

Tetraaquabis(3,5-dihydroxybenzoato- $\kappa$ O)nickel(II) trihydrateHuan-Yu Wang,<sup>a</sup> Shan Gao<sup>a</sup> and Seik Weng Ng<sup>b\*</sup><sup>a</sup>College of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China, and <sup>b</sup>Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia

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## Key indicators

Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.037  
 $wR$  factor = 0.121  
Data-to-parameter ratio = 13.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The covalently bonded monodentate carboxylate groups in the title compound,  $[\text{Ni}(\text{C}_7\text{H}_5\text{O}_4)_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ , are *trans* to each other; the octahedrally coordinated Ni atom lies on a pseudo-center of inversion that relates the carboxylate groups to each other as well as two coordinated water molecules to the other two. Extensive hydrogen bonding leads to the formation of a three-dimensional network.

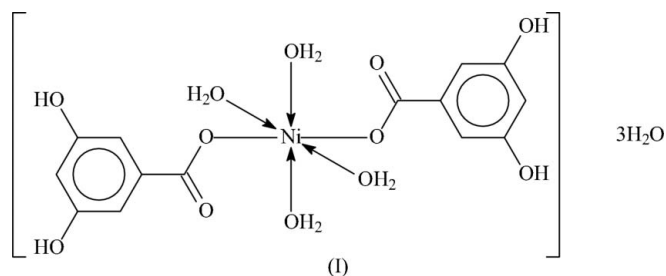
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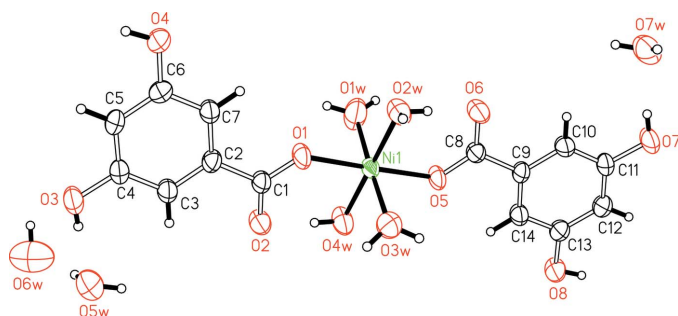
## Comment

Despite the huge number of metal benzoates that have been synthesized from benzoic acid and its substituted derivatives, there appears to be only one structurally authenticated example of a transition metal derivative of 3,5-dihydroxybenzoic acid. Nickel bis(3,5-dihydroxybenzoate) has been isolated as its adduct with 1,4,8,11-tetraazacyclotetradecane (Suh *et al.*, 2003). In the title complex, nickel bis(3,5-dihydroxybenzoate) exists as a tetraaqua-coordinated trihydrate, (I) (Fig. 1), whose metal atom exists in an octahedral environment; the metal atom is covalently linked to each carboxylate. The hydroxy substituents of the benzoate together with the coordinated and uncoordinated water molecules connect with each other to give rise to a tightly bound three-dimensional network of hydrogen bonds (Table 2). The metal atom lies on a pseudo-center of inversion that relates one carboxylate to the other; the pseudo-center also relates two of the coordinated water molecules to the other two and the solvent molecule O5 $w$  to O6 $w$ . Curiously, the excess electron density (that could not be refined as water) is also related to O7 $w$  by this pseudo-symmetry, although the electron density is found in a cavity of approximately 12 Å<sup>3</sup>, thought to be too small to accommodate a water molecule.



## Experimental

Nickel(II) nitrate hexahydrate (2.9 g, 10 mmol) and 3,5-dihydroxybenzoic acid (1.5 g, 10 mmol) were dissolved in a small volume of hot water. The pH of the solution was adjusted to 5 with 0.2 M sodium hydroxide. Green prismatic crystals were obtained after several days.



**Figure 1**  
ORTEP (Johnson, 1976) plot of  $[\text{Ni}(\text{C}_7\text{H}_5\text{O}_4)_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ . Displacement ellipsoids are drawn at the 70% probability level, and H atoms are drawn as spheres of arbitrary radii.

Analysis calculated for  $\text{C}_{14}\text{H}_{24}\text{NiO}_{15}$ : C 34.25, H 4.93%; found: C 34.26, H 4.96%.

**Crystal data**

$[\text{Ni}(\text{C}_7\text{H}_5\text{O}_4)_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$   
 $M_r = 491.04$   
 Monoclinic,  $P2_1/n$   
 $a = 9.250$  (2) Å  
 $b = 19.736$  (4) Å  
 $c = 10.797$  (2) Å  
 $\beta = 95.24$  (2)°  
 $V = 1962.9$  (7) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.662$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 18064 reflections  
 $\theta = 3.0$ – $27.5$ °  
 $\mu = 1.07$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 Prism, green  
 $0.38 \times 0.27 \times 0.21$  mm

**Data collection**

Rigaku R-AXIS RAPID IP diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
 $T_{\min} = 0.618$ ,  $T_{\max} = 0.807$   
 18979 measured reflections

4443 independent reflections  
 3727 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.016$   
 $\theta_{\text{max}} = 27.5$ °  
 $h = -11 \rightarrow 12$   
 $k = -25 \rightarrow 24$   
 $l = -13 \rightarrow 14$

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.121$   
 $S = 1.08$   
 4443 reflections  
 325 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0875P)^2 + 0.1403P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.74$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>

**Table 1**  
Selected geometric parameters (Å, °).

Ni1—O1	2.042 (1)	Ni1—O2w	2.098 (1)
Ni1—O5	2.042 (1)	Ni1—O3w	2.051 (2)
Ni1—O1w	2.041 (2)	Ni1—O4w	2.080 (1)
O1—Ni1—O5	178.47 (4)	O5—Ni1—O4w	88.62 (5)
O1—Ni1—O1w	90.16 (6)	O1w—Ni1—O2w	88.92 (8)
O1—Ni1—O2w	85.90 (5)	O1w—Ni1—O3w	178.04 (4)
O1—Ni1—O3w	91.48 (6)	O1w—Ni1—O4w	92.29 (8)
O1—Ni1—O4w	92.91 (5)	O2w—Ni1—O3w	90.13 (7)
O5—Ni1—O1w	89.85 (6)	O2w—Ni1—O4w	178.31 (4)
O5—Ni1—O2w	92.57 (5)	O3w—Ni1—O4w	88.70 (7)
O5—Ni1—O3w	88.48 (6)		

**Table 2**  
Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H3o $\cdots$ O5w	0.85 (1)	1.90 (1)	2.746 (2)	175 (3)
O4—H4o $\cdots$ O2 <sup>i</sup>	0.85 (1)	1.90 (1)	2.749 (2)	178 (2)
O7—H7o $\cdots$ O7w	0.84 (1)	1.98 (1)	2.818 (2)	175 (2)
O8—H8o $\cdots$ O6 <sup>ii</sup>	0.85 (1)	1.87 (1)	2.711 (2)	171 (2)
O1w—H1w1 $\cdots$ O3 <sup>iii</sup>	0.83 (1)	2.14 (1)	2.944 (2)	162 (2)
O1w—H1w2 $\cdots$ O7w <sup>iv</sup>	0.83 (1)	1.95 (1)	2.771 (2)	169 (2)
O2w—H2w1 $\cdots$ O6	0.84 (1)	1.75 (1)	2.578 (2)	170 (2)
O2w—H2w2 $\cdots$ O1 <sup>v</sup>	0.85 (1)	2.19 (1)	2.976 (2)	152 (2)
O3w—H3w1 $\cdots$ O7 <sup>vi</sup>	0.84 (1)	1.99 (1)	2.818 (2)	167 (2)
O3w—H3w2 $\cdots$ O5w <sup>vii</sup>	0.85 (1)	2.01 (1)	2.843 (2)	168 (2)
O4w—H4w1 $\cdots$ O2	0.85 (1)	1.77 (1)	2.606 (2)	168 (2)
O4w—H4w2 $\cdots$ O5 <sup>viii</sup>	0.84 (1)	2.15 (1)	2.921 (2)	153 (2)
O5w—H5w1 $\cdots$ O6w	0.84 (1)	1.86 (1)	2.685 (3)	169 (2)
O5w—H5w2 $\cdots$ O4 <sup>ix</sup>	0.85 (1)	2.00 (1)	2.848 (2)	178 (3)
O6w—H6w1 $\cdots$ O2w <sup>iv</sup>	0.86 (1)	2.20 (1)	3.031 (3)	162 (2)
O6w—H6w2 $\cdots$ O7 <sup>viii</sup>	0.87 (1)	2.47 (2)	3.108 (3)	131 (3)
O7w—H7w1 $\cdots$ O3 <sup>v</sup>	0.86 (1)	2.12 (1)	2.956 (2)	168 (2)
O7w—H7w2 $\cdots$ O8 <sup>x</sup>	0.85 (1)	1.98 (1)	2.808 (2)	168 (2)

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iv)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (v)  $-x + 1, -y + 1, -z + 2$ ; (vi)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (vii)  $-x + \frac{5}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (viii)  $-x + 1, -y + 1, -z + 1$ ; (ix)  $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (x)  $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ .

The C-bound H atoms were placed at calculated positions ( $C-H = 0.93$  Å) and were included in the refinement in the riding model approximation, with  $U_{\text{iso}}(\text{H})$  set to  $1.2U_{\text{eq}}(\text{C})$ . The water H atoms were located in difference Fourier maps and were refined with distance restraints of  $O-H = 0.85$  (1) Å and  $H \cdots H = 1.39$  (1) Å; their displacement parameters were similarly tied to  $U_{\text{eq}}(\text{O})$ . All  $H \cdots H$  contacts exceed  $2.2$  Å, except for one intermolecular contact of  $2.14$  Å. The final difference Fourier map had a large peak  $2.9$  Å from O7w and related by the false inversion center to O6w. The peak could not be refined as a water molecule, and further checks with PLATON (Spek, 2003) showed that, although the electron density coincided with a void, the void (approximately  $12$  Å<sup>3</sup>) was too small to accommodate a water molecule.

Data collection: RAPID-AUTO (Rigaku Corporation, 1998); cell refinement: RAPID-AUTO; data reduction: CrystalStructure (Rigaku/MSC, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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