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Poly[bis(μ_2-pyridine-2,6-dicarboxylato)-nickel(II)disodium(I)]

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The title compound, $[Na_2Ni(C_7H_3NO_4)_2]_n$, was synthesized by reaction of pyridyl-2,6-dicarboxylic acid (H_2PDC) and $NiCl_2$ in the presence of NaOH. Two PDC units ligate to the Ni^{II} cation in an *N*,*O*′,*O*″-tridentate manner and the Ni^{II} cation, which lies on a twofold rotation axis, has distorted tetragonal–bipyramidal octahedral geometry. The Na^+ ions are surrounded by the O atoms of the PDC anions and one-dimensional chains are constructed by interactions between O and Na.

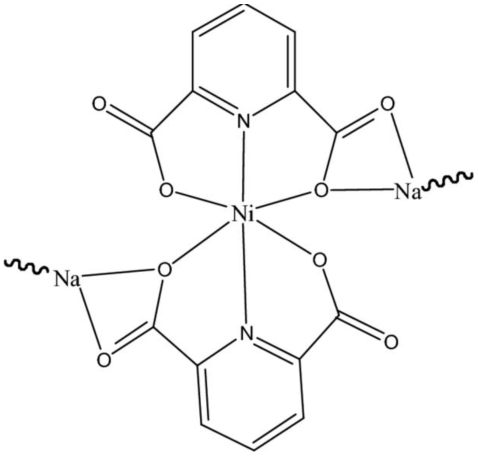
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
R factor = 0.028
wR factor = 0.075
Data-to-parameter ratio = 13.1

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

Comment

The multifunctional ligand pyridyl-2,6-dicarboxylic acid, H_2PDC, is of particular interest for obtaining metal–organic framework (MOF) systems, because it possesses potential carboxylic acid coordinating sites which can be deprotonated, resulting in a divalent anion, and a third, neutral, aromatic N coordinating site (MacDonald *et al.*, 2000). It usually acts as a tridentate NO_2 donor upon ligation to metal ions. Aiming to probe the size effects of metal ions on their hydration and binding to carboxylic acid O atoms, this work adopted H_2PDC as a ligand to prepare anionic Ni^{II} complexes with Na^+ and Ni^{2+} as counter-ions. The title complex, (I), and $[Ni_2(PDC)_2(H_2O)_5](H_2O)$, (II) (Wen *et al.*, 2002), were obtained by reacting different molar ratios of PDC, $NiCl_2$ and NaOH; complexes (I) and (II) were obtained in our experiments with mole ratios of 1:1:2 and 1:2:2, respectively.



(I)

In the structure of (I), the coordination environment about the Ni^{II} cation, which lies on a twofold rotation axis, is a distorted octahedron (Fig. 1 and Table 1). The various C—O bond lengths are in the range 1.2412 (7)–1.2447 (7) Å,

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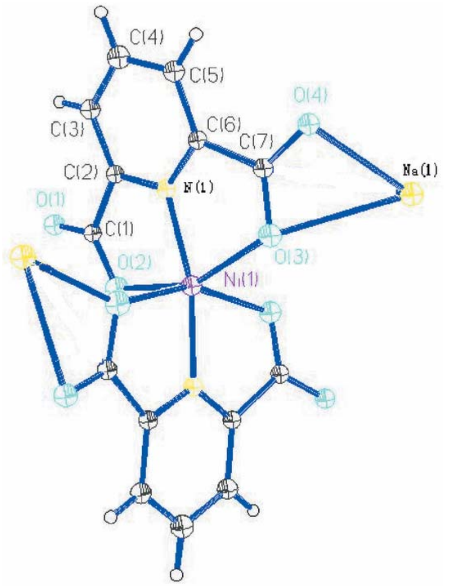

Figure 1
A plot of a fragment of polymeric $[Na_2Ni(PDC)_2]$. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

comparable to C—O bonds in analogues of PDC (Nathan & Mai, 2000).

The extended structure is a three-dimensional network linked by Na—O bonds. The Na^I cation has a coordination number of 6, linking three $[Ni(PDC)_2]^{2-}$ units. The Na—O distances vary from 2.321 (1) to 2.765 (1) Å and are in the range expected (2.25–2.78 Å; MacGillavry & Rieck, 1962). The resulting extended structure (Fig. 2) has a layered arrangement, with alternate sections of $[Ni(PDC)_2]^{2-}$ anions and complex Na—O networks.

The Na···Na distance in the sodium layer is 3.609 (2) Å, comparable with those observed in the clusters $[Na_2Fe_{18}S_{30}]^{8-}$ and $[Na_9Fe_{20}Se_{38}]$ (3.51–4.60 Å; You *et al.*, 1992), but somewhat shorter than those in the NaCl structure (3.973 Å). Fig. 3 illustrates the network structure constructed by interleaving rings, in which each ring is overlapped by six surrounding rings.

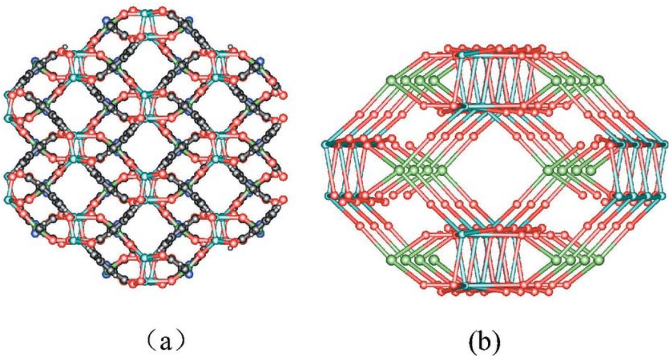
(a) (b)

Figure 2
(*a*) The network of (I), viewed along the *ab* plane, showing the interleaved ring structure. (*b*) The single ring is constructed by O (red), Ni (green) and Na (blue) atoms. All non-framework atoms have been omitted for clarity.

Experimental

To a methanol solution (15 ml) of nickel(II) chloride hexahydrate (0.12 g, 0.50 mmol) was added pyridyl-2,6-dicarboxylic acid (H_2PDC) (0.09 g, 0.50 mmol) [synthesized according to the literature procedure of Constable *et al.* (1990)] in the presence of NaOH (0.04 g, 1 mmol). The mixture was placed in a 25 ml Teflon-lined Parr bomb and heated at 413 K for 40 h. The bomb was then cooled to room temperature at about 5 K h^{-1}. Green block crystals of (I) were obtained from the cooled solution. CHN elemental analysis: calculated for $C_{14}H_6N_2Na_2NiO_8$: C 38.67, H 1.39, N 6.44%; found: C 38.88, H 1.35, N 6.40%. Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3060 (*w*), 1689 (*w*), 1603 (*vs*), 1470 (*s*), 1420 (*s*), 1344 (*s*), 1247 (*w*), 1023 (*m*), 771 (*m*).

Crystal data

$[Na_2Ni(C_7H_3NO_4)_2]$
$M_r = 434.88$
Orthorhombic, *Pnna*
$a = 14.4859\ (9)$ Å
$b = 12.5078\ (7)$ Å
$c = 8.3069\ (5)$ Å
$V = 1505.10\ (16)$ Å^3
$Z = 4$
$D_x = 1.919$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 405 reflections
$\theta = 2.2$–$26.0°$
$\mu = 1.40\ mm^{-1}$
$T = 295\ (2)$ K
Block, green
0.32 × 0.25 × 0.20 mm

Data collection

Bruker APEX area-dectector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.597$, $T_{max} = 0.756$
8655 measured reflections
1794 independent reflections
1631 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 27.9°$
$h = -19 \rightarrow 14$
$k = -16 \rightarrow 15$
$l = -10 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.075$
$S = 1.05$
1794 reflections
135 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.4474P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	1.9643 (11)	Na1—O4	2.4077 (13)
Ni1—O3	2.1390 (11)	Na1—O2^{iv}	2.4159 (12)
Ni1—O2^{i}	2.1423 (12)	Na1—O1^{iv}	2.5962 (13)
Na1—O4^{ii}	2.3205 (12)	Na1—O3	2.7649 (13)
Na1—O1^{iii}	2.3899 (13)		
N1—Ni1—N1^{i}	166.44 (7)	O4^{ii}—Na1—O2^{iv}	92.90 (4)
N1—Ni1—O3	112.13 (4)	O1^{iii}—Na1—O2^{iv}	115.45 (5)
N1^{i}—Ni1—O3	78.10 (4)	O4—Na1—O2^{iv}	138.02 (5)
O3—Ni1—O3^{i}	87.62 (6)	O4^{ii}—Na1—O1^{iv}	139.47 (5)
N1—Ni1—O2^{i}	92.98 (4)	O1^{iii}—Na1—O1^{iv}	84.38 (4)
O3—Ni1—O2^{i}	154.63 (4)	O4—Na1—O1^{iv}	139.52 (5)
N1—Ni1—O2	77.75 (4)	O2^{iv}—Na1—O1^{iv}	52.56 (4)
O3—Ni1—O2	94.32 (5)	O4^{ii}—Na1—O3	129.95 (4)
O2^{i}—Ni1—O2	94.59 (7)	O1^{iii}—Na1—O3	98.18 (4)
O4^{ii}—Na1—O1^{iii}	95.01 (4)	O4—Na1—O3	50.41 (3)
O4^{ii}—Na1—O4	79.55 (4)	O2^{iv}—Na1—O3	123.09 (4)
O1^{iii}—Na1—O4	106.37 (4)	O1^{iv}—Na1—O3	89.92 (4)

Symmetry codes: (i) $x, -y+\frac{3}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y+2, z$; (iii) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, y, -z$.

All H atoms were refined freely with individual U_{iso}(H) values; C—H bond lengths are in the range 0.9073 (5)–0.9491 (5) Å.

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Data collection: *SMART* (Bruker, 2002); cell refinement: *SMART* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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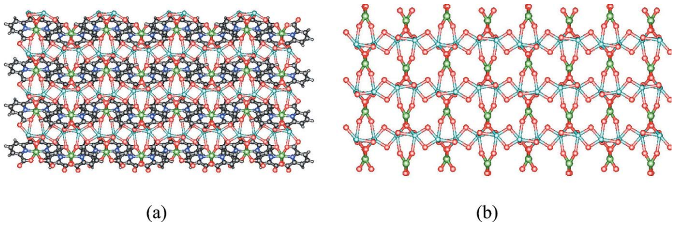

(a) (b)

Figure 3
(*a*) The layered arrangement in the structure of (I), with the alternate sections of $[\mathrm{Ni(PDC)_2}]^{2+}$ anions and complex Na–O network. Unlabelled atoms are related to labeled atoms by the symmetry operation ($x, \frac{3}{2} - y, \frac{1}{2} - z$). (*b*) A view showing the layered metal–organic structure. C and H atoms have been omitted.

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