Cobalt(II), nickel(II) and copper(II) complexes of isoquinoline-3-carboxylate

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The crystal structures of the title complexes, namely *trans*-bis(isoquinoline-3-carboxylato-$\kappa^2 N,O$)bis(methanol-κO)cobalt(II), $[Co(C_{10}H_6NO_2)_2(CH_3OH)_2]$, and the corresponding nickel(II) and copper(II) complexes, $[Ni(C_{10}H_6NO_2)_2(CH_3OH)_2]$ and $[Cu(C_{10}H_6NO_2)_2(CH_3OH)_2]$, are isomorphous and contain metal ions at centres of inversion. The three compounds have the same distorted octahedral coordination geometry, and each metal ion is bonded by two quinoline N atoms, two carboxylate O atoms and two methanol O atoms. Two isoquinoline-3-carboxylate ligands lie in *trans* positions, forming the equatorial plane, and the two methanol ligands occupy the axial positions. The complex molecules are linked together by O—H···O hydrogen bonds between the methanol ligands and neighbouring carboxylate groups.

Comment

Transition metal ions are well known to have many important biological functions, mainly as the cofactors of many metalloenzymes. Their complexes have remarkable anti-microbial or fungicidal activity (Okide *et al.*, 2000; Partel

(I) M=Co
(II) M=Ni
(III) M=Cu
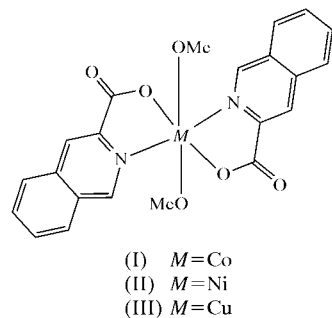
et al., 1999), or have redox activity and act as catalysts for metal-induced toxicity or carcinogenesis through processes which are interpreted as Fenton-type reactions (Kasprzak, 2002).
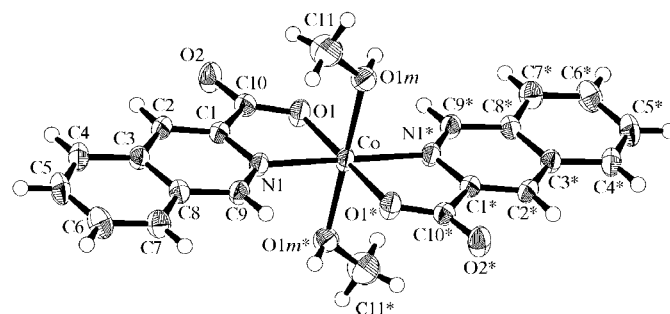

Figure 1
A drawing of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The corresponding drawings for (II) and (III) are similar. [Symmetry code: (*) $-x$, $-y$, $-z$.]

On the other hand, isoquinoline-3-carboxylic acid is a potent non-peptide inhibitor of the insulin-like growth-factor binding proteins (Zhu *et al.*, 2003). Its transition metal (mainly Fe) complexes act as oxidative catalysts in alkane oxidations (Shul'pin, 2002). In a previous paper, the crystal structure of the Fe^{II} complex of isoquinoline-3-carboxylate has been reported (Okabe & Muranishi, 2003c). We report here the structures of the corresponding Co^{II}, Ni^{II} and Cu^{II} complexes, denoted (I), (II) and (III), respectively, and compare their structural features.

The structure of (I) is shown in Fig. 1. The structures of (I), (II) and (III) are isomorphous with the aforementioned Fe^{II} analogue and have the same distorted octahedral coordination geometries, with the metal ion at a centre of inversion. The two bidentate ligands lie *trans* to one another and are coordinated to the central metal ion, through the isoquinoline N atoms and the carboxylate O atoms, to form a five-membered ring in the equatorial plane. Two O atoms of the methanol ligands complete the octahedron at the axial positions.

As shown in Table 1, the M—N coordination bond distances decrease in the order Fe^{II} > (I) > (II) > (III). The reverse of this order coincides well with the Irving–Williams series, which indicates the general stability sequence of octahedral metal complexes in the order Fe < Co < Ni < Cu. The axial coordination bond distances of the Cu^{II} complex, (III), are noticeably longer than those in (I) and (II), and also in the Fe^{II} complex. This may be explained by a strong Jahn–Teller effect in (III).

In the heterocyclic ring, the N1—C1 and N1—C9 bonds on both sides of the ring N atom and the C1—C2 bonds of (I), (II) and (III) are shorter than the other bonds in the same pyridine ring, *viz.* C2—C3, C3—C8 and C8—C9 (Table 1). This indicates the delocalization of the π electrons over these three bonds, which have double-bond character. This type of delocalization of π electrons is also present in the Fe^{II} complex and may be a general characteristic of the transition metal complexes of isoquinoline-3-carboxylate. Only the bonds on either side of the N atom have double-bond character in the metal complexes of analogous compounds, such as iso-quinoline-1-carboxylate complexes with Fe^{II} (Muranishi & Okabe, 2003), Co^{II} and Ni^{II} (Okabe & Muranishi, 2002), and

Zn^{II} (Okabe & Muranishi, 2003b), and quinoline-2-carboxylate complexes with Fe^{II} (Okabe & Makino, 1998), Co^{II} (Okabe & Makino, 1999), Ni^{II} (Odoko et al., 2001) and Zn^{II} (Okabe & Muranishi, 2003a).

When the Co(or Ni or Fe)—N coordination bond distances for (I) and (II) and analogous complexes of isoquinoline-1-carboxylate and quinoline-2-carboxylate are compared, they are found to decrease in the following order: for quinoline-2-carboxylate complexes with Co [2.226 (3) Å], Ni [2.182 (2) Å] or Fe [2.270 (1) Å], the M—N distances are longer than in (I), (II), (III) or Fe [2.167 (2) Å], which are in turn longer than those in isoquinoline-1-carboxylate complexes with Co [2.096 (2) Å], Ni [2.039 (3) Å], Cu [1.957 (3) and 1.969 (3) Å] or Fe [2.153 (2) Å]. The Cu^{II} complex of quinoline-2-carboxylate (Haendler, 1986) has been excluded from this discussion because of its pentacoordination geometry.

The Co(or Ni)—O bond distances in (I) and (II) and analogous complexes are in almost the reverse order of the M—N distances, and decrease in the following order: for isoquinoline-1-carboxylate complexes with Co [2.055 (2) Å] or Ni [2.036 (2) Å], the M—O distances are longer than in (I) or (II), which are in turn longer than those in quinoline-2-carboxylate complexes with Co [2.027 (3) Å] or Ni [2.004 (2) Å]. The Fe—O distances decrease in the following order: for the isoquinoline-1-carboxylate complex, the Fe—O distance of 2.091 (2) Å is longer than in the quinoline-2-carboxylate complex [2.087 (1) Å], which is in turn longer than that in the isoquinoline-3-carboxylate complex [2.050 (2) Å]. The Cu—O distances also vary across a range of compounds; Cu—O in (III) is longer than in the isoquinoline-1-carboxylate complex [1.927 (3) and 1.928 (3) Å; Pardo et al., 1999].

These data indicate that the same order of bond distances is present in the M—N distances of these complexes, but not in the M—O distances. These last may be changed under the influence of the electronegativity of the carboxylate anion, although the same order for M—O is present in the Co^{II} and Ni^{II} complexes.

The M—O bond distance is indicative of bond stability and may have an influence on the catalytic activity of isoquinoline-1- and -3-carboxylate complexes. For example, the Fe complex of isoquinoline-3-carboxylate, with a rather short M—O distance compared with the complex with isoquinoline-1-carboxylate, has a more effective catalytic activity in oxygen formation from cyclooctane in Gif oxidation (Shul'pin, 2002). The difference in double-bond character around the N atom of the heterocyclic ring may be one of the reasons for the difference in M—N(or O) coordination bond distances between the above analogous complexes.

The hydrogen-bonding parameters of the Fe^{II} complex and compounds (I), (II) and (III) are listed in Table 2. All structures are stabilized by a similar intermolecular O—H···O hydrogen-bonding pattern between methanol ligands and neighbouring carboxylate groups. The structures are also stabilized by a stacking interaction between the isoquinoline rings, at a mean distance of 3.358 (3) Å for (I), 3.362 (3) Å for (II) and 3.362 (3) Å for (III).

Experimental

Orange plate-shaped crystals of (I) were obtained by slow evaporation from a methanol solution of a mixture of isoquinoline-3-carboxylic acid and CoCl$_2$·6H$_2$O (molar ratio 4:1) at room temperature. Light-blue plate-shaped crystals of (II) were obtained by slow evaporation from a methanol solution of a mixture of isoquinoline-3-carboxylic acid and NiCl$_2$·6H$_2$O (molar ratio 4:1) at room temperature. Blue prismatic crystals of (III) were obtained by slow evaporation from a methanol solution of a mixture of isoquinoline-3-carboxylic acid and CuCl$_2$·2H$_2$O (molar ratio 4:1) at room temperature.

Compound (I)

Crystal data

[Co(C$_{10}$H$_6$NO$_2$)$_2$(CH$_4$O)$_2$]
$M_r = 467.33$
Monoclinic, $P2_1/c$
$a = 10.732$ (2) Å
$b = 6.268$ (2) Å
$c = 15.043$ (2) Å
$\beta = 101.00$ (1)°
$V = 993.3$ (4) Å^3
$Z = 2$
$D_x = 1.562$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 13.4–14.5°$
$\mu = 0.91$ mm^{-1}
$T = 296$ (1) K
Plate, light blue
$0.25 \times 0.15 \times 0.15$ mm

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North et al., 1968)
$T_{min} = 0.848$, $T_{max} = 0.873$
2613 measured reflections
2275 independent reflections
1618 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$

$\theta_{max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 8$
$l = -19 \rightarrow 19$
3 standard reflections
every 150 reflections
intensity decay: 0.1%

Refinement

Refinement on F^2
$R(F) = 0.032$
$wR(F^2) = 0.092$
$S = 1.01$
1618 reflections
144 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.2358P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Comparison of selected geometric parameters (Å, °).

	M = Fe†	(I) (M = Co)	(II) (M = Ni)	(III) (M = Cu)
M—O1	2.050 (2)	2.050 (2)	2.036 (2)	1.963 (2)
M—O1m	2.196 (2)	2.148 (2)	2.116 (2)	2.516 (2)
M—N1	2.167 (2)	2.110 (2)	2.049 (2)	1.979 (2)
N1—C1	1.372 (4)	1.376 (3)	1.368 (3)	1.372 (3)
N1—C9	1.315 (4)	1.314 (3)	1.314 (3)	1.315 (3)
C1—C2	1.366 (4)	1.357 (3)	1.357 (3)	1.361 (3)
C2—C3	1.414 (4)	1.414 (3)	1.412 (3)	1.412 (3)
C3—C8	1.415 (5)	1.416 (3)	1.416 (4)	1.418 (3)
C8—C9	1.416 (4)	1.414 (3)	1.417 (3)	1.414 (3)
O1—M—O1m	89.97 (9)	90.42 (6)	90.81 (7)	90.41 (7)
O1—M—N1	78.86 (9)	80.21 (6)	81.63 (7)	83.77 (7)
O1m—M—N1	92.43 (9)	92.51 (7)	92.55 (7)	88.14 (7)

† Okabe & Muranishi (2003c).

Compound (II)

Crystal data

$[Ni(C_{10}H_6NO_2)_2(CH_4O)_2]$
$M_r = 467.09$
Monoclinic, $P2_1/c$
$a = 10.638\ (2)$ Å
$b = 6.277\ (2)$ Å
$c = 15.068\ (2)$ Å
$\beta = 101.15\ (1)°$
$V = 987.2\ (4)$ Å^3
$Z = 2$

$D_x = 1.571$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25
  reflections
$\theta = 13.5–14.9°$
$\mu = 1.03$ mm^{-1}
$T = 296\ (1)$ K
Plate, colourless
$0.30 \times 0.20 \times 0.15$ mm

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan
  (North et al., 1968)
  $T_{min} = 0.821$, $T_{max} = 0.857$
2602 measured reflections
2267 independent reflections
1590 reflections with $I > 2\sigma(I)$

$R_{int} = 0.019$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 8$
$l = -19 \rightarrow 19$
3 standard reflections
  every 150 reflections
  intensity decay: 0.0%

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.096$
$S = 1.02$
1590 reflections
144 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2$
  $+ 0.449P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Compound (III)

Crystal data

$[Cu(C_{10}H_6NO_2)_2(CH_4O)_2]$
$M_r = 471.95$
Monoclinic, $P2_1/c$
$a = 10.265\ (2)$ Å
$b = 6.332\ (2)$ Å
$c = 15.764\ (1)$ Å
$\beta = 96.879\ (9)°$
$V = 1017.3\ (4)$ Å^3
$Z = 2$

$D_x = 1.541$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25
  reflections
$\theta = 14.7–15.0°$
$\mu = 1.12$ mm^{-1}
$T = 296\ (1)$ K
Plate, blue
$0.30 \times 0.30 \times 0.20$ mm

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan
  (North et al., 1968)
  $T_{min} = 0.720$, $T_{max} = 0.800$
2692 measured reflections
2339 independent reflections
1665 reflections with $I > 2\sigma(I)$

$R_{int} = 0.012$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 8$
$l = -20 \rightarrow 20$
3 standard reflections
  every 150 reflections
  intensity decay: 14.8%

Refinement

Refinement on F^2
$R(F) = 0.032$
$wR(F^2) = 0.094$
$S = 1.04$
2239 reflections
143 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2$
  $+ 0.4271P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

All H atoms were initially located in difference Fourier maps and were then regenerated in their ideal positions, with C—H = 0.96 (methyl) or 0.93 Å (other H atoms), and with U_{iso}(H) = $1.2U_{eq}$(parent) (methyl) or $1.5U_{eq}$(parent) (other H atoms). The weighting schemes for all three structures were optimized.

Table 2
Comparison of hydrogen-bonding geometry (Å, °).

Compound	D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
Fe†	O1m—H1m⋯O2^i	0.97	1.66	2.617 (3)	170
(I) (Co)	O1m—H1m⋯O2^i	0.81	1.65	2.607 (2)	172
(II) (Ni)	O1m—H1m⋯O2^i	0.91	1.70	2.600 (2)	178
(III) (Cu)	O1m—H1m⋯O2^i	0.82	1.86	2.679 (2)	175

Symmetry code: (i) $-x, -1 - y, -z$. † Okabe & Muranishi (2003c).

For the three title 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: *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*.

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