambiguously identify H atoms of the hydroxyl group in either structure, presumably because of disorder and as a consequence they were not included in the models.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *PROCESS_DATA* (Gable *et al.*, 1993); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997).

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