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Chloro[*N,N′-o*-phenylenebis(pyridine-2-carboxamido)]cobalt(III) chloroform disolvate

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Key indicators

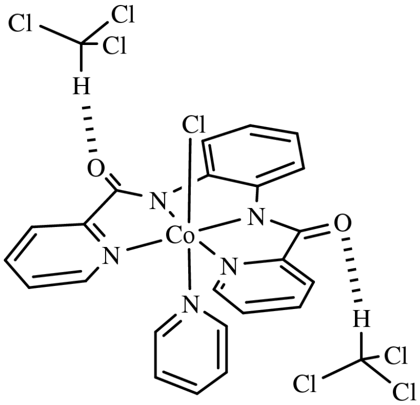
Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.019 Å
R factor = 0.099
wR factor = 0.299
Data-to-parameter ratio = 10.5

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

The title compound, [C(bpb)(Cl)(pyridine)]·2$CHCl_3$ [bpbH_2 is *N,N′-o*-phenylenebis(pyridine-2-carboxamide), $C_{18}H_{12}N_4O_2$], was obtained directly from [Co(bpb)(OO^{t}Bu)(pyridine)] upon storage in freshly distilled $CHCl_3$. The structure of this octahedral cobalt(III) complex reveals two chloroform molecules of solvation that form hydrogen bonds to the O atoms of the carboxamide group of the bpb^{2-} ligand.

Comment

When the complex [Co(bpb)(OO^{t}Bu)(pyridine)] was stored for a brief amount of time in $CHCl_3$ at room temperature, the title compound [Co(bpb)(Cl)(pyridine)], (I), crystallized out as yellow plates. The mechanism for the incorporation of the chloride ion into the cobalt(III) complex remains unknown at this time, although it is clear that the source of the chloride ion is the solvent $CHCl_3$. The mechanism of decomposition of various cobalt(III) alkylperoxides in many solvents has been discussed by Chavez *et al.* (1998). The decomposition of Co(bpb)(OO^{t}Bu)(pyridine) may proceed through a similar reaction pathway.



(I)

Since the initial report by Chapman & Vagg (1979), the *N,N′*-bis(2′-pyridinecarboxamide)-1,2-benzene or *N,N′-o*-phenylenebis(pyridine-2-carboxamide) (bpbH_2) ligand has been extensively employed as a tetradentate diamide ligand for various transition metal ions. This ligand was designed exclusively to investigate the unique bonding properties of deprotonated carboxamido N atoms toward M^{n+} ions. The square-planar cobalt(II) complex [Co(bpb)]·H_2O was reported in the initial account by Chapman & Vagg (1979). Later, bpbH_2 was utilized by Saussine *et al.* (1985) to stabilize

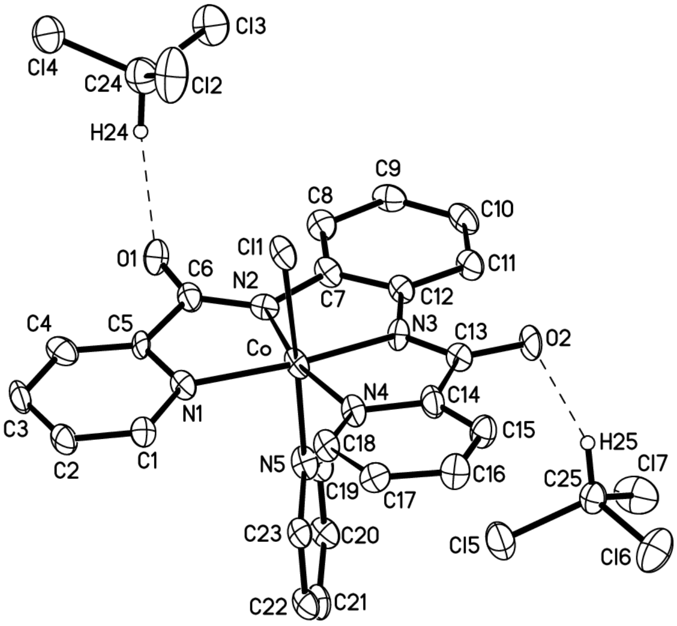


Figure 1

The molecular structure of [Co(bpb)(Cl)(pyridine)] showing the atom labeling scheme. Displacement ellipsoids are shown at the 35% probability level. H atoms have been omitted for clarity except on the two molecules of $CHCl_3$.

the cobalt(III) alkylperoxide complex [Co(bpb)(OO^{t}Bu)(4-Mepy)] (4-Mepy is 4-methylpyridine). Although this cobalt(III) alkylperoxide complex was not structurally characterized by X-ray diffraction, its activity as a catalyst for the oxidation of various hydrocarbon substrates in the presence of excess alkyhydroperoxide was investigated in detail. The role of cobalt(III) alkylperoxide complexes in the oxidation of hydrocarbon atoms has recently been highlighted in a review by Chavez & Mascharak (2000).

The structure of [Co(bpb)(Cl)(pyridine)] is presented in Fig. 1. The cobalt(III) center resides in an octahedral geometry with the bpb^{2-} ligand occupying the equatorial plane of the octahedron. The remaining coordination sites are occupied by one chloride and one pyridine ligand. The Co—N(amido) distances are similar in length [Co—N2, 1.890 (9) Å, Co—N3, 1.879 (9) Å] while the Co—N(py) distances are 1.980 (10) Å and 2.000 (11) Å. The single pyridine is coordinated to the cobalt(III) center at a distance of 1.978 (10) Å. The Co—Cl distance [2.251 (4) Å] is well within the range of Co^{III}—Cl distances. For example, the Co—Cl bond distances in $[Co(NH_3)_5(Cl)]Cl_2$ and $[Co(Metrenen)(Cl)](ClO_4)_2$ are 2.286 (2) and 2.248 (5) Å, respectively (Messmer & Amma, 1968; Buckingham *et al.*, 1972). As expected, the bpb^{2-} ligand frame remains completely planar in the complex. The structure reveals (Table 2) two $CHCl_3$ molecules of solvation which form weak hydrogen bonds with the carbonyl-O atoms of the bpb^{2-} ligand.

Experimental

[Co(bpb)(OO^{t}Bu)(pyridine)] was synthesized by following the procedure outlined by Saussine *et al.* (1985); pyridine was used in place of 4-methylpyridine. Single crystals of [Co(bpb)(Cl)(pyridine)] were obtained directly from [Co(bpb)(OO^{t}Bu)(pyridine)] when the parent compound was dissolved in freshly distilled $CHCl_3$ and the solution was stored for a period of ~20 min.

Crystal data

$[CoCl(C_{18}H_{12}N_4O_2)(C_5H_5N)]\cdot 2CHCl_3$
$M_r = 728.53$
Triclinic, $P\overline{1}$
$a = 8.374$ (5) Å
$b = 12.762$ (10) Å
$c = 14.381$ (9) Å
$\alpha = 98.08$ (6)°
$\beta = 90.12$ (5)°
$\gamma = 107.44$ (5)°
$V = 1450.1$ (17) Å^3
$Z = 2$
$D_x = 1.669$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 45 reflections
$\theta = 8$–25°
$\mu = 10.87$ mm^{-1}
$T = 130$ (2) K
Plate, yellow
0.52 × 0.16 × 0.01 mm

Data collection

Siemens *P*4 diffractometer
$2\theta-\omega$ scans
Absorption correction: empirical (*XABS*2, Parkin *et al.*, 1995)
$T_{min} = 0.070$, $T_{max} = 0.899$
3802 measured reflections
3802 independent reflections
2389 reflections with $I > 2\sigma(I)$
$R_{int} = 0.075$
$\theta_{max} = 56.7$°
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 15$
2 standard reflections every 198 reflections intensity decay: <2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.099$
$wR(F^2) = 0.299$
$S = 1.03$
3802 reflections
361 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1923P)^2 + 3.7422P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.09$ e Å^{-3}
$\Delta\rho_{min} = -1.01$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Co—N3	1.879 (9)	Co—N1	1.980 (10)
Co—N2	1.890 (9)	Co—N4	2.000 (11)
Co—N5	1.978 (10)	Co—Cl1	2.252 (4)
N3—Co—N2	84.6 (4)	N5—Co—N4	91.1 (4)
N3—Co—N5	90.9 (4)	N1—Co—N4	109.5 (4)
N2—Co—N5	92.4 (4)	N3—Co—Cl1	91.7 (3)
N3—Co—N1	167.4 (4)	N2—Co—Cl1	88.7 (3)
N2—Co—N1	83.0 (4)	N5—Co—Cl1	177.2 (3)
N5—Co—N1	87.2 (4)	N1—Co—Cl1	90.4 (3)
N3—Co—N4	83.0 (4)	N4—Co—Cl1	88.3 (3)
N2—Co—N4	167.2 (4)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C24—H24···O1	1.00	2.17	3.144 (19)	164.3
C25—H25···O2	1.00	2.16	3.107 (16)	157.3

Data collection: *P*3/*P*4-*PC* (Siemens, 1991); cell refinement: *P*3/*P*4-*PC*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL XP* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

Acta Cryst. (2001). E**57**, m368–m370 John M. Rowland *et al.* • $[CoCl(C_{18}H_{12}N_4O_2)(C_5H_5N)]\cdot 2CHCl_3$ **m369**

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