

Tris[*N*-(4-fluorophenyl)pyridine-2-carboxamidato- κ^2 *N,N'*]cobalt(III) trihydrate: a novel meridional complex

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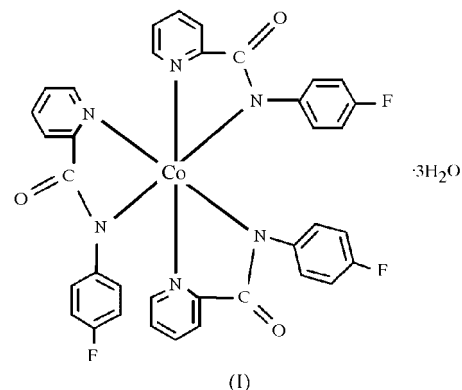
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The title complex, $[\text{Co}(\text{C}_{12}\text{H}_8\text{FN}_2\text{O})_3]\cdot 3\text{H}_2\text{O}$, has been synthesized for the first time. The complex comprises three bidentate ligands containing the pyridine-2-carboxamide stem. The distorted octahedral coordination around the Co atom is formed *via* the pyridine (py) N atom and the deprotonated amide N atom of each ligand, with the three pyridine rings in a meridional arrangement. For each ligand, the pyridine ring and the carbonyl group are nearly coplanar, with torsion angles in the range 0.4 (3)–4.8 (4)°. The Co–N_{py} distances [1.9258 (16)–1.9656 (17) Å] are shorter than the corresponding Co–N_{amide} distances [1.9372 (17)–1.9873 (15) Å]. In addition, the Co–N_{py} distances are closely related to the magnitudes of the chelate angles, a shorter Co–N_{py} distance corresponding to a larger angle. Five intermolecular hydrogen bonds, involving carbonyl O atoms of the ligands and lattice water molecules, lead to the formation of a mesh structure.

Comment

The selective oxidation of hydrocarbons using molecular oxygen as the primary oxidant is an important technology and is an area of continued research and development because of the low cost and environmentally friendly nature of the oxidant (Bolm *et al.*, 1994; Neumann & Dahan, 1998; Brink *et al.*, 2000). Much effort has been made in the past to activate dioxygen using metal complexes (Shilov & Shul'pin, 2000). Ishii *et al.* (1996) reported a novel catalytic system using *N*-hydroxyphthalimide combined with $\text{Co}(\text{acac})_n$ (acac is acetylacetonate; $n = 2$ or 3) as catalysts in the oxidation of alkylbenzene; thus, ethylbenzene was successfully oxidized to acetophenone in excellent yield. However, this method has a

corrosive and environmentally unfriendly nature because of the use of acetic acid as solvent. We found recently in our laboratory that the title complex, (I), is an efficient catalyst for the direct oxidation of ethylbenzene with dioxygen, without the need any solvent and reducing reagent, giving 86.0% acetophenone selectivity on 65.7% conversion under moderate conditions. This economical and environmentally friendly system shows excellent potential for industrial application. The synthesis and structure of complex (I) are described here.



Complex (I) contains three ligands, coordinated *via* the pyridine N atom and the negatively charged amide N atom instead of the neutral amide N atom or the carbonyl O atom. There are two possible geometric isomers for this compound; one is facial, having all three pyridine (py) rings in a *cis* conformation, and the other is meridional, having two of the pyridine rings in *trans* positions. The crystal structure shows that this complex is the latter isomer; two pyridine rings are mutually *trans*, two amide groups are mutually *trans* and one pyridine ring is *trans* to one amide group. Therefore, various situations exist for competitive *trans* effects. In each of the three ligands, the Co–N_{py} distance [1.9258 (16)–1.9656 (17) Å] is always shorter than the corresponding Co–N_{amide} distance [1.9372 (17)–1.9873 (15) Å], while the Co–N_{py} distance for one ligand can be longer than the Co–N_{amide} distance for another; for instance, the Co–N3 distance [1.9656 (17) Å] is longer than the Co–N6 distance [1.9372 (17) Å]. Moreover, the Co–N_{py} distances depend on the size of the chelate angles; the longer the Co–N_{py} distance, the smaller the corresponding angle. In (I), the Co–N3 distance is the longest Co–N_{py} distance and the N3–Co–N4 angle [81.92 (7)°] is the smallest chelate angle. Since the distances of the six coordination bonds are not equal, the complex has the form of a distorted octahedron. The structural features described above have been reported in analogous complexes (Qi *et al.*, 2003).

For every ligand in (I), the pyridine ring and the carbonyl group are nearly coplanar, with C4–C5–C6–O1, C16–C17–C18–O2 and C28–C29–C30–O3 torsion angles of 0.4 (3), 4.8 (3) and 3.2 (3)°, respectively. In addition, the deprotonated amide N atom facilitates the aerobic oxidation of Co^{II} to Co^{III} during the formation of the complex. The three anionic ligands neutralize the trivalent cobalt cation.

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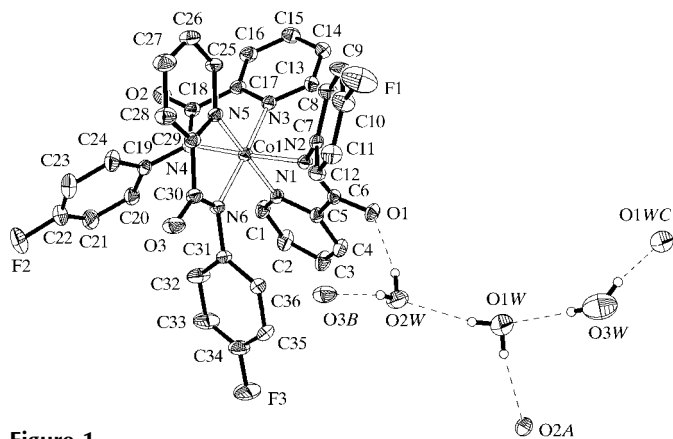


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

There are four intermolecular hydrogen bonds in the crystal structure of (I) (Fig. 1 and Table 1): (i) carbonyl atom O2 of one molecule interacts with the O1W–H11W group of a lattice water molecule; (ii) the O3W–H3WA lattice water group interacts with water atom O1W; (iii) carbonyl atom O1 interacts with the O2W–H21W group of an adjacent water molecule; (iv) carbonyl atom O3 interacts with the O2W–H22W group of another lattice water molecule. Through these intermolecular hydrogen-bonding interactions, every molecule of (I) is linked to adjacent molecules, thus forming a mesh structure.

Experimental

The carboxamide ligand was synthesized from 2-pyridinecarboxylic acid and 4-fluoroaniline according to a published procedure (Ray *et al.*, 1997). The ligand was dissolved in EtOH under ambient conditions, and to this solution was added cobalt dichloride dissolved in EtOH and 25% NH₃. The mixture was stirred magnetically for 30 min. The precipitate was filtered off, washed with ethanol and air-dried, yielding a deep-red powder. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent from a saturated ethanol–water solution at room temperature.

Crystal data

[Co(C ₁₂ H ₈ FN ₂ O) ₃]·3H ₂ O	<i>Z</i> = 2
<i>M_r</i> = 758.59	<i>D_x</i> = 1.433 Mg m ^{−3}
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 12.1443 (12) Å	Cell parameters from 7832 reflections
<i>b</i> = 12.2258 (12) Å	<i>θ</i> = 1.5–27.5°
<i>c</i> = 14.5543 (14) Å	<i>μ</i> = 0.56 mm ^{−1}
<i>α</i> = 99.774 (2)°	<i>T</i> = 294 (2) K
<i>β</i> = 103.547 (2)°	Prism, red
<i>γ</i> = 117.775 (2)°	0.22 × 0.20 × 0.14 mm
<i>V</i> = 1758.3 (3) Å ³	

Data collection

Bruker SMART CCD diffractometer	6160 independent reflections
<i>φ</i> and <i>ω</i> scans	4984 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.028
<i>T</i> _{min} = 0.727, <i>T</i> _{max} = 0.925	<i>θ</i> _{max} = 25.0°
9817 measured reflections	<i>h</i> = −14 → 14
	<i>k</i> = −14 → 12
	<i>l</i> = −15 → 17

Refinement

Refinement on *F*²
R(*F*) = 0.041
wR(*F*²) = 0.112
S = 1.01
 6160 reflections
 469 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.49 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

Table 1
Hydrogen-bonding geometry (Å, °).

<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–H11W···O2 ⁱ	0.85	2.04	2.856 (3)	162
O1W–H12W···O2W	0.85	2.19	2.855 (3)	135
O2W–H21W···O1	0.85	2.02	2.850 (2)	165
O2W–H22W···O3 ⁱⁱ	0.85	1.96	2.788 (2)	164
O3W–H31W···O1W	0.85	2.19	3.035 (3)	180

Symmetry codes: (i) *x*, *y*, *z* − 1; (ii) 1 − *x*, 1 − *y*, −*z*.

C-bound H atoms were placed in calculated positions, with C–H distances of 0.93 Å, and were thereafter treated as riding. Water H atoms were positioned from difference maps, and their coordinates were allowed for with the O–H distance constrained to 0.85 Å; *U*_{iso}(H) values were set at 1.2*U*_{eq} of the attached atom.

Data collection: SMART (Siemens, 1995); cell refinement: SMART; data reduction: SAINT (Siemens, 1995) and SHELXTL-NT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-NT; software used to prepare material for publication: SHELXTL-NT.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1443). Services for accessing these data are described at the back of the journal.

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