

Qi Yun Yang,^a Da Wu Yang,^a
Jian Ying Qi,^{a,b,*} Zhong Yuan
Zhou^b and Albert S. C. Chan^{b,*}^aDepartment of Chemistry, Changsha University of Science and Technology, Changsha, Hunan, People's Republic of China, and ^bDepartment of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong KongCorrespondence e-mail: jqi@itsa.ucsf.edu,
bcachan@polyu.edu.hk

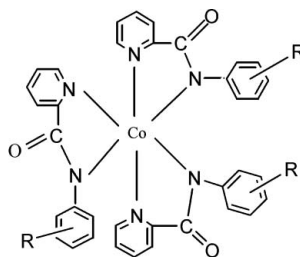
Key indicators

Single-crystal X-ray study
T = 294 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.075
wR factor = 0.209
Data-to-parameter ratio = 16.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Tris[*N*-(3-chlorophenyl)pyridine-2-carboxamido- $\kappa^2\text{N},\text{N}'$]cobalt(III) monohydrate

The title complex, $[\text{Co}(\text{C}_{12}\text{H}_8\text{ClN}_2\text{O})_3]\cdot\text{H}_2\text{O}$, has been synthesized for the first time. The complex comprises three bidentate ligands containing the pyridine-2-carboxamide nucleus. The distorted octahedral coordination around the Co atom is formed *via* the pyridine N atom and the deprotonated amide N atom of each ligand. One intermolecular hydrogen bond forms between a carbonyl O atom of one ligand and the single water molecule.

Comment

We reported recently that cobalt complexes (2) and (3) containing ligands based on a pyridine-2-carboxamide nucleus were found to be highly effective catalysts in the direct oxidation of ethylbenzene to acetophenone using dioxygen as oxidant, without the need for any solvent (Qi *et al.*, 2003, 2004). In order to develop further this economical and environmentally friendly catalytic system, we synthesized another complex, (1)·H₂O, containing *N*-(3-chlorophenyl)pyridine-2-carboxamide ligands. This complex is highly active and remarkably selective in the oxidation of ethylbenzene, a reaction of high scientific and commercial interest. Typical results showed that, when the reaction temperature was increased from 393 to 423 K, the conversion of ethylbenzene increased rapidly from 50 to 65%. The main product was acetophenone with its selectivity up to 90% at 423 K. The selectivity was increased by 4% compared to the result reported previously (Qi *et al.*, 2004).



(1) R = m-Cl (2) R = p-Cl (3) R = p-F

The crystal structure of the monohydrate shows similar structural features to the analogous complexes (2) and (3) (Qi *et al.*, 2003, 2004). All three contain three ligands, coordinated *via* the pyridine N atom and the negatively charged amide N atom. They also are all meridional geometric isomers with two of the pyridine rings in positions *trans* to one another. In addition, two amide groups are mutually *trans* and one pyridine ring is *trans* to one amide group. In this complex, one ligand has a Co–N_{2py} distance [1.940 (3) Å] that is very slightly longer than its Co–N_{1amide} distance [1.932 (3) Å].

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This differs from the other two ligands in (1)·H₂O and from all ligands in (2) and (3), where the Co—N_{py} distance is shorter than the Co—N_{amide} distance. Since the distances of the six coordination bonds are not equal, the complex has the form of a distorted octahedron.

For every ligand in (1)·H₂O, the pyridine ring and the carbonyl group are nearly coplanar, with C9—C8—C7—O1, C21—C20—C19—O2 and C33—C32—C31—O3 torsion angles of 5.2 (5), 1.7 (6) and 3.8 (6)°, 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. There is also an intermolecular hydrogen bond formed by carbonyl atom O2 of one ligand to O1W, the single included water molecule.

Experimental

The ligand of the complex was synthesized from 2-pyridinecarboxylic acid and 3-chloroaniline following a published procedure (Ray *et al.*, 1997). The ligand (0.354 g, 1.52 mmol) was dissolved in EtOH (5 ml) and to it was added cobalt dichloride hexahydrate (0.181 g, 0.76 mmol) dissolved in EtOH (2 ml). The resulting red solution was stirred magnetically for 0.5 h. After about 20 d, a red precipitate resulted. The crystal used for the data collection was obtained by slow evaporation of an ethanol–water saturated solution at room temperature.

Crystal data

[Co(C ₁₂ H ₈ ClN ₂ O) ₃]·H ₂ O	Z = 2
<i>M_r</i> = 771.91	<i>D_x</i> = 1.507 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 9.484 (4) Å	Cell parameters from 4728 reflections
<i>b</i> = 10.796 (4) Å	<i>θ</i> = 1–27.5°
<i>c</i> = 18.716 (8) Å	<i>μ</i> = 0.79 mm ⁻¹
<i>α</i> = 102.378 (7)°	<i>T</i> = 294 (2) K
<i>β</i> = 93.416 (7)°	Block, brown
<i>γ</i> = 113.011 (8)°	0.20 × 0.14 × 0.12 mm
<i>V</i> = 1700.8 (12) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	7631 independent reflections
<i>φ</i> and <i>ω</i> scans	3641 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.046
<i>T</i> _{min} = 0.858, <i>T</i> _{max} = 0.911	<i>θ</i> _{max} = 27.7°
10958 measured reflections	<i>h</i> = -11 → 12
	<i>k</i> = -14 → 5
	<i>l</i> = -23 → 24

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.075	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.095 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.209	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>S</i> = 1.01	(Δσ) _{max} = 0.001
7631 reflections	Δρ _{max} = 0.97 e Å ⁻³
451 parameters	Δρ _{min} = -0.98 e Å ⁻³

Table 1

Hydrogen-bond 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—H1WB···O2	0.85	2.36	2.934 (5)	125

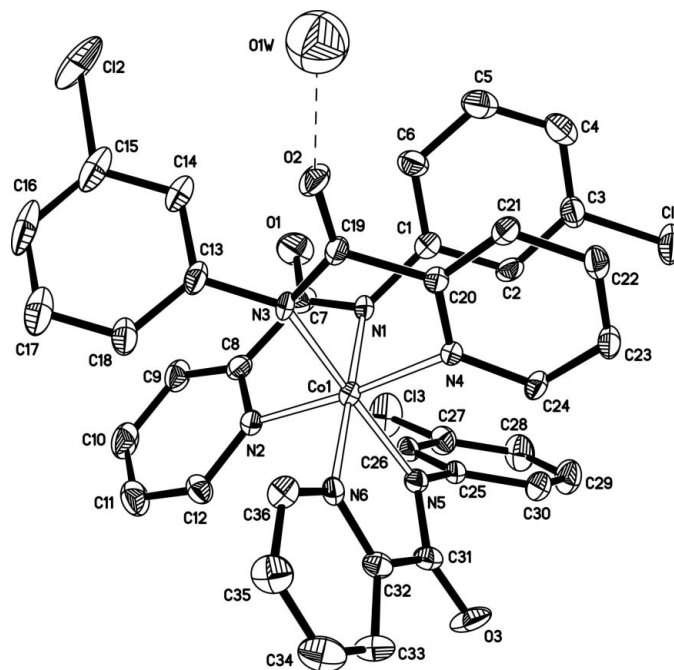


Figure 1

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

Table 2

Comparison of bond lengths (Å) and angles (°) for compounds (1), (2) and (3).

	(1)	(2)	(3)
Co—N _{py}	N2—Co1 1.940 (3) N4—Co1 1.942 (3) N6—Co1 1.957 (3)	N1—Co1 1.9615 (18) N3—Co1 1.9365 (16) N5—Co1 1.9447 (17)	N1—Co1 1.9395 (17) N3—Co1 1.9652 (18) N5—Co1 1.9270 (17)
Co—N _{amide}	N1—Co1 1.932 (3) N3—Co1 1.953 (2) N5—Co1 1.968 (3)	N2—Co1 1.9666 (17) N4—Co1 1.9420 (17) N6—Co1 1.9502 (16)	N2—Co1 1.9508 (16) N4—Co1 1.9859 (16) N6—Co1 1.9366 (17)
N1—Co1—N2	83.22 (13)	81.72 (7)	82.75 (7)
N3—Co1—N4	82.99 (11)	82.81 (7)	81.96 (7)
N5—Co1—N6	82.84 (12)	82.43 (7)	82.94 (7)

C-bound H atoms were positioned geometrically (C—H = 0.93 Å) and refined in the riding-model approximation, with *U*_{iso}(H) = 1.2*U*_{eq}(C). 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}(O).

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

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