

Interpenetrating nets in *cis*-bis(pyridine-4-carboxylate)nickel(II)

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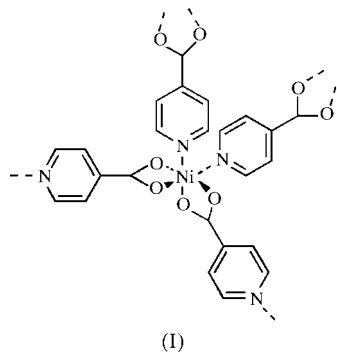
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The title compound, $[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_2)_2]$, crystallized in a three-dimensional framework consisting of three interpenetrating diamond-like nets. The Ni atom is on a twofold axis, the coordination is '(O₂)₂N₂' in a *cis* arrangement and the ligands are bridging.

Comment

Molecules containing bifunctional and multifunctional pyridine or carboxylate groups, such as 4,4'-bipyridine (Fujita *et al.*, 1994; Stang *et al.*, 1995; Yaghi & Li, 1995; Kondo *et al.*, 1997; Hagrman *et al.*, 1997; Kumar *et al.*, 1998; Keller & Lopez, 1999; Biradha *et al.*, 1999; Gudbjartson *et al.*, 1999; Zhang *et al.*, 1999), benzene-1,4-dicarboxylate (Eddaoudi *et al.*, 2001; Groeneman *et al.*, 1998; Guilera & Steed, 1999; Lo *et al.*, 2000), pyridine-4-carboxylate (pyca) (MacGillivray *et al.*, 1998; Evans, Wang *et al.*, 1999; Evans, Xiong *et al.*, 1999; Ma *et al.*, 1999; Evans & Lin, 2000), benzene-1,3,5-tricarboxylate (Chui *et al.*, 1999; Chen *et al.*, 2001; Choi & Suh, 1998) and other bridging molecules (Batten & Robson, 1998; Batten, 2001; Leininger *et al.*, 2000; Fujita *et al.*, 2001; Yaghi *et al.*, 1998) are often used as ligands in the construction of coordination



polymers with different nanostructures and interpenetrating nets. Diamond-related nets constitute the largest class of interpenetrating structures and most of these involve Zn^{II},

Cd^{II}, Cu^I and Ag^I metals (Batten & Robson, 1998). So far, no diamond-like net arrangement has been reported with Ni^{II} as the transition metal (Allen *et al.*, 1983).

The Ni^{II} ion in the title compound, (I), is six-coordinated by two *cis*-pyridyl N atoms of two μ -pyca anions and two *O,O'*-chelating carboxylate groups of two additional μ -pyca anions (Fig. 1). The two Ni–O bond distances of the chelating μ -pyca anion are significantly different. One [Ni1–O2 2.074 (3) Å] is significantly longer than the Ni–N bond distance [Ni1–N1 2.041 (3) Å], and the other [Ni1–O1

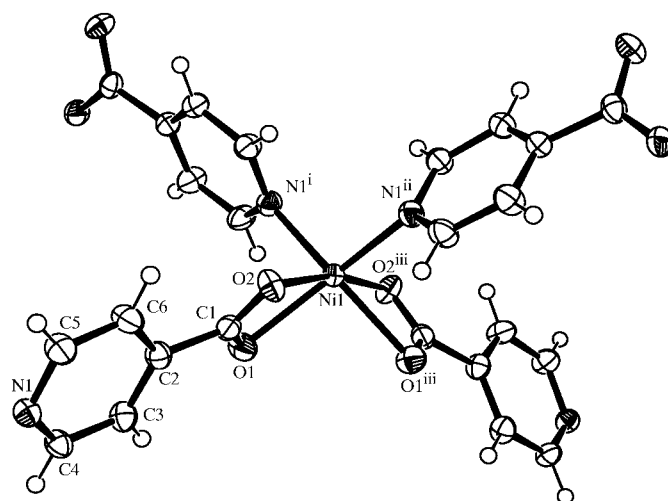


Figure 1
ORTEP-3 (Farrugia, 1997) view of (I) shown with 50% probability displacement ellipsoids. [Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{4} - z$; (ii) $\frac{1}{2} - y, \frac{1}{2} + x, \frac{3}{4} + z$; (iii) $y, x, -z$.]

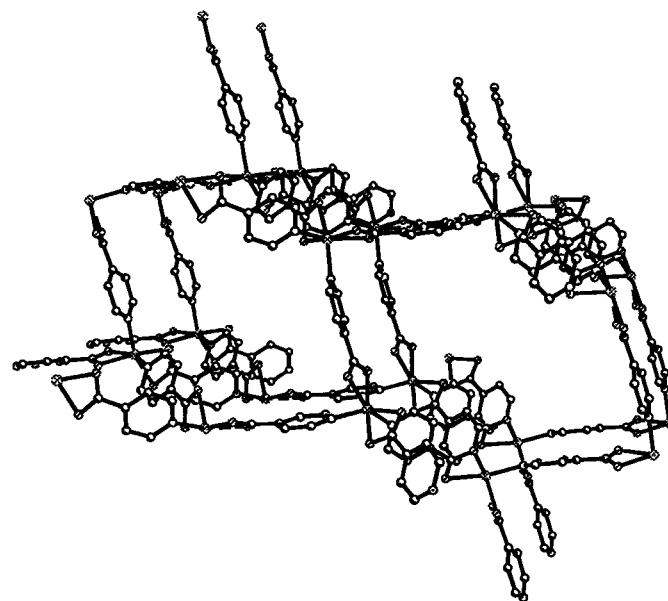


Figure 2
The three-dimensional framework of (I).

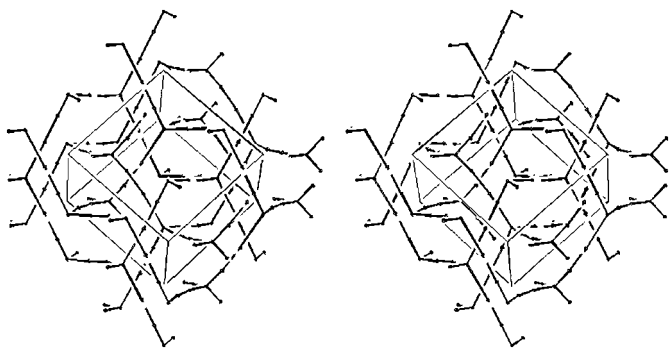


Figure 3

Stereoview of (I) using the Ni, C1 and N1 atoms connected by lines, displaying the threefold interpenetrating diamond-like nets.

2.208 (2) Å] is much longer. The angles around the Ni^{II} ion are also very different. The O1–Ni1–O2 and N18–Ni1–O1 angles are 61.88 (9) and 156.06 (10)°, respectively, while the other angles are closer to 90° [88.22 (10)–100.65 (15)°] and 180° [166.71 (14)°]; thus, the octahedral geometry of the Ni^{II} ion is highly distorted. The pyca ligand is not planar and has a dihedral angle of 19.5 (2)° between the planes defined by the carboxylate group and the pyridine moiety.

The extended arrangement consists of each Ni^{II} ion connected with four neighboring Ni^{II} ions through pyca bridges, forming a three-dimensional diamond-like net (Fig. 2). Three independent three-dimensional diamond-like nets interpenetrate with each other (Fig. 3). The Ni···Ni separation in each three-dimensional net is 8.760 (5) Å.

Experimental

A mixture of Eu₂O₃ (0.088 g, 0.25 mmol), NiCl₂·6H₂O (0.119 g, 0.5 mmol), pyridine-4-carboxylic acid (0.246 g, 0.2 mmol) and water (15 ml) was sealed in a 35 ml Teflon-capped ace pressure tube, heated to 453 K and held at that temperature for 12 h. During this time, the solid Eu₂O₃ dissolved completely and deep-green crystals of (I) (10% based on nickel) formed at the bottom of the tube. When the tube was cooled to room temperature, blue crystals of *trans*-tetraaquabis(pyridine-4-carboxylate-*κ*N)nickel(II) (Batten & Harris, 2001) (40% based on nickel) formed. These were mechanically separated under a microscope from the green crystals. In this reaction, the Eu₂O₃ compound presumably acts as a weak base. If the reaction temperature is below 413 K, only *trans*-tetraaquabis(pyridine-4-carboxylate-*κ*N)nickel(II) is obtained (Batten & Harris, 2001). This suggests that the formation of the highly distorted structure in (I) requires more vigorous reaction conditions.

Crystal data

[Ni(C₆H₄NO₂)₂]
 $M_r = 302.90$
 Tetragonal, $P4_32_12$
 $a = 11.678$ (3) Å
 $c = 8.6608$ (12) Å
 $V = 1181.1$ (4) Å³
 $Z = 4$
 $D_x = 1.703$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10$ –15°
 $\mu = 1.65$ mm⁻¹
 $T = 293$ (2) K
 Prism, green
 $0.50 \times 0.45 \times 0.40$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Non-profiled $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.451$, $T_{\max} = 0.516$
 1448 measured reflections
 1043 independent reflections
 1021 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.04$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 13$
 $l = -1 \rightarrow 10$
 3 standard reflections
 frequency: 166 min
 intensity decay: 1%

Refinement

Refinement on F^2
 $R(F) = 0.029$
 $wR(F^2) = 0.092$
 $S = 1.18$
 1043 reflections
 87 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 0.3267P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³
 Absolute structure: (Flack, 1983),
 327 Friedel pairs
 Flack parameter = 0.01 (3)

H atoms were treated as riding, with C–H distances of 0.93 Å and isotropic displacement parameters set to 1.2 times the equivalent isotropic displacement parameter of the C atoms to which they were attached.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1362). Services for accessing these data are described at the back of the journal.

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