

Cobalt(II) and nickel(II) complexes of quinoline-2-carboxylate

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Received 31 March 2003

Accepted 16 April 2003

Online 20 May 2003

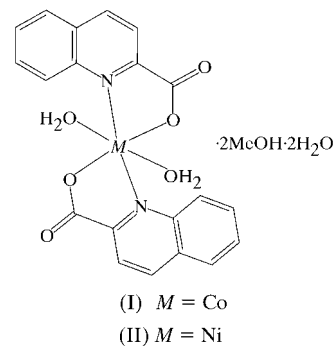
The title complexes, *trans*-diaquabis(quinoline-2-carboxylato- κ^2N,O)cobalt(II)–water–methanol (1/2/2), $[\text{Co}(\text{C}_{10}\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{CH}_4\text{O} \cdot 2\text{H}_2\text{O}$, and *trans*-diaquabis(quinoline-2-carboxylato- κ^2N,O)nickel(II)–water–methanol (1/2/2), $[\text{Ni}(\text{C}_{10}\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{CH}_4\text{O} \cdot 2\text{H}_2\text{O}$, are isomorphous and contain Co^{II} and Ni^{II} ions at centers of inversion. Both complexes have the same distorted octahedral coordination geometry, and each metal ion is coordinated by two quinoline N atoms, two carboxylate O atoms and two water O atoms. The quinoline-2-carboxylate ligands lie in *trans* positions with respect to one another, forming the equatorial plane, with the two water ligands occupying the axial positions. The complex molecules are linked together by hydrogen bonding involving a series of ring patterns which include the uncoordinated water and methanol molecules.

Comment

Quinoline-2-carboxylic acid (quinaldinic acid or quinaldic acid) is known to be a potent chelator of various divalent metal ions (Martell & Smith, 1974). It may be engaged in metal-catalyzed oxidation reactions in solution (Shul'pin, 2002). The structures of the Co^{II} (Okabe & Makino, 1999) and Ni^{II} (Odoko *et al.*, 2001) complexes of this ligand have been determined previously as the water/ethanol solvates. In the present study, crystals of the same Co^{II} , (I), and Ni^{II} , (II), complexes were prepared as their water/methanol solvates, and their structures were determined so as to clarify the solvent effect.

The structures of (I) (Fig. 1) and (II) are isomorphous and have the same distorted octahedral coordination geometries with the metal ion at a center of inversion. The two bidentate quinoline-2-carboxylate ligands are coordinated to the central metal ion, either Co^{II} or Ni^{II} , through the quinoline N and the carboxylate O atoms, forming a five-membered ring in the equatorial plane. Two aqua O atoms complete the octahedron by occupying the axial positions. These coordination geometries are fundamentally the same as found in *trans*-diaquabis(quinoline-2-carboxylato- κ^2N,O)cobalt(II)–water–ethanol

(1/2/2) (Okabe & Makino, 1999), *trans*-diaquabis(quinoline-2-carboxylato- κ^2N,O)nickel(II)–water–ethanol (1/2/2) (Odoko *et al.*, 2001) and *trans*-diaquabis(quinoline-2-carboxylato- κ^2N,O)iron(II)–water–ethanol (1/2/2) (Okabe & Makino, 1998). The equatorial coordination bond lengths between the quinoline N atom and the metal ion, and between the carboxylate O atom and the metal ion (Tables 1 and 3), agree with the corresponding bond lengths in the same complex molecules in the structures of their water/ethanol solvates, *viz.* $\text{Co}-\text{N} = 2.226(2) \text{ \AA}$ and $\text{Co}-\text{O} = 2.037(3) \text{ \AA}$ in the Co^{II} complex (Okabe & Makino, 1999), and $\text{Ni}-\text{N} = 2.185(2) \text{ \AA}$ and $\text{Ni}-\text{O} = 2.013(2) \text{ \AA}$ in the Ni^{II} complex (Odoko *et al.*, 2001). The coordination bond lengths of the metal complexes of quinoline-2-carboxylate decrease in the order of Mn^{II} [$\text{Mn}-\text{N} = 2.324(3) \text{ \AA}$ and $\text{Mn}-\text{O} = 2.125(2) \text{ \AA}$ (Haendler, 1996), and $\text{Mn}-\text{N} = 2.315(2) \text{ \AA}$ and $\text{Mn}-\text{O} = 2.131(2) \text{ \AA}$ (Okabe & Koizumi, 1997)] > Fe^{II} [$\text{Fe}-\text{N} = 2.270(1) \text{ \AA}$ and $\text{Fe}-\text{O} = 2.087(1) \text{ \AA}$; Okabe & Makino, 1998] > Co^{II} (Okabe & Makino, 1999; this work) > Ni^{II} (Odoko *et al.*, 2001; this work) > Cu^{II} ($\text{Cu}-\text{N} = 2.014$ and 2.012 \AA , and $\text{Cu}-\text{O} = 1.954$ and 1.962 \AA ; Haendler, 1986, 1996). The reverse of this order coincides well with the Irving–Williams series, which indicates the general stability sequence of octahedral metal complexes as being in the order $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni} < \text{Cu}$.



The hydrogen-bonding parameters for (I) and (II) are listed in Tables 2 and 4. Both structures are stabilized by identical hydrogen-bonding patterns involving several ring motifs (Bernstein *et al.*, 1995). One centrosymmetric hydrogen-bonded ring involves one carboxylate O atom from each of two metal complex molecules, one aqua ligand from each of another two metal complex molecules, two solvent water molecules and two ethanol molecules. This produces an $R_8^6(16)$ ring motif. A larger centrosymmetric hydrogen-bonded ring with an $R_6^6(20)$ motif involves one carboxylate O atom and one aqua ligand from each of two metal complex molecules, two solvent water molecules and two ethanol molecules. Within this large ring are two smaller rings. One is a centrosymmetric ring involving just two solvate water and two ethanol molecules; this ring contains a total of eight atoms, four of them donors and two acceptors, and has an $R_4^2(8)$ motif. The second ring is not centrosymmetric and involves just one metal complex molecule, one solvent water molecule and one methanol molecule, giving an $R_3^3(10)$ motif. Finally, another centrosymmetric ring is formed between two adjacent metal

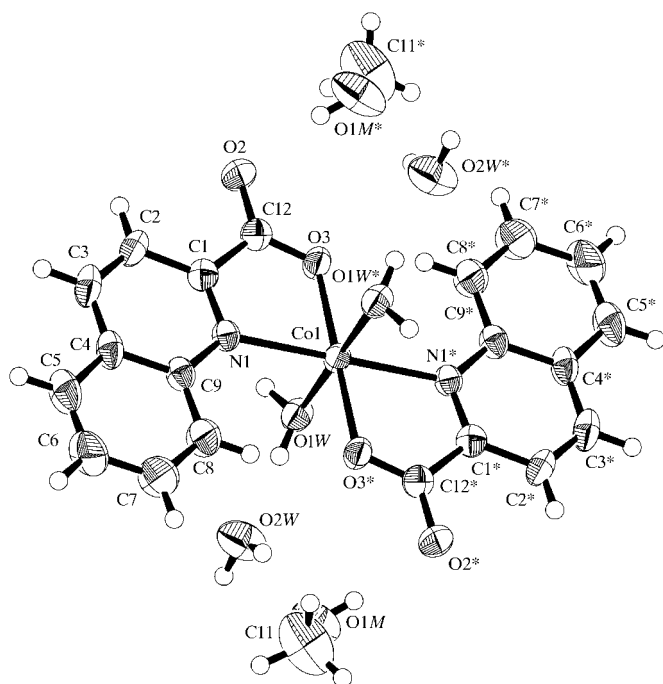


Figure 1
ORTEP (Johnson, 1976) drawing of (I) with the atomic numbering scheme. Ellipsoids for non-H atoms are drawn at the 50% probability level. Atoms marked with an asterisk are at the symmetry position $(1-x, -y, 2-z)$.

complex molecules and involves the water ligand as a donor on one molecule and the carboxylate O atom as an acceptor on the second molecule, thereby generating a graph-set motif of $R_2^2(12)$. All of these hydrogen-bonding patterns are clearly visible in Fig. 2. Similar hydrogen-bonding patterns are also formed in the water/ethanol solvate of the Ni^{II} complex

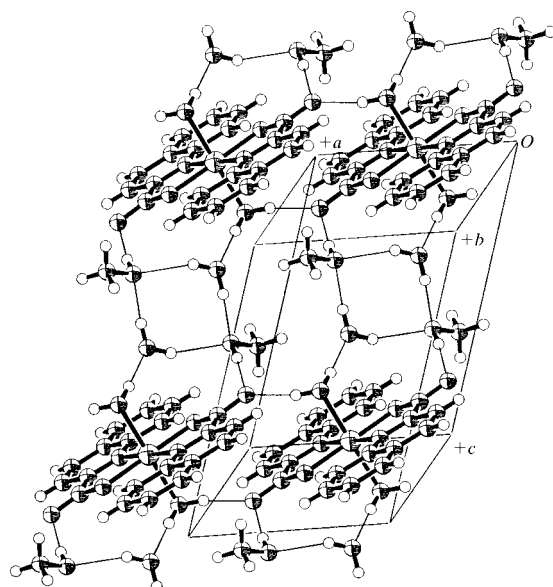


Figure 2
The molecular packing of (I). Hydrogen bonds are indicated by thin lines.

(Odoko *et al.*, 2001), as confirmed by recalculation of the data for this compound (the results are not given here). The hydrogen-bonding patterns in the water/ethanol solvate of the Co^{II} complex (Okabe & Makino, 1999) also seem to be the same as those observed in this study, even though the H atoms of the solvent water molecules were not located in their work. The supramolecular networks exhibited by the Co^{II} and Ni^{II} complexes in both their water/methanol solvates and water/ethanol solvates are much the same and the structures are even almost isomorphous. The change of the solvate molecule from methanol to ethanol merely expands the cell slightly to accommodate the extra methylene group, without causing significant rearrangement of the supramolecular networks.

Experimental

Orange plate-shaped crystals of (I) were obtained by slow evaporation of a water–methanol solution (10:90%, *v/v*) of a mixture of quinoline-2-carboxylic acid and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (molar ratio 4:1) at room temperature. Light-blue plate-shaped crystals of (II) were obtained by slow evaporation of a water–methanol solution (40:60%, *v/v*) of a mixture of quinoline-2-carboxylic acid and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (molar ratio 4:1) at room temperature.

Compound (I)

Crystal data

$[\text{Co}(\text{C}_{10}\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{CH}_4\text{O} \cdot 2\text{H}_2\text{O}$
 $M_r = 539.39$
 Triclinic, $P\bar{1}$
 $a = 7.170$ (2) Å
 $b = 8.965$ (2) Å
 $c = 10.827$ (2) Å
 $\alpha = 76.35$ (2)°
 $\beta = 74.38$ (2)°
 $\gamma = 69.86$ (2)°
 $V = 621.3$ (3) Å³

$Z = 1$
 $D_x = 1.442$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 20 reflections
 $\theta = 12.7\text{--}14.7^\circ$
 $\mu = 0.75$ mm⁻¹
 $T = 296.2$ K
 Plate, orange
 0.20 × 0.20 × 0.10 mm

Data collection

Rigaku AFC-5R diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.870$, $T_{\text{max}} = 0.928$
 3034 measured reflections
 2855 independent reflections
 1677 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -9 \rightarrow 8$
 $k = -11 \rightarrow 0$
 $l = -14 \rightarrow 13$
 3 standard reflections every 150 reflections
 intensity decay: 38.1%

Refinement

Refinement on F^2
 $R(F) = 0.046$
 $wR(F^2) = 0.129$
 $S = 1.04$
 2855 reflections
 162 parameters

H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0516P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.62$ e Å⁻³

Table 1

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

Co1—O1	2.026 (3)	Co1—N1	2.224 (3)
Co1—O1W	2.120 (2)		
O1—Co1—O1W	92.03 (9)	O1—Co1—N1	77.36 (10)

Table 2

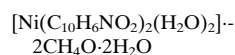
Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1A...O2W	0.89	1.83	2.719 (4)	177
O1W—H1B...O2 ⁱ	0.89	1.84	2.711 (3)	168
O1M—H1M...O2 ⁱⁱ	0.82	1.90	2.720 (4)	173
O2W—H2A...O1M ⁱⁱⁱ	0.89	1.90	2.750 (4)	160
O2W—H2B...O1M	0.88	2.17	3.007 (4)	158

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

Compound (II)

Crystal data


 $M_r = 539.15$

 Triclinic, $P\bar{1}$
 $a = 7.127$ (2) Å

 $b = 8.909$ (3) Å

 $c = 10.769$ (2) Å

 $\alpha = 76.74$ (2)°

 $\beta = 74.39$ (1)°

 $\gamma = 70.66$ (2)°

 $V = 613.9$ (3) Å³
 $Z = 1$
 $D_x = 1.458$ Mg m⁻³

 Mo $K\alpha$ radiation

Cell parameters from 25 reflections

 $\theta = 13.9$ – 14.9 °

 $\mu = 0.85$ mm⁻¹
 $T = 296.2$ K

Plate, light blue

 $0.20 \times 0.20 \times 0.10$ mm

Data collection

 Rigaku AFC-5R diffractometer
 ω - 2θ scans

 Absorption correction: ψ scan
 (North *et al.*, 1968)

 $T_{\min} = 0.879$, $T_{\max} = 0.919$

3003 measured reflections

2823 independent reflections

 2234 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 27.5$ °

 $h = -9 \rightarrow 8$
 $k = -11 \rightarrow 10$
 $l = -13 \rightarrow 13$

 3 standard reflections
 every 150 reflections
 intensity decay: 5.5%

Refinement

 Refinement on F^2
 $R(F) = 0.038$
 $wR(F^2) = 0.111$
 $S = 1.04$

2823 reflections

162 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0624P)^2]$

 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.002$
 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.62$ e Å⁻³

A linear correction was applied to the intensities to correct for the decay that occurred during each data collection. Initially, all H atoms were located from difference Fourier maps. Subsequently, the methyl and hydroxy H atoms were constrained to an ideal geometry (C—H = 0.96 Å and O—H = 0.82 Å), with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but were allowed to rotate freely about the C—O bonds. All other H atoms, except those of the water molecules, were placed in geometrically

Table 3

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

Ni1—O1	2.003 (2)	Ni1—N1	2.182 (2)
Ni1—O1W	2.088 (2)		
O1—Ni1—O1W	91.65 (7)	O1W—Ni1—N1	90.20 (7)
O1—Ni1—N1	78.83 (8)		

Table 4

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1A...O2W	0.90	1.83	2.725 (3)	179
O1W—H1B...O2 ⁱ	0.91	1.82	2.716 (2)	170
O1M—H1M...O2 ⁱⁱ	0.82	1.90	2.723 (3)	177
O2W—H2A...O1M ⁱⁱⁱ	0.90	1.89	2.759 (4)	162
O2W—H2B...O1M	0.88	2.16	3.002 (4)	159

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

idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the water molecules were kept fixed at the positions located from the Fourier maps and their U_{iso} values were initially refined and thereafter held fixed. The crystals of (I) and (II) were very unstable in air and so were mounted in capillaries before data collection.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999) and *DIRDIF94* (Beurskens *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1166). Services for accessing these data are described at the back of the journal.

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