

## Cobalt(II) and nickel(II) complexes of isoquinoline-1-carboxylate

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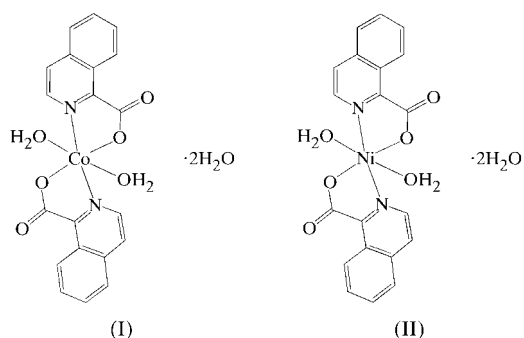
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*trans*-Diaquabis(isoquinoline-1-carboxylato- $\kappa^2N,O$ )cobalt(II) dihydrate,  $[\text{Co}(\text{C}_{10}\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , and *trans*-diaquabis(isoquinoline-1-carboxylato- $\kappa^2N,O$ )nickel(II) dihydrate,  $[\text{Ni}(\text{C}_{10}\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , contain the same isoquinoline ligand, with both metal atoms residing on a centre of symmetry and having the same distorted octahedral coordination. In the former complex, the Co—O(water) bond length in the axial direction is 2.167 (2) Å, which is longer than the Co—O(carboxylate) and Co—N bond lengths in the equatorial plane [2.055 (2) and 2.096 (2) Å, respectively]. In the latter complex, the corresponding bond lengths for Ni—O(water), Ni—O(carboxylate) and Ni—N are 2.127 (2), 2.036 (2) and 2.039 (3) Å, respectively. Both crystals are stabilized by similar stacking interactions of the ligand, and also by hydrogen bonds between the hydrate and coordinated water molecules.

### Comment

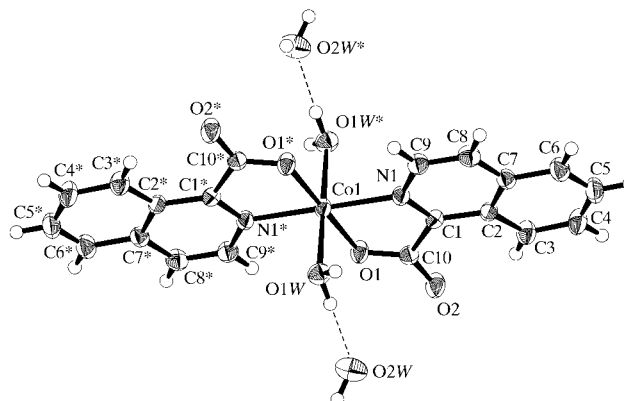
Isoquinoline-1-carboxylic acid (IQCA) is a potent inhibitor of the copper enzyme dopamine  $\beta$ -hydroxylase, which catalyses the biosynthesis of norepinephrine and lowers endogenous levels of norepinephrine and epinephrine in the brain, heart, spleen and adrenal glands (Townes *et al.*, 1990). These authors reported the strong binding affinity of IQCA to dopamine



$\beta$ -hydroxylase compared with the analogous compound quinoline-2-carboxylic acid (QCA), which also inhibits the same enzyme. Their explanation for the large difference (a

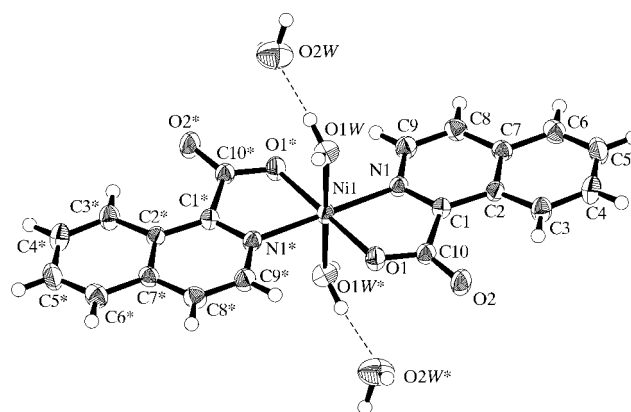
factor of more than 100) in the apparent affinities of these two inhibitors is that the hydrophobic portions of these molecules would be oriented very differently with regard to the enzyme surface if the coordination of the ligand atoms to the  $\text{Cu}^{\text{II}}$  centre(s) in the oxidized enzyme was the same for both compounds. To date, the crystal structure of the  $\text{Cu}^{\text{II}}$  (Tomas *et al.*, 1999) and  $\text{Sn}^{\text{IV}}$  (Smith *et al.*, 1995) complexes of IQCA have been reported. Based on these findings, we aimed to clarify the interaction mode between IQCA and transition metal ions, and have determined the crystal structures of both the  $\text{Co}^{\text{II}}$  complex, (I), and the  $\text{Ni}^{\text{II}}$  complex, (II).

The molecular structure of (I) is shown in Fig. 1. The Co atom has a distorted octahedral coordination in the *trans* form, defined by two N atoms and two O atoms of the bidentate isoquinoline ligands in the equatorial plane, and two axial O atoms of the water molecules. The coordination bond length in the axial direction [Co1—O1W = 2.167 (2) Å] is longer than those in the equatorial plane (Table 1). In the crystal packing of (I), the isoquinoline rings are stacked in relation to each other at a mean distance of 3.403 (4) Å, and hydrogen bonds are formed between the coordinated water molecule, the carboxylate group and the hydrated water molecule (Table 2).



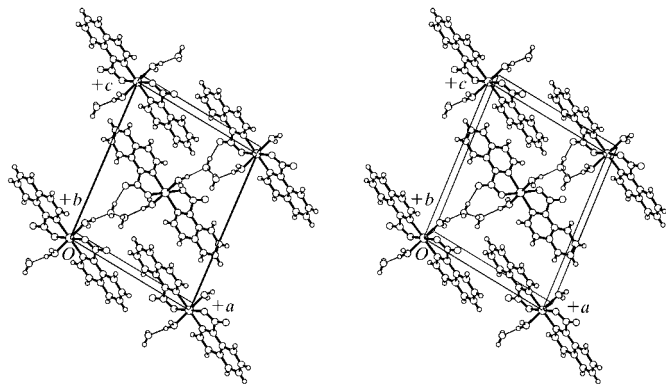
**Figure 1**

A view of the structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms marked with an asterisk (\*) are related by the symmetry operation ( $-x, -y, -z$ ).



**Figure 2**

A view of the structure of (II) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms marked with an asterisk (\*) are related by the symmetry operation ( $-x, -y, -z$ ).


**Figure 3**

A stereoview of the molecular packing of (I). Hydrogen bonds are indicated by thin lines.

The molecular structure of (II) is shown in Fig. 2. In this complex, the Ni atom has the same distorted octahedral coordination geometry, bonded by the same ligand atoms, as the Co atom in (I). The bond length in the axial direction [Ni1—O1W = 2.127 (2) Å] is also longer than the other coordination bond lengths (Table 3). These long bonds in the axial direction compared with the equatorial plane, which are observed in the octahedral coordination geometry of these two complexes, may be explained by a Jahn–Teller effect. In the crystal packing of (II), the isoquinoline rings are stacked in relation to each other at a mean distance of 3.681 (12) Å.

The distorted octahedral coordination mode observed in this study has also been observed in the transition metal complexes of QCA [Co<sup>II</sup> (Okabe & Makino, 1999), Ni<sup>II</sup> (Odoko *et al.*, 2001), Mn<sup>II</sup> (Haendler, 1996; Okabe & Koizumi, 1997), Fe<sup>II</sup> (Okabe & Makino, 1998) and V<sup>IV</sup> (Okabe & Muranishi, 2002)], with an exception being the pentacoordination of the Cu<sup>II</sup> complex (Haendler, 1986).

In complexes (I) and (II), the central metal atom forms a five-membered ring with the O and N atoms of the bidentate isoquinoline ligand, as observed in the QCA complexes, as well as in the Cu<sup>II</sup> complex with IQCA. The O—Co—N angle in (I) [101.75 (7)°] is larger than that in the Co<sup>II</sup> complex with QCA [77.23 (7)°; Okabe & Makino, 1999]. Similarly, the O—Ni—N angle in (II) [100.00 (9)°] is larger than that in the Ni<sup>II</sup> complex with QCA [78.53 (6)°; Odoko *et al.*, 2001]. The O—Cu—N angles of the Cu<sup>II</sup> complex with IQCA [82.96 (12)–97.04 (12)°; Tomas *et al.*, 1999] are somewhat larger than those of the complex with QCA [82.1 (1)–82.5 (1)°; Haendler, 1986]. Thus, the included angle, O—M—N, in the five-membered ring of the IQCA complex is larger than that in the QCA complex.

The Cu atom in the Cu<sup>II</sup> complex of IQCA, *trans*-bis(isoquinoline-1-carboxylato)copper(II), also displays octahedral coordination to two axial O atoms from the adjacent carboxylate groups (Tomas *et al.*, 1999). It is noted that water is not coordinated to the central Cu atom, although the crystal was prepared in the presence of water (Tomas *et al.*, 1999).

The results of the present study indicate that the coordination geometry of (I) and (II) is the same as that in the Cu<sup>II</sup>

complex with IQCA, but the ligating atoms of (I) and (II) are different from those of the Cu<sup>II</sup> complex. In all the complexes of QCA with transition metal ions (Co<sup>II</sup>, Ni<sup>II</sup>, Mn<sup>II</sup> and Fe<sup>II</sup>), as well as those of compounds (I) and (II), the central metal atom is coordinated to two water molecules, although the Cu<sup>II</sup> and V<sup>IV</sup> complexes of QCA contain only one coordinated water molecule. The absence of coordinated water in the Cu<sup>II</sup> complex of IQCA may have some role in the potent inhibitory activity of IQCA against dopamine  $\beta$ -hydroxylase, although this must be further confirmed by solution studies in a biological environment.

## Experimental

Orange plate-like crystals of (I) were obtained by slow evaporation of a solution in methanol–water (90:10 v/v) of a mixture of isoquinoline-1-carboxylic acid and CoCl<sub>4</sub>·6H<sub>2</sub>O (molar ratio 4:1). Blue needle-like crystals of (II) were obtained by slow evaporation of a solution in methanol–water (70:30 v/v) of a mixture of isoquinoline-1-carboxylic acid and NiCl<sub>2</sub>·6H<sub>2</sub>O (molar ratio 4:1).

### Compound (I)

#### Crystal data

|   |   |
|---|---|
| [Co(C <sub>10</sub> H <sub>6</sub> NO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> ·2H <sub>2</sub> O | $D_x = 1.610 \text{ Mg m}^{-3}$           |
| $M_r = 475.31$  | Mo $K\alpha$ radiation                    |
| Monoclinic, $P2_1/n$  | Cell parameters from 25 reflections       |
| $a = 12.271 (2) \text{ \AA}$  | $\theta = 14.3\text{--}15.0^\circ$        |
| $b = 5.324 (2) \text{ \AA}$   | $\mu = 0.93 \text{ mm}^{-1}$              |
| $c = 15.150 (1) \text{ \AA}$  | $T = 296.2 \text{ K}$                     |
| $\beta = 97.85 (1)^\circ$   | Plate, orange                             |
| $V = 980.5 (4) \text{ \AA}^3$   | $0.40 \times 0.15 \times 0.10 \text{ mm}$ |
| $Z = 2$   |   |

#### Data collection

|   |                                    |
|---|------------------------------------|
| Rigaku AFC-5R diffractometer                                    | $R_{\text{int}} = 0.016$           |
| $\omega/2\theta$ scans  | $\theta_{\text{max}} = 27.5^\circ$ |
| Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968) | $h = 0 \rightarrow 15$             |
| $T_{\text{min}} = 0.846$ , $T_{\text{max}} = 0.911$             | $k = 0 \rightarrow 6$              |
| 2594 measured reflections                                       | $l = -19 \rightarrow 19$           |
| 2241 independent reflections                                    | 3 standard reflections             |
| 1675 reflections with $I > 2\sigma(I)$                          | every 150 reflections              |
|   | intensity decay: none              |

#### Refinement

|                     |  |
|---------------------|--|
| Refinement on $F^2$ | H-atom parameters constrained                        |
| $R(F) = 0.031$      | $w = 1/[\sigma^2(F_o^2) + (0.10P)^2]$                |
| $wR(F^2) = 0.116$   | where $P = (F_o^2 + 2F_c^2)/3$                       |
| $S = 0.84$          | $(\Delta/\sigma)_{\text{max}} < 0.001$               |
| 2241 reflections    | $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$  |
| 142 parameters      | $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$ |

**Table 1**

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

|                        |            |            |           |
|------------------------|------------|------------|-----------|
| Co1—O1                 | 2.055 (2)  | Co1—N1     | 2.096 (2) |
| Co1—O1W                | 2.167 (2)  |            |           |
| O1—Co1—O1W             | 90.52 (6)  | Co1—O1—C10 | 116.6 (1) |
| O1—Co1—N1              | 78.25 (7)  | Co1—N1—C1  | 115.4 (1) |
| O1—Co1—N1 <sup>i</sup> | 101.75 (7) | Co1—N1—C9  | 124.8 (1) |
| O1W—Co1—N1             | 91.42 (7)  |            |           |

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

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

| D—H...A                     | D—H  | H...A | D...A     | D—H...A |
|-----------------------------|------|-------|-----------|---------|
| O1W—H1A...O2W               | 0.86 | 1.97  | 2.829 (3) | 173     |
| O1W—H1B...O1 <sup>i</sup>   | 0.84 | 2.03  | 2.829 (2) | 160     |
| O2W—H2A...O2W <sup>ii</sup> | 0.91 | 2.07  | 2.949 (2) | 160     |
| O2W—H2B...O2 <sup>iii</sup> | 0.87 | 1.86  | 2.723 (3) | 172     |

Symmetry codes: (i)  $x, 1 + y, z$ ; (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (iii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ .

## Compound (II)

### Crystal data

|   |   |
|---|---|
| [Ni(C <sub>10</sub> H <sub>6</sub> NO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O | $D_x = 1.619 \text{ Mg m}^{-3}$           |
| $M_r = 475.07$  | Mo $K\alpha$ radiation                    |
| Monoclinic, $P2_1/n$  | Cell parameters from 25 reflections       |
| $a = 12.171 (2) \text{ \AA}$  | $\theta = 14.0\text{--}14.6^\circ$        |
| $b = 5.351 (4) \text{ \AA}$   | $\mu = 1.05 \text{ mm}^{-1}$              |
| $c = 15.107 (2) \text{ \AA}$  | $T = 296.2 \text{ K}$                     |
| $\beta = 97.91 (1)^\circ$   | Needle, blue                              |
| $V = 974.5 (8) \text{ \AA}^3$   | $0.50 \times 0.10 \times 0.05 \text{ mm}$ |
| $Z = 2$   |   |

### Data collection

|  |                                    |
|--|------------------------------------|
| Rigaku AFC-5R diffractometer                     | $R_{\text{int}} = 0.018$           |
| $\omega/2\theta$ scans                           | $\theta_{\text{max}} = 27.5^\circ$ |
| Absorption correction: $\psi$ scan               | $h = 12 \rightarrow 15$            |
| (North <i>et al.</i> , 1968)                     | $k = 0 \rightarrow 6$              |
| $T_{\text{min}} = 0.882, T_{\text{max}} = 0.949$ | $l = -19 \rightarrow 19$           |
| 2573 measured reflections                        | 3 standard reflections             |
| 2225 independent reflections                     | every 150 reflections              |
| 1620 reflections with $I > 2\sigma(I)$           | intensity decay: none              |

### Refinement

|                     |  |
|---------------------|--|
| Refinement on $F^2$ | H-atom parameters constrained                        |
| $R(F) = 0.040$      | $w = 1/[\sigma^2(F_o^2) + (0.10P)^2]$                |
| $wR(F^2) = 0.143$   | where $P = (F_o^2 + 2F_c^2)/3$                       |
| $S = 0.99$          | $(\Delta/\sigma)_{\text{max}} < 0.001$               |
| 2225 reflections    | $\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$  |
| 142 parameters      | $\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$ |

All H atoms in (I) and (II) were treated as riding, with C—H distances of 0.93 Å and O—H distances in the range 0.86–0.95 Å.

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

|            |           |            |           |
|------------|-----------|------------|-----------|
| Ni1—O1     | 2.036 (2) | Ni1—N1     | 2.039 (3) |
| Ni1—O1W    | 2.127 (2) |            |           |
| O1—Ni1—O1W | 89.14 (8) | Ni1—O1—C10 | 115.6 (2) |
| O1—Ni1—N1  | 80.00 (9) | Ni1—N1—C1  | 115.0 (2) |
| O1W—Ni1—N1 | 88.56 (9) | Ni1—N1—C9  | 125.0 (2) |

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

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

| D—H...A                      | D—H  | H...A | D...A     | D—H...A |
|------------------------------|------|-------|-----------|---------|
| O1W—H1A...O2W                | 0.94 | 1.87  | 2.810 (4) | 178     |
| O1W—H1B...O1 <sup>i</sup>    | 0.92 | 1.95  | 2.833 (3) | 161     |
| O2W—H2B...O2 <sup>ii</sup>   | 0.95 | 1.79  | 2.739 (4) | 172     |
| O2W—H2A...O2W <sup>iii</sup> | 0.95 | 2.09  | 2.969 (4) | 154     |

Symmetry codes: (i)  $-x, 1 - y, -z$ ; (ii)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (iii)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 1999); 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: GG1140). Services for accessing these data are described at the back of the journal.

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