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Tetraaqua[(3-carboxyphenoxy)acetato]nickel(II)

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Key indicators

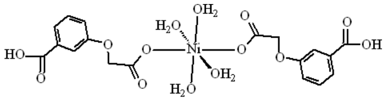
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.084
Data-to-parameter ratio = 14.4

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

The title complex, $[Ni(C_9H_7O_5)_2(H_2O)_4]$, a neutral mononuclear molecule, consists of an Ni^{II} ion, a 3-carboxyphenoxyacetate (3-CPOAH$^-$) ligand and four coordinated water molecules. The Ni^{II} atom, located on a symmetry center, has octahedral coordination involving two oxoacetate O atoms of two 3–CPOAH$^-$ ligands and four water molecules. Intermolecular hydrogen bonds form a supramolecular network structure.

Comment

Carboxyphenoxyacetic acids, which have been known to show biological activities and are widely used in agriculture, are a family of multidentate flexible ligands, with versatile binding ability. To the best of our knowledge, investigations of the complexes of carboxyphenoxyacetic acids (CPOAH$_2$) have mainly focused on complexes of the 4-CPOAH$_2$ acid ligand with metals such as sodium, nickel, manganese and cobalt (Wai *et al.*, 1990; Kennard *et al.*, 1984), while complexes of the 3-CPOAH$_2$ acid have not been reported to date. The reaction of 3-CPOAH$_2$ acid with Ni(CH$_3$COO)$_2$ yielded a new Ni^{II} complex, (I), whose crystal structure is reported here.



(I)

As shown in Fig. 1, the title complex has a mononuclear structure, in which the 3-carboxyphenoxyacetate groups are bonded to the Ni^{II} atom in a monodentate fashion. It should be noted that the 3-carboxyphenoxyacetate group is a singly charged anion. The Ni^{II} atom, located on a center of symmetry, is coordinated by two oxoacetate O atoms of different 3-CPOAH$^-$ ligands and four water molecules, forming an octahedral coordination geometry. The average Ni—O*W* distance [2.059 (2) Å] is almost the same as the Ni—O distance [2.062 (1) Å], but the two Ni—O*W* distances differ significantly by 0.056 (3) Å. This may be attributed to the

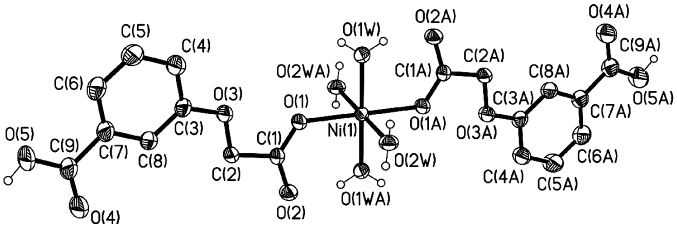


Figure 1
View of the title compound, with 30% probability displacement ellipsoids [symmetry code: (A) $3 - x, 2 - y, 1 - z$].

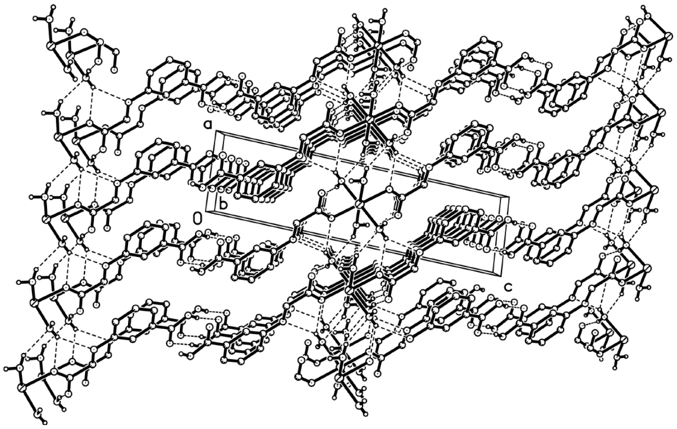


Figure 2
The hydrogen-bonding framework in the structure of (I).

formation of three intermolecular hydrogen bonds for O2*W* but only two for O1*W*. The bond angles around the center Ni^{II} atom are close to 90°, the idealized octahedral geometry. The coordinated oxyacetate group and benzene ring are almost coplanar, with a C3—O3—C2—C1 torsion angle of 176.7 (2)°, and the mean deviation from this plane is 0.072 (3) Å. The molecules form layers in which the shortest Ni···Ni distance is 21.89 (5) Å, whereas the closest Ni···Ni distance between neighboring layers is 5.79 (6) Å, In addition, as shown in Fig. 2, the uncoordinated carboxylate groups of adjacent molecules form O—H···O hydrogen bonds with each other, resulting in a one-dimensional chain, with an O···O distance of 2.631 (3) Å and an O—H···O angle of 171° (symmetry code: $1 - x, 3 - y, -z$). These one-dimensional chains are linked by the other hydrogen bonds listed in Table 2, forming a supramolecular network.

Experimental

The title complex was prepared by the addition of a stoichiometric amount of $Ni(CH_3COO)_2$ (20 mmol) and NaOH (30 mmol) to a hot aqueous solution of 3-CPOAH$_2$ (20 mmol), with subsequent filtration. Green single crystals were obtained from the solution at room temperature over several days.

Crystal data

$[Ni(C_9H_7O_5)_2(H_2O)_4]$
$M_r = 521.07$
Triclinic, $P\bar{1}$
$a = 4.9412$ (10) Å
$b = 5.7963$ (12) Å
$c = 18.362$ (4) Å
$\alpha = 96.94$ (3)°
$\beta = 94.82$ (3)°
$\gamma = 97.91$ (3)°
$V = 514.36$ (18) Å^3

$Z = 1$
$D_x = 1.682$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5791 reflections
$\theta = 3.4$–27.5°
$\mu = 1.02$ mm^{-1}
$T = 293$ (2) K
Prism, green
0.32 × 0.30 × 0.30 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.721$, $T_{max} = 0.735$
3641 measured reflections

2294 independent reflections
2076 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 27.5°$
$h = -5 \rightarrow 6$
$k = -7 \rightarrow 7$
$l = -23 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.084$
$S = 1.05$
2294 reflections
159 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.1735P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1*W*	2.0311 (15)	Ni1—O2*W*	2.0870 (16)
Ni1—O1	2.0617 (14)		
O1*W*—Ni1—O1	87.28 (6)	O1—Ni1—O2*W*	92.05 (6)
O1—Ni1—O2*W*^{i}	87.95 (6)	C3—O3—C2	116.68 (15)
O1*W*—Ni1—O2*W*	89.23 (6)		

Symmetry code: (i) $3 - x, 2 - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*A*···O2^{i}	0.82	1.92	2.670 (2)	152
O2*W*—H12*A*···O2^{ii}	0.82	1.90	2.704 (2)	167
O5—H10···O4^{iii}	0.82	1.82	2.631 (3)	171
O2*W*—H12*B*···O1^{iv}	0.72 (3)	2.29 (3)	2.871 (2)	140 (3)
O2*W*—H12*B*···O3^{iv}	0.72 (3)	2.36 (3)	3.011 (2)	152 (3)
O1*W*—H11*B*···O2*W*^{v}	0.74 (3)	2.18 (3)	2.861 (2)	153 (3)

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

The H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and O—H = 0.82 Å, and included in the final cycles of refinement using a riding model, with $U_{iso}(H) = 1.2U_{eq}$(parent atom), except for H11*B* and H12*B* in the two water molecules, which were located in a difference Fourier map and refined isotropically.

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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References

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Kennard, C. H. L., Smith, G. & O'Reilly, E. J. (1984). *Inorg. Chim. Acta*, **82**, 35–40.
Rigaku Corporation (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Wai, H. Y., Ru, J. W. & Mak, T. C. W. (1990). *J. Crystallogr. Spectrosc. Res.* **20**, 307–312.

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