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8-Hydroxyquinaldinic acid and its nickel(II) complex

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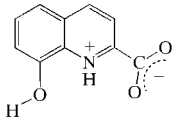
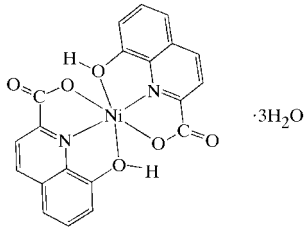
The molecules of 8-hydroxyquinolinium-2-carboxylate, $C_{10}H_7NO_3$, have a planar structure, in which the carboxyl group is ionized and the ring N atom is protonated. The derived nickel(II) complex, bis(8-hydroxyquinoline-2-carboxylato-κ^3O^2,N,O^8)nickel(II) trihydrate, $[Ni(C_{10}H_6NO_3)_2]\cdot 3H_2O$, contains an octahedral central Ni^{II} ion coordinated by the hydroxyl O atom, the ring N atom and the carboxylate O atom of each of the two tridentate ligands, with a perpendicular orientation of the quinoline rings.

Comment

8-Hydroxyquinaldic acid (8-hydroxyquinoline-2-carboxylic acid), (I), is one of the tryptophan metabolites formed through the kynurenine metabolic pathway (Rodwell, 1983). This compound is known as a tridentate chelating agent with three ligand atoms, *viz*. the hydroxyl O atom, the quinoline ring N atom and the carboxyl O atom (Irving & Pinnington, 1954; Moberg & Weber, 1984). The physiological role of this compound or of its metal complexes are as yet unclear, but the analogous compound 8-hydroxyquinoline and its metal complexes have various biological properties, such as antimicrobial or fungicidal activity (Okide *et al.*, 2000; Patel *et al.*, 1999) or antitumour activity (Smith *et al.*, 1998). These findings drive the structural studies of various quinoline derivatives because of their therapeutic value.



(I)



(II)

Until now, the solid-state structures of 8-hydroxyquinaldinic acid and its metal complexes have not been determined, except for the structure of the cobalt(II) complex, which we reported recently (Okabe & Muranishi, 2002). Therefore, it is of interest to clarify the detailed structure of this compound and the coordinating behaviour of its metal complexes, in connection with their physiological role as well as their use as selective chelating reagents for metal ions (Högberg *et al.*, 1985). In this study, the structure of (I) and of its nickel(II) complex, (II), have been determined, and the results are presented here.

The structure of (I) is shown in Fig. 1. It is planar, with a slight torsion of the carboxylate group [O2—C10—C1—N1 −4.2 (3)°]. The carboxyl group is ionized, the ring N atom is protonated, and the hydroxyl group remains unchanged. The net charge of the molecule is kept neutral by this H-atom transfer. Bifurcated intramolecular hydrogen bonds are formed between the protonated NH^+ group and the carboxyl O atom, and between NH^+ and the hydroxyl O atoms (Table 2). Neighbouring molecules are linked together along the *c* axis by intermolecular hydrogen bonds between the carboxylate and hydroxyl groups (Fig. 2). The quinoline rings are stacked along the *a* axis, with a mean distance between the rings of 3.380 (5) Å.

The molecular structure of complex (II) is shown in Fig. 3. In this complex, two tridentate ligand molecules coordinate to the central Ni^{II} ion in a bisected octahedral coordination geometry, in which the two quinoline rings are oriented

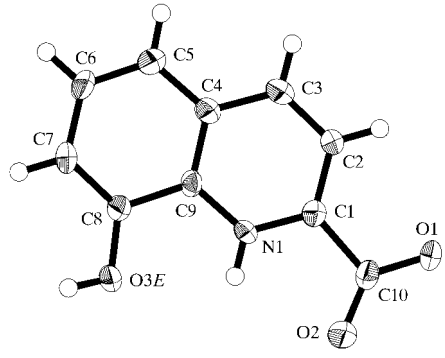


Figure 1
A view of the molecule of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

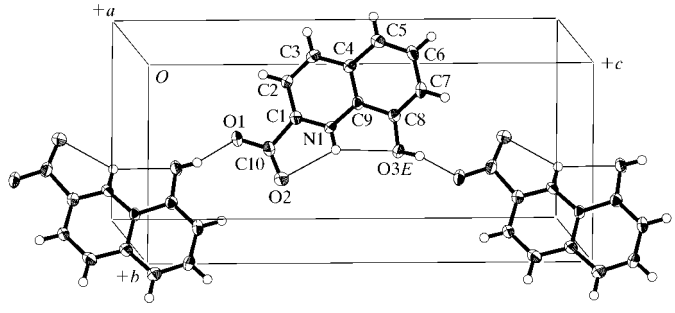


Figure 2
A packing diagram for (I), showing the hydrogen-bonding scheme.

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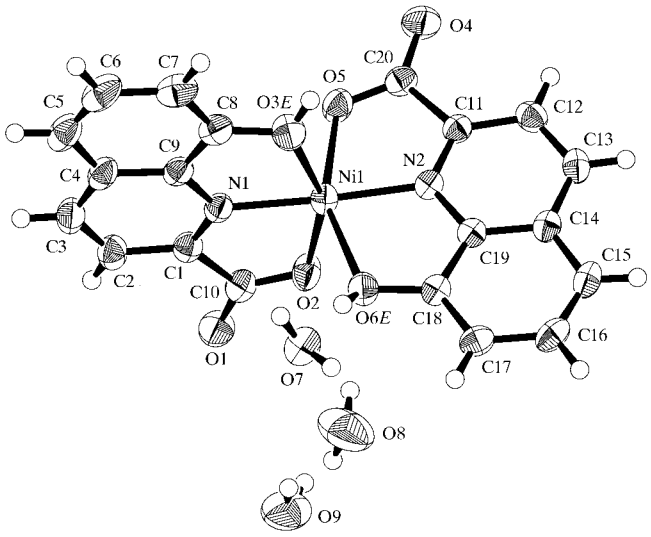

Figure 3
A view of the molecule of (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

perpendicularly. The two carboxyl groups of the two ligand molecules are ionized and are essentially coplanar with the quinoline ring planes, as shown by the relevant torsion angles [O2—C10—C1—N1 −4.2 (3)° and O5—C20—C11—N2 −8.2 (4)°].

The overall structure of (II) is the same as the cobalt(II) complex (Okabe & Muranishi, 2002). Three ligand atoms (the hydroxyl O, the quinoline N and the carboxyl O atoms) and the central Ni^{II} ion form five-membered rings. The distances between Ni^{II} and the carboxylate O atoms [2.080 (3)–2.124 (2) Å] are shorter than those between Ni^{II} and the hydroxyl O atoms [2.227 (2)–2.290 (3) Å]. The Ni—N distance is the shortest of those involving the three coordinated ligand atoms.

In an NMR study of the manganese(II) complexes of quinaldinic acid derivatives (Moberg & Weber, 1984), a bisected octahedral structure with a perpendicular orientation of the quinoline rings was postulated as one of the possible coordination modes around the central metal ion. However, the manganese(II) complex of 8-hydroxyquinaldinic acid could not be clearly deduced as a bisected octahedral structure from the NMR study. The bisected octahedral coordination mode of the cobalt(II) complex (Okabe & Muranishi, 2002) and the nickel(II) complex, (II), may be a common feature of the metal complexes of 8-hydroxyquinaldinic acid, although further structural studies are needed for confirmation.

In the crystal packing of (II), stacking interactions are present between the C1–C9/N1 quinoline rings and between the C11–C19/N2 rings. The mean distances are 3.454 (4) Å for the C1–C9/N1 rings and 3.378 (4) Å for the C11–C19/N2 rings. Neighbouring nickel(II) complex molecules are also connected together by a hydrogen-bonding network involving the water molecules (Table 4).

Experimental

Yellow plate crystals of (I) and light-yellow prismatic crystals of (II) were obtained by, respectively, slow evaporation of an ethanol–water solution of (I) (*ca* 70:30 *v*/*v*), and of an ethanol–water solution (*ca* 70:30 *v*/*v*) of a mixture of (I) and nickel(II) acetate tetrahydrate (molar ratio 4:1).

Compound (I)

Crystal data

$C_{10}H_7NO_3$
M_r = 189.17
Monoclinic, $C2/c$
a = 12.748 (2) Å
b = 7.476 (3) Å
c = 16.657 (2) Å
β = 90.68 (1)°
V = 1587.4 (7) Å^3
Z = 8
D_x = 1.583 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16 reflections
θ = 10.2–12.9°
μ = 0.12 mm^{-1}
T = 296.2 K
Plate, yellow
0.20 × 0.10 × 0.05 mm

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
2068 measured reflections
1838 independent reflections
691 reflections with $I > 2\sigma(I)$
R_{int} = 0.066
θ_{max} = 27.5°
$h = 12 \rightarrow 16$
$k = 0 \rightarrow 9$
$l = -21 \rightarrow 21$
3 standard reflections
every 150 reflections
intensity decay: 0.8%

Refinement

Refinement on F^2
$R(F)$ = 0.053
$wR(F^2)$ = 0.197
S = 0.87
1838 reflections
128 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C10	1.255 (4)	C3—C4	1.405 (6)
O2—C10	1.230 (5)	C4—C5	1.405 (6)
O3*E*—C8	1.338 (5)	C4—C9	1.406 (6)
N1—C1	1.332 (4)	C5—C6	1.364 (6)
N1—C9	1.367 (5)	C6—C7	1.409 (6)
C1—C2	1.388 (6)	C7—C8	1.368 (6)
C1—C10	1.533 (5)	C8—C9	1.438 (5)
C2—C3	1.369 (6)		
N1—C1—C10	115.8 (3)	O1—C10—O2	130.2 (4)
C2—C1—C10	124.8 (3)	O1—C10—C1	113.7 (3)
O3*E*—C8—C7	126.7 (3)	O2—C10—C1	116.0 (3)
O3*E*—C8—C9	115.6 (3)		

Table 2
Hydrogen-bonding and short intermolecular contact geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.86	2.30	2.662 (4)	105
N1—H1···O3*E*	0.86	2.35	2.692 (4)	104
O3*E*—H3*E*···O1^{i}	0.82	1.76	2.562 (4)	164

Symmetry code: (i) $x, -y, z - \frac{1}{2}$.

Table 3
Selected geometric parameters (Å, °) for (II).

Ni1—O2	2.080 (3)	Ni1—O6*E*	2.227 (2)
Ni1—O3*E*	2.290 (3)	Ni1—N1	1.979 (2)
Ni1—O5	2.124 (2)	Ni1—N2	1.972 (2)
O2—Ni1—O3*E*	153.13 (9)	O6*E*—Ni1—N1	104.29 (8)
O2—Ni1—O5	97.86 (9)	O6*E*—Ni1—N2	75.93 (8)
O2—Ni1—O6*E*	89.13 (8)	N1—Ni1—N2	175.2 (1)
O2—Ni1—N1	78.96 (10)	Ni1—O2—C10	114.3 (2)
O2—Ni1—N2	105.83 (9)	Ni1—O3*E*—C8	111.8 (2)
O3*E*—Ni1—O5	91.84 (9)	Ni1—O5—C20	113.9 (1)
O3*E*—Ni1—O6*E*	93.02 (8)	Ni1—O6*E*—C18	111.9 (2)
O3*E*—Ni1—N1	74.6 (1)	Ni1—N1—C1	117.3 (2)
O3*E*—Ni1—N2	100.67 (10)	Ni1—N1—C9	121.8 (2)
O5—Ni1—O6*E*	154.03 (8)	Ni1—N2—C11	119.1 (1)
O5—Ni1—N1	101.60 (8)	Ni1—N2—C19	120.7 (2)
O5—Ni1—N2	78.10 (8)		

Compound (II)

Crystal data

$[Ni(C_{10}H_6NO_3)_2]\cdot 3H_2O$	$Z = 2$
$M_r = 489.05$	$D_x = 1.681$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 9.237$ (1) Å	Cell parameters from 25 reflections
$b = 15.865$ (3) Å	$\theta = 14.5$–$15.0°$
$c = 7.200$ (1) Å	$\mu = 1.06$ mm^{-1}
$\alpha = 97.63$ (1)°	$T = 296.2$ K
$\beta = 106.95$ (1)°	Prismatic, yellow
$\gamma = 101.90$ (1)°	0.25 × 0.10 × 0.10 mm
$V = 966.4$ (3) Å^3	

Data collection

Rigaku AFC-5*R* diffractometer	$R_{int} = 0.024$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 11$
$T_{min} = 0.880$, $T_{max} = 0.899$	$k = -20 \rightarrow 20$
4703 measured reflections	$l = -9 \rightarrow 8$
4434 independent reflections	3 standard reflections every 150 reflections
3202 reflections with $I > 2\sigma(I)$	intensity decay: 0.3%

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R(F) = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.134$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.90$	$\Delta\rho_{max} = 0.64$ e Å^{-3}
4434 reflections	$\Delta\rho_{min} = -0.32$ e Å^{-3}
307 parameters	

For compound (I), all H atoms were initially located from difference Fourier maps and were then refined at their ideal positions using a riding model [*SHELXL*97 *HFIX* instruction (Sheldrick, 1997)], with C—H = 0.93, O—H = 0.82 and N—H = 0.86 Å. For complex (II), all H atoms were also initially located from difference Fourier maps, and then all except those of the 8-hydroxyl groups were refined at their ideal positions using a riding model (*SHELXL*97 *HFIX* instruction), with C—H = 0.93 Å. The H atoms of the 8-hydroxyl groups were fixed in the positions located from the difference Fourier maps. The water H atoms were idealized using the *SHELXL*97 *SADI* restriction.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*E*—H3*E*···O9^{i}	0.78	1.79	2.556 (4)	167
O6*E*—H6*E*···O7	0.81	1.66	2.465 (3)	173
O7—H7*A*···O1^{ii}	0.85 (2)	1.73 (2)	2.576 (3)	169 (4)
O7—H7*A*···O2^{ii}	0.85 (2)	3.10 (3)	3.757 (3)	135 (3)
O7—H7*B*···O4^{iii}	0.85 (2)	1.85 (2)	2.689 (3)	168 (4)
O7—H7*B*···O5^{iii}	0.85 (2)	3.12 (4)	3.687 (3)	126 (3)
O8—H8*B*···O4^{iv}	0.87 (3)	2.20 (5)	2.943 (4)	144 (7)
O8—H8*B*···O5^{iv}	0.87 (3)	3.03 (7)	3.872 (4)	162 (5)
O8—H8*A*···O6*E*	0.87 (3)	2.51 (6)	2.888 (4)	107 (5)
O8—H8*A*···O2	0.87 (3)	2.63 (4)	3.447 (5)	157 (7)
O9—H9*A*···O8	0.85 (6)	1.98 (5)	2.821 (6)	172 (6)
O9—H9*B*···O5^{iii}	0.84 (5)	2.27 (4)	2.952 (4)	138 (5)

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

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation & Rigaku Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku Corporation, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999) and *DIRDIF*94 (Beurskens *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1077). Services for accessing these data are described at the back of the journal.

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