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mer-Tris(1*H*-benzotriazole-κ*N*)(pyridine-2,6-dicarboxylato-κ^3*N*,*O*,*O*′)nickel(II)

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Key indicators

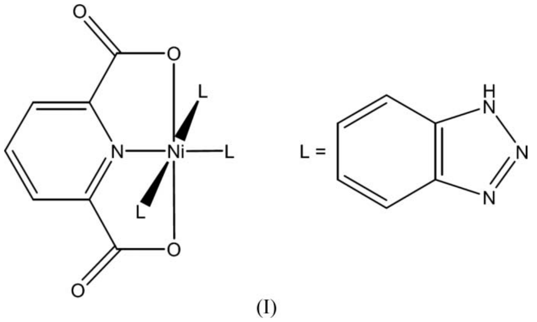
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.094
Data-to-parameter ratio = 17.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title complex, [Ni($C_7H_3NO_4$)($C_6H_5N_3$)$_3$], has been prepared hydrothermally. Three neutral monodentate benzotriazole ligands occupy meridional sites about the octahedrally coordinated nickel(II) cation. The remaining sites are occupied by the N and two O atoms of a tridentate pyridine-2,6-dicarboxylate dianion.

Comment

As part of our work on transition metal salts of pyridine-2,6-dicarboxylic acid (dipicolinic acid, dipicH$_2$) (Kumaresan *et al.*, 2004; Kumaresan & Ramadevi, 2005), we prepared the title compound, (I), from nickel(II) acetate, dipicolinic acid and benzotriazole (see *Experimental*).



(I)

The mononuclear complex contains an octahedrally coordinated nickel(II) cation. One N and two O atoms of a planar dipic^{2-} dianion occupy three coordination sites and the remaining three meridional sites are occupied by donor N atoms of identically coordinated benzotriazole ligands (Fig. 1). The molecule can be viewed as a four-bladed paddle wheel, with the Ni—O1 bond as axis and the four ligands, each nearly planar, as paddles.

The Cambridge Structural Database (CSD, Version 5.26, November 2004 update; Allen, 2002) contains results for nine complexes in which a nickel(II) cation is coordinated in a κ^3-*N*,*O*,*O*′ fashion by a dipic^{2-} dianion. These compounds display Ni—N bond lengths in the narrow range 1.952–1.979 Å, more variable Ni—O distances of 2.092–2.182 Å and O—Ni—O angles of 154.4–156.5°. In the title complex (Table 1), the only non-typical feature of the Ni–dipic bonding is the Ni—N1 distance [1.992 (2) Å], which falls just outside the expected range. The difference in length between the Ni—O1 and Ni—O3 bonds of 0.068 (2) Å is not unusual. Here it is accompanied by differences in the conformations of the two chelate rings formed by the dipic^{2-} ligand. Both rings are envelopes with Ni at the flap; the N1—C5—C7—O3—Ni ring is the more puckered, with endocyclic torsion angles about Ni—O3 and Ni—N1 of −4.7 (1) and 4.8 (1)°, respectively. The corre-

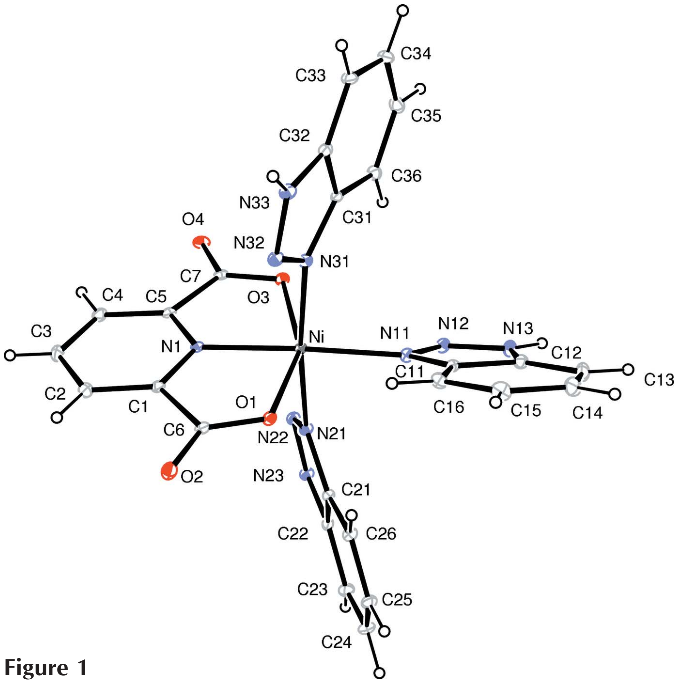


Figure 1
A view of the title molecule, with the atom-numbering scheme and 20% probability displacement ellipsoids.

sponding values for the N1—C1—C6—O1—Ni ring are only 1.3 (1) and −1.3 (1)°, respectively. We also note that the structurally characterized examples of nickel(II) bonded to neutral dipicH_2 and to monanionic dipicH^- have Ni—N and Ni—O bond lengths which fall in similar ranges to those found in Ni–dipic^{2-} complexes (Zhang *et al.*, 2003; Nathan & Mai, 2000).

Each benzotriazole ligand in (I) binds to the metal atom through a single unprotonated N atom. This is by far the most common form of coordination of the benzotriazole molecule to a metal, as a search of the CSD makes clear, but it has not previously been reported for nickel(II). However, a complex in which this ligand bridges two nickel(II) ions has been described (Meunier-Piret *et al.*, 1976). The mutually *trans* Ni—N21 and Ni—N31 bonds of 2.088 (2) and 2.079 (2) Å, respectively, are significantly longer than the Ni—N11 distance of 2.049 (2) Å, suggesting that the triazole N atom exerts a stronger *trans* influence than pyridine N. Corresponding bond lengths in the three triazole ligands agree well with each other (Table 2) and with values in benzotriazole ligands and free molecules from the CSD. Evidently, coordination has little effect on the character of the N—N bonds or on the slight tendency to bond alternation in the C_6 rings.

The mononuclear complexes are linked by N—H⋯O hydrogen bonds (Table 3). All three benzotriazole N—H bonds act as donors, two to the free carboxylate atoms O2 and O4, and one to the metal-coordinated atom O3 (Fig. 2). This may explain the lengthening of Ni—O3 by 0.068 (2) Å relative to Ni—O1.

The atomic U^{ij} values are moderately well reproduced by a TLS analysis (Schomaker & Trueblood, 1968): $R_2 = (\Sigma\Delta U^2/\Sigma U^2)^{\frac{1}{2}} = 0.20$. The worst discrepancy in the Hirshfeld (1976) rigid-bond test is $\Delta U = 0.004$ (11) Å^2 for C6—O1.

Experimental

A mixture of $[Ni(CH_3CO_2)_2]\cdot 4H_2O$ (31 mg), dipicolinic acid (20 mg), benzotriazole (24 mg) and water (2.5 ml) in a mole ratio of 1.03:1:1.68:1.15 was homogenized for 30 min. It was then sealed in a 23 ml polyfluoroethylene-lined stainless steel bomb and kept at 423 K under autogenous pressure for 72 h. On cooling to room temperature at 10 K h^{-1}, blue crystals of (I) formed. These were collected by filtration, washed in de-ionized water and then in diethyl ether, and finally dried.

Crystal data

$[Ni(C_7H_3NO_4)(C_6H_5N_3)_3]$
$M_r = 581.2$
Monoclinic, $P2_1/c$
$a = 9.8964$ (1) Å
$b = 10.3253$ (1) Å
$c = 26.0261$ (4) Å
$\beta = 98.971$ (1)°
$V = 2626.90$ (6) Å^3
$Z = 4$

$D_x = 1.47$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15068 reflections
$\theta = 1$–27°
$\mu = 0.79$ mm^{-1}
$T = 100$ K
Needle, blue
0.56 × 0.18 × 0.18 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.731$, $T_{max} = 0.867$
35667 measured reflections
6231 independent reflections

5149 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 27.9$°
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 12$
$l = -32 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.094$
$S = 1.06$
6231 reflections
361 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 1.0906P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—N1	1.9922 (15)	O1—C6	1.265 (2)
Ni—N11	2.0489 (15)	O2—C6	1.245 (2)
Ni—N31	2.0788 (14)	O3—C7	1.270 (2)
Ni—N21	2.0879 (15)	O4—C7	1.246 (2)
Ni—O1	2.1124 (12)	C35—C36	1.375 (3)
Ni—O3	2.1802 (12)		
N1—Ni—N11	177.23 (6)	O1—Ni—O3	154.82 (5)
N31—Ni—N21	173.43 (6)		
O1—Ni—N11—N12	151.94 (13)	O1—Ni—N31—N32	−15.81 (13)
O1—Ni—N21—N22	149.03 (13)		

Table 2
Comparison of selected ligand bond lengths (Å).

Ligand	$n = 1$	$n = 2$	$n = 3$
N*n*1—N*n*2	1.310 (2)	1.311 (2)	1.318 (2)
N*n*1—C*n*1	1.373 (2)	1.379 (2)	1.379 (2)
N*n*2—N*n*3	1.334 (2)	1.339 (2)	1.336 (2)
N*n*3—C*n*2	1.361 (2)	1.360 (2)	1.355 (2)
C*n*1—C*n*2	1.393 (3)	1.395 (2)	1.395 (2)
C*n*1—C*n*6	1.406 (2)	1.408 (2)	1.407 (3)
C*n*2—C*n*3	1.404 (3)	1.404 (3)	1.403 (3)
C*n*3—C*n*4	1.369 (3)	1.369 (3)	1.373 (3)
C*n*4—C*n*5	1.413 (3)	1.412 (3)	1.417 (3)
C*n*5—C*n*6	1.375 (3)	1.379 (3)	1.375 (3)

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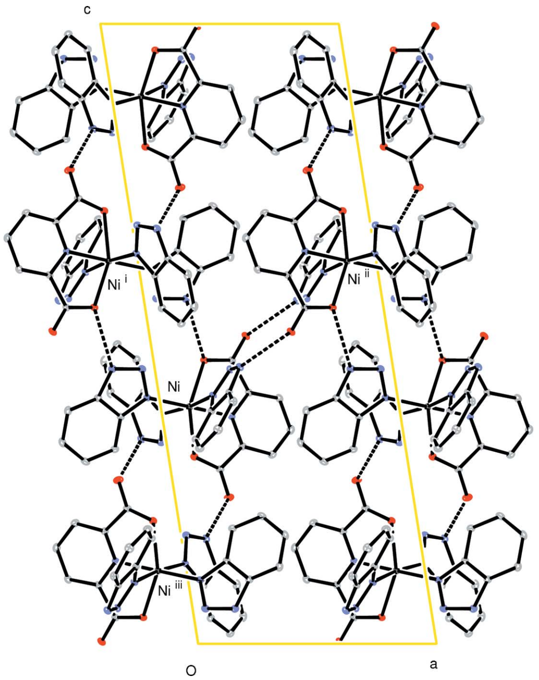

Figure 2
The unit-cell contents of (I), viewed in projection down *b*. Dotted lines represent hydrogen bonds. H atoms have been omitted. Symmetry codes are as defined in Table 3.

Table 3
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N13-H13\cdots O3^{i}$	0.86	1.96	2.7777 (19)	160
$N23-H23\cdots O4^{ii}$	0.86	1.88	2.6612 (18)	151
$N33-H33\cdots O2^{iii}$	0.86	1.78	2.617 (2)	165

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

The interpretation of the structure depends critically on the positioning of the H atoms and it is therefore important to note that all H atoms were unambiguously located in difference maps. In the final refinement, their positions were idealized geometrically and they then rode on their parent atoms, with C—H = 0.93 Å and N—H = 0.86 Å, and with $U_{iso}(H) = 1.2U_{eq}(C \text{ or } N)$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SORTAV* in *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX*.

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