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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.046
 wR factor = 0.112
Data-to-parameter ratio = 16.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Aqua(benzene-1,3-dioxyacetato- κO)tetrakis-
(1*H*-imidazole- κN^3)nickel(II) monohydrate

In the title complex {systematic name: aqua[*p*-phenylenebis(dioxyacetato)- κO]tetrakis(1*H*-imidazole- κN^3)nickel(II) monohydrate}, $[\text{Ni}(\text{C}_{10}\text{H}_8\text{O}_6)(\text{C}_3\text{H}_4\text{N}_2)_4(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, the Ni^{II} atom shows a distorted octahedral configuration, defined by one carboxyl O atom of the benzene-1,3-dioxyacetate group, four N atoms from four imidazole ligands and one water molecule. A three-dimensional supramolecular network is constructed by hydrogen-bonding and π - π stacking interactions.

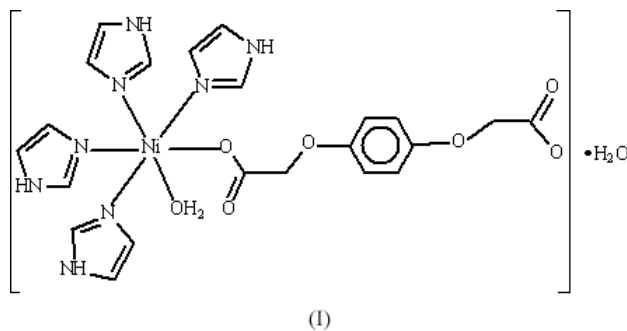
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Comment

In recent decades, considerable effort has been dedicated to the design and synthesis of supramolecular architectures directed by robust covalent bonds and/or weak intermolecular interactions such as hydrogen-bonding and π - π stacking interactions (Bacaa *et al.*, 2003; Iglesias *et al.*, 2003). As multidentate flexible ligands, phenylenedioxydiacetic acids (BDOAH₂) are good candidates for the construction of supramolecular complexes with versatile binding modes. However, complexes of the related benzene-1,3-dioxyacetic acid have been less well documented thus far. As a contribution to this field, we have previously reported the structures of three one-dimensional chain Zn^{II} , Cd^{II} and Cu^{II} polymers (Gao, Li *et al.*, 2004; Gao, Liu & Ng, 2004; Liu *et al.*, 2004) and a mononuclear $[\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6](1,3\text{-BDOA})$ complex (Gao, Liu, Dong *et al.*, 2004), within which 1,3-BDOA²⁻ acts as the bridging ligand in the polymers and the 1,3-BDOA²⁻ dianion functions as counter-ion in the Ni^{II} complex. In order to further explore the coordination behavior of metal ions with 1,3-BDOAH₂, we have synthesized a new Ni^{II} complex, $[\text{Ni}(1,3\text{-BDOA})(\text{C}_3\text{H}_4\text{N}_2)_4(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (I).



As illustrated in Fig. 1, the title complex consists of a neutral mononuclear $[\text{Ni}(1,3\text{-BDOA})(\text{C}_3\text{H}_4\text{N}_2)_4(\text{H}_2\text{O})]$ complex and one water molecule; the 1,3-BDOA²⁻ group is bonded to the Ni^{II} atom through only one of the two oxyacetate groups in a monodentate fashion, whereas the other is not involved in

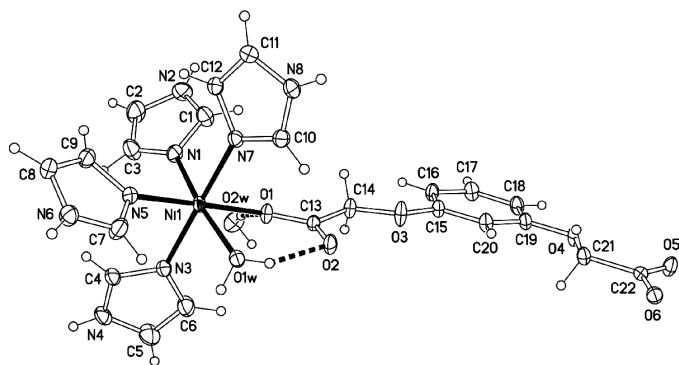


Figure 1
ORTEP plot (Johnson, 1976) of the title complex, drawn with 30% probability ellipsoids. The dashed line indicates an intramolecular hydrogen bond.

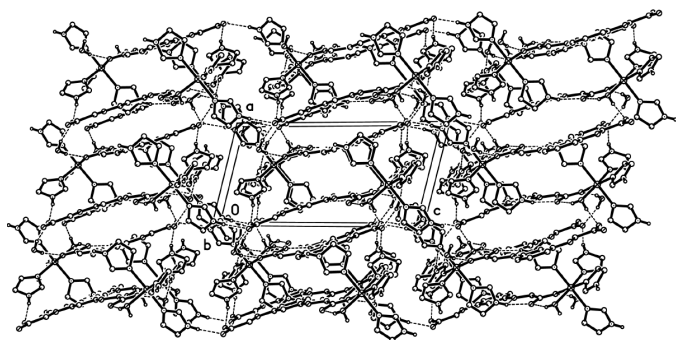


Figure 2
Packing diagram of the title complex. Dashed lines indicate hydrogen bonds.

coordination to Ni. The Ni^{II} atom is coordinated by four imidazole N atoms, one carboxyl O atom of the 1,3-BDOA²⁻ ligand and one water molecule, displaying a distorted octahedral geometry. Its equatorial plane is defined by the atoms O1, N3, N5 and N7 [r.m.s. deviation = 0.01 (4) Å; the deviation of Ni from the mean plane = 0.04 (4) Å]. Atoms N1 and O1W occupy the axial sites around Ni. The dihedral angles between the benzene ring and the four different imidazole co-ligands are: 42.5 (3) (imidazole containing N1), 73.5 (3) (imidazole containing N3), 34.6 (3) (imidazole containing N5) and 83.0 (3)° (imidazole containing N7).

It is noted that the C13–O1 bond distance is slightly longer than C13–O2, agreeing with the monodentate coordination mode of the carboxyl group (O1/C13/O2). The two oxyacetate groups and the benzene ring are almost in the same plane, as indicated by the torsion angles C15–O3–C14–C13 and C19–O4–C21–C22 [172.2 (2) and 177.7 (2)°, respectively].

In contrast to the title compound with close to planar BDOA, the mononuclear [Ni(C₃H₄N₂)₆](1,3-BDOA) complex (Gao, Liu, Dong *et al.*, 2004) contains oxyacetate groups twisted out the benzene ring plane.

Extensive intermolecular hydrogen bonding is observed between the uncoordinated imidazole N atoms, the carboxyl O atoms, one of the ether O atoms and water molecules (Table 2). There are also weak π – π stacking interactions between benzene rings, with a shortest $Cg \cdots Cg$ (Cg is the

centroid of the benzene ring) contact of 3.904 (3) Å. In this way, a three-dimensional supramolecular network structure is constructed, as shown in Fig. 2.

Experimental

Benzene-1,3-dioxyacetic acid was prepared following the method described for the synthesis of benzene-1,2-dioxyacetic acid by Mirci (1990). The title complex was prepared by the addition of benzene-1,3-dioxyacetic acid (4.52 g, 20 mmol) to an aqueous solution of imidazole (5.70 g, 60 mmol) and nickel diacetate tetrahydrate (4.98 g, 20 mmol), and the pH was adjusted to 6 with 0.1 M sodium hydroxide. Green crystals separated from the filtered solution after several days. Analysis calculated for C₂₂H₂₈NiN₈O₈: C 44.70, H 4.77, N 18.95%; found: C 44.82, H 4.70, N 19.01%.

Crystal data

[Ni(C₁₀H₈O₆)(C₃H₄N₂)₄·(H₂O)]·H₂O
 $M_r = 591.21$
 Triclinic, $P\bar{1}$
 $a = 8.3099$ (17) Å
 $b = 9.896$ (2) Å
 $c = 16.986$ (3) Å
 $\alpha = 75.95$ (3)°
 $\beta = 75.93$ (3)°
 $\gamma = 87.62$ (3)°
 $V = 1314.2$ (5) Å³

$Z = 2$
 $D_x = 1.494$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 12270 reflections
 $\theta = 3.2$ – 27.5 °
 $\mu = 0.80$ mm⁻¹
 $T = 293$ (2) K
 Prism, green
 $0.38 \times 0.27 \times 0.19$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.751$, $T_{\max} = 0.863$
 12870 measured reflections

5980 independent reflections
 4469 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 27.5$ °
 $h = -10 \rightarrow 10$
 $k = -12 \rightarrow 12$
 $l = -22 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.112$
 $S = 1.03$
 5980 reflections
 364 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.4263P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.60$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1–N1	2.092 (2)	Ni1–O1W	2.140 (2)
Ni1–N3	2.094 (2)	O1–C13	1.272 (3)
Ni1–N5	2.090 (2)	O2–C13	1.249 (3)
Ni1–N7	2.101 (2)	O5–C22	1.241 (3)
Ni1–O1	2.143 (2)	O6–C22	1.255 (3)
N1–Ni1–N3	92.89 (9)	N5–Ni1–N3	89.41 (9)
N1–Ni1–N7	89.90 (9)	N5–Ni1–N7	88.63 (9)
N1–Ni1–O1	84.99 (8)	N5–Ni1–O1	178.62 (8)
N1–Ni1–O1W	172.46 (8)	N5–Ni1–O1W	90.85 (8)
N3–Ni1–N7	176.75 (9)	N7–Ni1–O1	91.35 (8)
N3–Ni1–O1	90.55 (8)	N7–Ni1–O1W	88.19 (8)
N3–Ni1–O1W	89.25 (8)	O1W–Ni1–O1	87.77 (7)
N5–Ni1–N1	96.40 (9)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H22···O5 ⁱ	0.86	1.88	2.720 (3)	164
N4—H23···O6 ⁱⁱ	0.86	2.02	2.869 (3)	170
N6—H24···O2W ⁱⁱⁱ	0.86	1.96	2.739 (4)	151
N8—H25···O2 ^{iv}	0.86	1.96	2.792 (3)	163
N8—H25···O3 ^{iv}	0.86	2.52	3.001 (3)	116
O1W—H1W1···O2	0.85 (3)	1.90 (3)	2.688 (3)	154 (3)
O1W—H1W2···O6 ^v	0.85 (3)	1.92 (3)	2.758 (3)	167 (3)
O2W—H2W1···O5 ^{vi}	0.85 (3)	2.02 (3)	2.857 (3)	167 (4)
O2W—H2W2···O1	0.85 (3)	2.02 (3)	2.854 (3)	168 (3)

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

H atoms on carbon and nitrogen were placed in calculated positions [$C-H = 0.93$ (aromatic) or 0.97 Å (aliphatic), and $N-H = 0.86$ Å (imidazole), and $U_{iso}(H) = 1.2U_{eq}(C,N)$] using the riding-model approximation. Water H atoms were located in a difference map and refined with $O-H$ and $H\cdots H$ distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); 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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