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5-*n*-Butylpyridine-2-carboxylate–copper(II) and –iron(III) complexes

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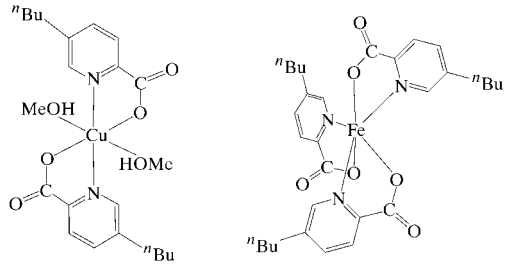
In *trans*-bis(5-*n*-butylpyridine-2-carboxylato-κ^2N,O)bis(methanol-κO)copper(II), $[Cu(C_{10}H_{12}NO_2)_2(CH_4O)_2]$, the Cu atom lies on a centre of symmetry and has a distorted octahedral coordination. The Cu—O(methanol) bond length in the axial direction is 2.596 (3) Å, which is much longer than the Cu—O(carboxylate) and Cu—N distances in the equatorial plane [1.952 (2) and 1.977 (2) Å, respectively]. In *mer*-tris(5-*n*-butylpyridine-2-carboxylato-κ^2N,O)iron(III), $[Fe(C_{10}H_{12}NO_2)_3]$, the Fe atom also has a distorted octahedral geometry, with Fe—O and Fe—N bond-length ranges of 1.949 (4)–1.970 (4) and 2.116 (5)–2.161 (5) Å, respectively. Both crystals are stabilized by stacking interactions of the 5-*n*-butylpyridine-2-carboxylate ligand, although hydrogen bonds also contribute to the stabilization of the copper(II) complex.

Comment

Fusaric acid (5-butylpicolinic acid or 5-butylpyridine-2-carboxylic acid) is a well known fusarium mycotoxin produced by certain fungi which cause infections in cereal grains and other agricultural commodities (Nagatsu *et al.*, 1970; Wang & Ng, 1999; D'Mello *et al.*, 1999). It is a potent inhibitor of the copper enzyme dopamine β-hydroxylase, which catalyzes the biosynthesis of norepinephrine, and lowers endogenous levels of norepinephrine and epinephrine in the brain, heart, spleen and adrenal glands. It is suggested that the inhibitory action of fusaric acid is due to complex interactions with the enzyme–substrate complex (Nagatsu *et al.*, 1970). Fusaric acid also possesses a marked growth-inhibitory action on rice seedlings *via* the Fenton reaction, which produces reactive oxygen species, such as hydroxyl radicals, in the presence of reactive transition metals, such as copper, iron *etc*., and hydrogen peroxide (Iwahashi *et al.*, 1999; Kasprzak, 2002). The formation of chelates of fusaric acid with the transition metals Fe^{III}, Cu^{II}, Co^{II}, Ni^{II} or Mn^{II} has been confirmed spectrophotometrically (Malini, 1966). These findings prompted us to clarify the structure of fusaric acid and the mode of interaction between fusaric acid and metal ions, and we have determined the crystal structures of the title Cu^{II} and Fe^{III} complexes, *viz*. (I) and (II), respectively.



(I) (II)

The molecular structure of (I) is shown in Fig. 1. The Cu atom has a distorted octahedral coordination geometry in the *trans* form, defined by two N atoms and two O atoms of the bidentate pyridinecarboxylate ligand molecules in the equatorial plane, and two O atoms of the methanol molecules in axial positions. The coordination bond length in the axial direction [Cu1—O3*M* 2.596 (3) Å] is longer than those in the equatorial plane (Table 1).

A similar coordination geometry was observed in hydrated bis(pyridine-2-carboxylato)copper(II), in which the corresponding Cu—O(aq) distance in the axial direction and the Cu—O(carboxylate) bond length in the equatorial plane are 2.752 (2) and 1.940 (2) Å, respectively (Faure *et al.*, 1973). These long bond lengths in the axial direction, compared with those in the equatorial plane, are usually observed in copper complexes of octahedral coordination geometry and are explained by a Jahn–Teller effect.

The butyl side chains of the fusaric acid ligands are in the fully extended *trans* zigzag conformation in (I), the zigzag

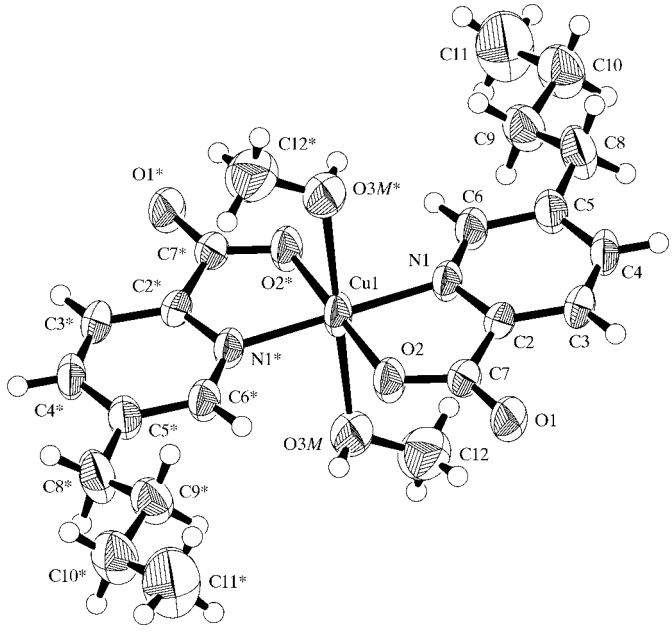


Figure 1
A view of the molecule of (I) with the atomic numbering scheme; asterisks indicate symmetry-related atoms (symmetry code: $2-x, 1-y, 2-z$). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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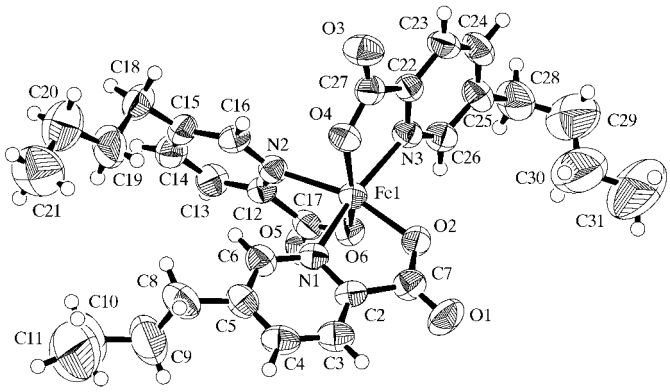

Figure 2
A view of the molecule of (II) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

plane nearly coinciding with the planes of the pyridine ring and the carboxylate [O2—C7—C2—N1 −3.0 (4)°, C6—C5—C8—C9 −17.5 (5)° and C8—C9—C10—C11 −179.6 (4)°].

In the crystal packing of (I), neighbouring molecules are stacked with a mean separation of 3.403 (4) Å, and strong hydrogen bonds are formed between the coordinated methanol molecules and the carboxylate groups of neighbouring molecules (Table 2). The hydrocarbon side chains of the ligands and the coordinated methanol molecules form hydrophobic moieties by association.

The molecular structure of (II) is shown in Fig. 2. In this complex, the Fe atom has a distorted octahedral coordination geometry in the meridional form, formed by three N and three O atoms from three bidentate ligands (Table 3). The orientation of the hydrocarbon chains in (II) is very different from that in (I), with the chains roughly perpendicular to the pyridine ring plane [C14—C15—C18—C19 92.0 (7)°, C24—C25—C28—C29 80.0 (10)° and C4—C5—C8—C9 −76.7 (10)°]. The conformations of the three chains are different, being *trans–gauche* [C5—C8—C9—C10 −179.3 (8)° and C8—C9—C10—C11 −63 (1)°], *trans–trans* [C15—C18—C19—C20 −174.1 (7)° and C18—C19—C20—C21 −178.6 (7)°] and *gauche–trans* [C25—C28—C29—C30 68 (1)° and C28—C29—C30—C31 166 (1)°].

The model of the coordination mode of the Fe^{II} complex of picolinic acid (pyridine-2-carboxylic acid) has been proposed from UV–visible absorption spectra (Iwahashi *et al.*, 1999), in which the central Fe^{II} atom was expected to be coordinated by three N and three O atoms of the three ligands in the facial form. In the present study, only the meridional isomer of the Fe^{III} complex was obtained, although there was a probability that both meridional and facial isomers were obtained in the preparation of compound (II). It is noted that the crystal structures of the Fe^{II} complexes of picolinic acid or fusaric acid have not yet been determined.

In the crystal packing of (II), one of the three pyridine rings (N1/C2–C6) stacks at a mean distance of 3.681 (12) Å.

In both (I) and (II), the central metal atom forms a five-membered ring through the O and N atoms of the bidentate ligand, as was also observed in the Cd^{II} complex of fusaric acid (Okabe, Wada & Muranishi, 2002), as well as in the analogous metal complexes, such as the Mo^{V} complex of picolinic acid (Okabe, Isomoto & Odoko, 2002) and the Ce^{III} complex of dipicolinic acid (pyridine-2,6-dicarboxylic acid; Okabe, Kyoyama & Fujimoto, 2002).

The major conformational differences found in the butyl side chain of fusaric acid in complexes (I) and (II) suggest that the conformational change of the butyl side chain occurs as required to accommodate the structure of its binding site on biological target molecules.

Experimental

Blue crystals of (I) were obtained by slow evaporation of a methanol–water solution (90:10 *v*/*v*) of a mixture of fusaric acid and $CuSO_4{\cdot}5H_2O$ (molar ratio 4:1). Colourless prismatic crystals of (II) were obtained by slow evaporation of an ethanol–water solution (30:70 *v*/*v*) of a mixture of fusaric acid and $Fe(SO_4)_3{\cdot}nH_2O$ (n = 6–9; molar ratio *ca* 4:1 assuming n = 7).

Compound (I)

Crystal data

$[Cu(C_{10}H_{12}NO_2)_2(CH_4O)_2]$
M_r = 484.05
Monoclinic, $P2_1/n$
a = 8.462 (4) Å
b = 6.612 (4) Å
c = 21.456 (3) Å
β = 99.88 (2)°
V = 1182.7 (9) Å^3
Z = 2
D_x = 1.359 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
θ = 14.9–15.0°
μ = 0.96 mm^{-1}
T = 296.2 K
Plate, blue
0.5 × 0.4 × 0.2 mm

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.636, T_{max} = 0.825
3139 measured reflections
2707 independent reflections
1998 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.5°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 8$
$l = -27 \rightarrow 27$
3 standard reflections
every 150 reflections
intensity decay: 20.2%

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

Cu1—O2	1.952 (2)	O1—C7	1.234 (4)
Cu1—O3*M*	2.596 (3)	O2—C7	1.268 (3)
Cu1—N1	1.977 (2)		
O2—Cu1—O3*M*	86.80 (9)	Cu1—O3*M*—C12	121.2 (3)
O2—Cu1—N1	83.66 (9)	Cu1—N1—C2	111.2 (2)
O3*M*—Cu1—N1	90.65 (9)	Cu1—N1—C6	128.6 (2)
Cu1—O2—C7	114.2 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*M*—H3*M*···O1^{i}	0.82	1.92	2.716 (4)	164

Symmetry code: (i) $2-x, 2-y, 2-z$.

Refinement

Refinement on F^2	H-atom parameters constrained
$R(F) = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.166$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.22$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
2707 reflections	$\Delta\rho_{min} = -0.77$ e Å^{-3}
145 parameters	

Compound (II)

Crystal data

$[Fe(C_{10}H_{12}NO_2)_3]$	$D_x = 1.272$ Mg m^{-3}
$M_r = 590.47$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 24 reflections
$a = 9.946$ (5) Å	$\theta = 10.2$–$11.5°$
$b = 22.271$ (5) Å	$\mu = 0.53$ mm^{-1}
$c = 14.072$ (4) Å	$T = 296.2$ K
$\beta = 98.40$ (3)°	Prismatic, colourless
$V = 3083.6$ (19) Å^3	0.2 × 0.1 × 0.1 mm
$Z = 4$	

Data collection

Rigaku AFC-5*R* diffractometer	$h = 0 \rightarrow 12$
$\omega/2\theta$ scans	$k = 0 \rightarrow 28$
7678 measured reflections	$l = -18 \rightarrow 18$
7090 independent reflections	3 standard reflections every 150 reflections
2368 reflections with $I > 2\sigma(I)$	intensity decay: 0.7%
$R_{int} = 0.075$	
$\theta_{max} = 27.5°$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R(F) = 0.062$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.225$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.93$	$\Delta\rho_{max} = 0.50$ e Å^{-3}
7090 reflections	$\Delta\rho_{min} = -0.55$ e Å^{-3}
364 parameters	

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

Fe1—O2	1.949 (4)	O1—C7	1.209 (7)
Fe1—O4	1.970 (4)	O2—C7	1.296 (7)
Fe1—O6	1.969 (4)	O3—C27	1.214 (7)
Fe1—N1	2.161 (5)	O4—C27	1.298 (7)
Fe1—N2	2.159 (4)	O5—C17	1.223 (8)
Fe1—N3	2.116 (5)	O6—C17	1.293 (7)
O2—Fe1—O4	106.5 (2)	N1—Fe1—N2	90.9 (2)
O2—Fe1—O6	91.6 (2)	N1—Fe1—N3	162.0 (2)
O2—Fe1—N1	78.6 (2)	N2—Fe1—N3	103.0 (2)
O2—Fe1—N2	163.1 (2)	Fe1—O2—C7	120.8 (4)
O2—Fe1—N3	90.2 (2)	Fe1—O4—C27	120.4 (4)
O4—Fe1—O6	158.9 (2)	Fe1—O6—C17	120.6 (4)
O4—Fe1—N1	91.4 (2)	Fe1—N1—C2	111.3 (4)
O4—Fe1—N2	86.7 (2)	Fe1—N1—C6	130.3 (4)
O4—Fe1—N3	78.3 (2)	Fe1—N2—C12	112.4 (3)
O6—Fe1—N1	103.0 (2)	Fe1—N2—C16	128.4 (4)
O6—Fe1—N2	77.7 (2)	Fe1—N3—C22	113.8 (4)
O6—Fe1—N3	91.3 (2)	Fe1—N3—C26	127.5 (4)

The reflection data for (I) were corrected for an intensity decay of 20.2%. In (I), only one H atom, H3*M*, attached to the methanol hydroxy group, was fixed at the position located from a difference Fourier map. The remaining H atoms were placed in calculated positions and treating as riding, with C—H distances in the range 0.93–0.97 Å. The large atomic displacement parameters of the *n*-butyl groups of (II) suggest positional disorder.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation and Rigaku, 2000); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation and Rigaku, 2000). For compound (I), program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989) and *DIRDIF*94 (Beurskens *et al.*, 1994). For compound (II), program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1999) and *DIRDIF*94. For both compounds, 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: OB1079). Services for accessing these data are described at the back of the journal.

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