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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.038
 wR factor = 0.098
Data-to-parameter ratio = 17.6

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

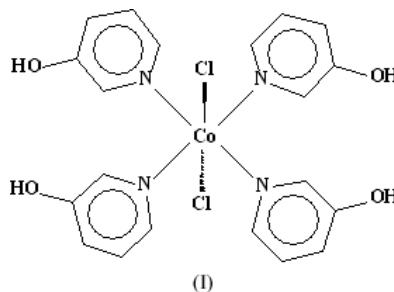
Dichlorotetrakis(3-hydroxypyridine)cobalt(II)

In the title complex, $[\text{CoCl}_2(\text{C}_5\text{H}_5\text{NO})_4]$, the Co atom is in an elongated octahedral environment, defined by two Cl^- ions and four N atoms of 3-hydroxypyridine ligands. The Co atom lies on a special position with crystallographic twofold rotation symmetry. Individual molecules are linked by intermolecular $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bonds into a layer structure.

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Comment

Hydroxypyridines (PyOH), including 2-OH, 3-OH and 4-OH, are all widely used in pharmaceutical synthesis and are potential bifunctional ligands with versatile binding modes. However, only a few complexes with neutral pyridone as ligand have been structurally characterized thus far (Goodgame *et al.*, 1989; Breeze & Wang, 1993; Ohgo & Ohashi, 1996) and the majority of these contain 2-PyOH or its tautomer, the lactam 2-pyridone (Maity *et al.*, 2002; Chattopadhyay *et al.*, 2004). As a contribution to this field, we have reported the structures of two cobalt complexes, $[\text{CoCl}_2(4\text{-pyridone})_2]$ and $[\text{Co}(\text{NO}_3)(4\text{-pyridone})_2(\text{H}_2\text{O})_2](\text{NO}_3)$, in which the Co atoms exhibit tetrahedral and octahedral geometries, coordinated by the O atoms of 4-pyridone ligands (Gao *et al.*, 2004; Lu *et al.*, 2004). Unlike 2-PyOH or 4-PyOH, 3-PyOH does not have the corresponding tautomeric form, '3-pyridone', so the N atom of this ligand may become a preferred binding site for metal ions (Breeze & Wang, 1993), while deprotonated 3-PyOH, *viz.* pyridin-3-onate, may act as a bridging ligand (Castillo *et al.*, 2000). For this reason, we used 3-PyOH instead of 4-PyOH in the reaction, and have synthesized a novel cobalt complex, $[\text{CoCl}_2(\text{C}_5\text{H}_5\text{NO})_4]$, (I), whose crystal structure is reported here.



As show in Fig. 1, the crystal structure of (I) is a neutral mononuclear complex, in which the Co atom occupies a special position having crystallographic twofold rotation symmetry, and in which the Co atom is coordinated by four N atoms of the 3-PyOH ligands and two Cl^- ions in an elongated octahedral environment. The axial positions are occupied by the two Cl^- ions, with $\text{Co}-\text{Cl}$ distances of 2.5132 (7) Å. The four N atoms are in the equatorial plane, with $\text{Co}-\text{N}$ bond

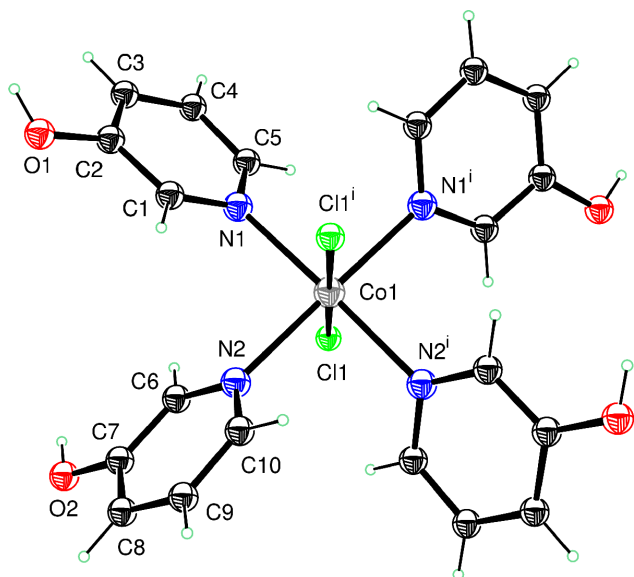


Figure 1
ORTEP plot of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $\frac{1}{2} - x, 1 - y, z$.]

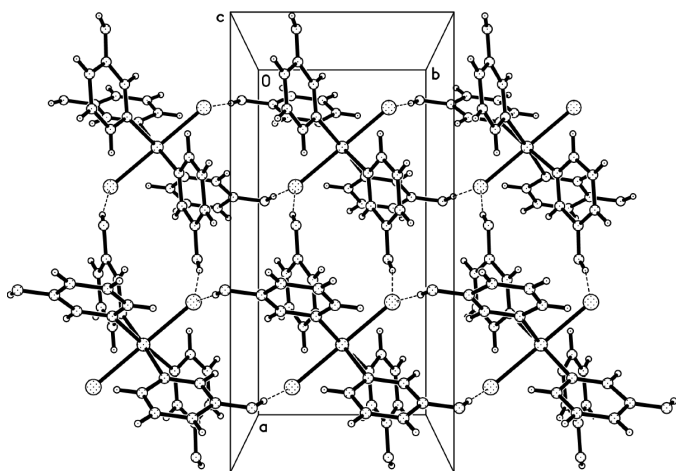


Figure 2
The packing of (I), with the O—H...Cl hydrogen bonds denoted by dashed lines.

lengths of 2.158 (2) and 2.172 (2) Å (Table 1). The C—C and C—N bond lengths are as expected, while the C—O bond distances [1.351 (3) and 1.359 (3) Å] of the title complex are slightly longer than those in other related complexes (1.31–1.34 Å; see references below). The dihedral angle between the pyridine rings is 65.72 (5)°.

To our knowledge, only eight structures of complexes containing the 3-PyOH ligand have been reported. These are three mononuclear complexes coordinated by the N atom of 3-PyOH (Breeze & Wang, 1993; Ohgo & Ohashi, 1996); one Co^{II} and one Ni^{II} complex with oxalate and 3-PyOH ligands (Castillo, Luque, Lloret & Roman, 2001; one Cu^{II} complex with oxalate and 3-PyOH ligands (Castillo, Luque, Julve *et al.*, 2001); and one- and two-dimensional polynuclear copper complexes bridged by *N,O*-bidentate pyridin-3-onate ligands (Kawata *et al.*, 1997; Castillo *et al.*, 2000).

The uncoordinated hydroxyl O atoms form intermolecular hydrogen bonds with the Cl[−] ions (Table 2 and Fig. 2), giving rise to a layer structure.

Experimental

The title complex was prepared by the addition of CoCl₂·6H₂O (2 mmol) to an ethanol solution of 3-PyOH (6 mmol). The solution was allowed to evaporate at room temperature, and pink single crystals were isolated from the solution after eight days. Analysis calculated for C₂₀H₂₀Cl₂CoN₄O₄: C 47.08, H 3.95, N 10.98%; found: C 47.21, H 3.72, N 10.83%.

Crystal data

[CoCl₂(C₅H₅NO)₄]
M_r = 510.23
Orthorhombic, *Pcca*
a = 15.651 (3) Å
b = 7.597 (2) Å
c = 18.848 (4) Å
V = 2241.0 (9) Å³
Z = 4
D_x = 1.512 Mg m^{−3}

Mo Kα radiation
Cell parameters from 15 032 reflections
θ = 3.1–27.5°
μ = 1.04 mm^{−1}
T = 293 (2) K
Prism, pink
0.38 × 0.26 × 0.18 mm

Data collection

Rigaku R-Axis RAPID
diffractometer
ω scans
Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)
T_{min} = 0.694, T_{max} = 0.835
20 059 measured reflections

2581 independent reflections
2004 reflections with *I* > 2σ(*I*)
R_{int} = 0.042
θ_{max} = 27.5°
h = −19 → 20
k = −9 → 9
l = −21 → 24

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.038
wR(F²) = 0.098
S = 1.05
2581 reflections
147 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.8539P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.34 e Å^{−3}
Δρ_{min} = −0.21 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Co1—Cl1	2.5132 (7)	O1—C2	1.359 (3)
Co1—N1	2.158 (2)	O2—C7	1.351 (3)
Co1—N2	2.172 (2)		
Cl1—Co1—Cl1 ⁱ	178.75 (3)	N1—Co1—Cl1	87.80 (5)
N1 ⁱ —Co1—N1	90.62 (9)	N2 ⁱ —Co1—Cl1	90.29 (5)
N1 ⁱ —Co1—N2 ⁱ	90.75 (7)	N2—Co1—Cl1	90.61 (5)
N1—Co1—N2 ⁱ	177.68 (6)	N2 ⁱ —Co1—N2	87.94 (9)
N1 ⁱ —Co1—Cl1	91.32 (5)		

Symmetry code: (i) $\frac{1}{2} - x, 1 - y, z$.

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H11...Cl1 ⁱⁱ	0.84 (2)	2.23 (2)	3.052 (2)	168 (3)
O2—H12...Cl1 ⁱⁱⁱ	0.84 (2)	2.23 (3)	3.068 (2)	175 (3)

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

H atoms attached to O atoms were located in difference Fourier synthesis maps and refined with an O–H distance restraint of 0.85 (1) Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Other H atoms were placed in calculated positions and were allowed to ride on their parent C atoms [$\text{C}–\text{H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$].

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK & Rigaku Corporation, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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