

catena- $[\mu_6$ -1,2,4,5-Benzenetetracarboxylato-tetraaqua-dinickel(II)] dihydrate

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Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

H-atom completeness 72%

Disorder in solvent or counterion

R factor = 0.046

w R factor = 0.108

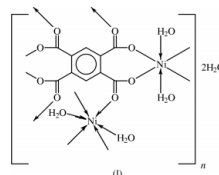
Data-to-parameter ratio = 16.9

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

The two Ni atoms and the μ_6 -1,2,4,5-benzenetetracarboxylate ligand in the crystal structure of *catena*- $[\mu_6$ -1,2,4,5-benzenetetracarboxylato-tetraaqua-dinickel(II)] dihydrate, $[\text{Ni}_2(\text{C}_{10}\text{H}_2\text{O}_8)(\text{H}_2\text{O})_4]\cdot 2(\text{H}_2\text{O})$, occupy special positions at three independent inversion centers. One of the Ni atoms is chelated by two 1,2,4,5-benzenetetracarboxylates $[\text{Ni}-\text{O}$ 2.018 (3) and 2.021 (3) \AA ; $\text{O}-\text{Ni}-\text{O}$ 91.7 (1) $^\circ$]; the two remaining sites of the coordination octahedron of this atom are taken up by water molecules. The second Ni atom is coordinated by four carbonyl O atoms belonging to four benzenetetracarboxylate ligands $[\text{Ni}-\text{O}$ 2.045 (3), 2.069 (3) \AA]; its coordination sphere also includes two water molecules. Each tetraanionic benzenetetracarboxylate ligand links together six Ni atoms, the linkages giving rise to a three-dimensional network motif. The structure is consolidated by hydrogen bonds involving coordinated as well as uncoordinated water molecules.

Comment

The 1,2,4,5-benzenetetracarboxylate ligand, by virtue of the positions of its four carboxyl groups on the benzene ring, should be capable of a variety of linkages to several metal centers. However, attempts to synthesize transition-metal derivatives by the reaction of the metal salts with the carboxylic acid or acid anhydride in the presence of sodium hydroxide do not always yield the desired compounds. For example, the reaction involving a cobalt(II) reagent affords hexaaquacobalt(II) dihydrogen 1,2,4,5-benzenetetracarboxylate (Ward & Luehrs, 1983), a compound where the carboxylic acid retains two of its four acid protons; the nickel(II) analog has an identical formulation (Jessen *et al.*, 1992). Neither of these compounds displays any metal-carboxylate bonds. The sodium component of the reaction can also be incorporated into the crystal structure (Wu *et al.*, 2001) as the counterion that balances the charge of the anionic entity. For steric reasons, few metal 1,2,4,5-benzenetetracarboxylates have been crystallographically authenticated owing to the fact that four carboxyl $-\text{CO}_2$ groups are rather unlikely to participate in bonding simultaneously (Murugavel *et al.*, 2002); the documented cases are limited to the tetrathallium (Day & Luehrs, 1988) and monocesium (Luehrs & Bowman-James, 1994) derivatives.



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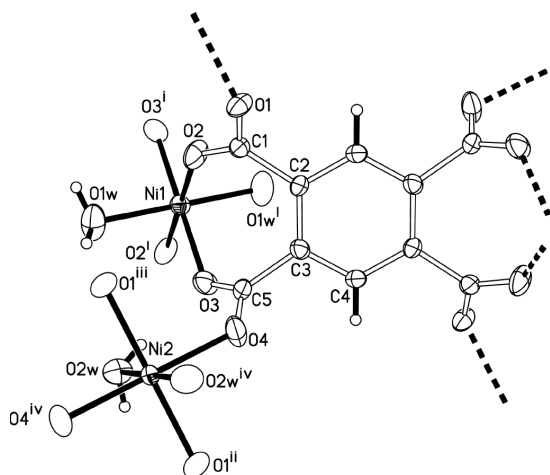


Figure 1
ORTEP (Johnson, 1976) plot of a fragment of the structure of the title compound, with displacement ellipsoids drawn at the 75% probability level. H atoms are drawn as spheres of arbitrary radii. The disordered water molecule is not shown [Symmetry translational codes: (i) $-x, 1 - y, -z$; (ii) $x, 1 + y, z$; (iii) $1 - x, 1 - y, -z$; (iv) $1 - x, 2 - y, -z$].

In the title compound, (I), the two independent Ni atoms both lie at inversion centers. One of them is chelated by two 1,2,4,5-benzenetetracarboxylato tetraanions, which bind via their *ortho*-carboxyl $-\text{CO}_2$ groups [Ni1–O2 2.018 (3) and Ni1–O3 2.021 (3) Å; O2–Ni1–O3 91.7 (1)°]; the two remaining sites of the coordination octahedron of Ni1 are taken up by water molecules [Ni1–O1w 2.106 (3) Å] (Fig. 1). The Ni2 atom is coordinated by four carbonyl O atoms belonging to four benzenetetracarboxylate ligands [Ni2–O1ⁱⁱ 2.069 (3), Ni2–O4 2.045 (3) Å] (see Fig. 1 for symmetry codes); its coordination sphere also includes two water molecules [Ni2–O2w 2.057 (3) Å].

Each tetraanionic benzenetetracarboxylate ligand links together six Ni atoms, the linkages giving rise to a three-dimensional network motif. The structure is consolidated by hydrogen bonds involving the coordinated (O1w, O2w) and disordered uncoordinated (O3w') water molecules (Table 2).

Experimental

1,2,4,5-Benzenetetracarboxylic acid anhydride (pyromellitic anhydride, 0.22 g, 1 mmol) and sodium hydroxide (0.16 g, 4 mmol) were dissolved in water (15 ml); nickel nitrate hexahydrate (0.58 g, 2 mmol), dissolved in water (3 ml), was then added to the solution. The green solution was placed in a 20 ml Teflon-lined stainless-steel bomb, heated at 453 for 100 h, and then cooled to room temperature at 5 K h⁻¹ to give prismatic crystals.

Crystal data

[Ni₂(C₁₀H₂O₈)(H₂O)₄]₂·2H₂O
 $M_r = 475.63$
 Triclinic, $P\bar{1}$
 $a = 6.910$ (1) Å
 $b = 7.389$ (1) Å
 $c = 8.223$ (1) Å
 $\alpha = 90.08$ (7)°
 $\beta = 109.83$ (8)°
 $\gamma = 93.37$ (7)°
 $V = 394.2$ (1) Å³

$Z = 1$
 $D_x = 2.003$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.0$ – 15.0 °
 $\mu = 2.47$ mm⁻¹
 $T = 298$ (2) K
 Prism, green
 $0.18 \times 0.11 \times 0.11$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.674$, $T_{\max} = 0.758$
 2476 measured reflections
 2300 independent reflections
 1594 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 30.0$ °
 $h = 0 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -11 \rightarrow 10$
 2 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.108$
 $S = 1.03$
 2300 reflections
 136 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.0381P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.06$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.83$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1–O2	2.018 (3)	Ni2–O1 ⁱⁱ	2.069 (3)
Ni1–O3	2.021 (3)	Ni2–O4	2.045 (3)
Ni1–O1w	2.106 (3)	Ni2–O2w	2.057 (3)
O2–Ni1–O2 ⁱ	180.0	O1 ⁱⁱ –Ni2–O1 ⁱⁱⁱ	180.0
O2–Ni1–O3	91.7 (1)	O1 ⁱⁱ –Ni2–O4	88.3 (1)
O2–Ni1–O3 ⁱ	88.3 (1)	O1 ⁱⁱ –Ni2–O4 ^{iv}	91.7 (1)
O2–Ni1–O1w	85.5 (1)	O1 ⁱⁱ –Ni2–O2w ^{iv}	83.8 (1)
O2–Ni1–O1w ⁱ	94.5 (1)	O1 ⁱⁱ –Ni2–O2w	96.2 (1)
O3 ⁱ –Ni1–O3	180.0 (2)	O4–Ni2–O4 ^{iv}	180.0 (2)
O3–Ni1–O1w	85.2 (1)	O4–Ni2–O2w	94.3 (1)
O3 ⁱ –Ni1–O1w	94.8 (1)	O4–Ni2–O2w ^{iv}	85.7 (1)
O1w–Ni1–O1w ⁱ	180.0 (2)	O2w–Ni2–O2w ^{iv}	180.0

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1w–H1w1 \cdots O1 ⁱⁱⁱ	0.85	2.07	2.897 (4)	162
O1w–H1w2 \cdots O3w'	0.85	2.04	2.865 (9)	164
O2w–H2w2 \cdots O2 ⁱⁱ	0.84	2.04	2.785 (4)	147
O2w–H2w1 \cdots O3	0.85	1.96	2.743 (4)	152

Symmetry codes: (ii) $x, 1 + y, z$; (iii) $1 - x, 1 - y, -z$.

The carbon-bound atom H4 was positioned geometrically and was allowed to ride on the C4 atom; the water H atoms were located and refined, subject to O–H 0.85 (1) and H \cdots H 1.39 (1) Å restraints. The displacement parameters of all H atoms were set to 1.2 times U_{eq} of the carrier C or O atoms.

One of the uncoordinated water molecules is disordered, and as the disorder refined to nearly 1/1, the occupancy for each of the components (O3w and O3w') was set to 0.5; their displacement parameters were restrained to be equal to each other. The H atoms of the disordered water molecule were not located and were not included in the refinement.

The largest peak was approximately 1 Å from atoms O3w and O3w'.

Data collection: *CAD-4 Software* (Enraf–Nonius Delft, 1988); cell refinement: *CAD-4 Software*; data reduction: *XCAD4/PC* (Harms, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick,

1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-II* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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