Crystal Structure of Tetraethylammonium Dichloro[1,2-bis(2-pyridine-2-carboxamido)benzene]cobalt(III) Monohydrate

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The structure of the tetradentate Co(III) complex was determined by the X-ray diffraction method. Four N atoms of the 1,2-bis(2-pyridine-2-carboxamido)benzene (bpb²⁻) ligand and two chloro ligands are coordinated to the Co(III) atom with a Cl-Co-Cl angle of 176.18(7)°. The coordination geometry of the Co atom is distorted octahedral(Oh).

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The cobalt-catalyzed oxidation of hydrocarbons by oxygen molecules represents one of the largest scale applications of homogeneous catalysis, and is widely used in industry.¹ Therefore, in order to develop new cobalt complexes, we synthesized the title complex and obtained a crystal of its cobalt(III) complex. We report here on the crystal structure of a

Co(III) complex that contains the N4-type tetradentate ligand, 1,2-bis(pyridine-2-carboxamido)benzene (H2bpb).

All chemicals used were of analytical reagent grade, and were used directly without further purification. The title complex, [Et₄N][CoCl₂(bpb)], was prepared according to the literature.² Single crystals for X-ray crystallography were prepared by slow evaporation from an acetonitrile-diethyl ether solution at room temperature. The X-ray diffraction data for the title compound were collected on an Enraf-Nonius CAD-4 Mach3 diffractometer equipped with a monochromator in the Mo K_α (λ = 0.71073 Å) incident beam. A dark-green crystal was mounted on a glass fiber. The final cell parameters were obtained from a

Table 1 Crystal data and experimental data

Formula: C ₂₆ H ₃₄ Cl ₂ CoN ₅ O ₃
Formula weight: 594.40
Temperature: 293(2)K
Crystal size: 0.2 × 0.15 × 0.1 mm ³
Crystal color: dark green
Crystal description: block
Crystal system: monoclinic
Space group: P2 ₁ /n (No. 14) Z = 4
a = 10.674(2) Å
b = 10.7903(10) Å
c = 22.838(4) Å
β = 90.096(10)°
V = 2630.4(7) Å ³
Calculated density: 1.496 Mg/cm ³
Radiation: 0.71073 Å (Mo K _α)
2θ _{max} = 51.92 R = 0.0591 [3170 reflections, I > 2σ(I)]
wR = 0.1919
Goodness-of-fit = 1.047
(Δ/σ) _{max} final cycle = 0.001
(Δρ) _{min,max} = -0.545, 0.606 e Å ⁻³
No. of reflections collected = 5442
No. of reflections used = 5155
No. of parameters = 335
Diffractometer: Enraf-Nonius CAD4 Mach 3
Monochromator: graphite
Structure determination: SHELXS-97 and SHELXL-97
Refinement: full-matrix least-squares on F ²

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Fig. 1 Structural chemical diagram.

Fig. 2 Molecular structure along with the labeling atoms. One of disordered sets of ethyl groups in a cation is displayed; the hydrogen atoms of crystalline water molecules were not located.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U(eq)
Co(1)	8235(1)	6823(1)	4287(1)	33(1)
Cl(1)	6945(1)	8063(1)	4811(1)	47(1)
Cl(2)	9571(1)	5534(1)	3822(1)	44(1)
O(1)	10132(5)	9604(5)	3577(2)	72(2)
O(2)	5282(4)	5170(4)	3567(2)	58(1)
N(1)	9644(4)	7510(4)	4747(2)	35(1)
N(2)	8656(4)	8106(5)	3769(2)	41(1)
N(3)	6971(4)	6467(4)	3746(2)	36(1)
N(4)	7513(4)	5379(4)	4702(2)	34(1)
C(1)	10080(6)	7231(6)	5282(3)	45(2)
C(2)	11018(6)	7875(6)	5548(3)	52(2)
C(3)	11563(6)	8861(6)	5261(3)	53(2)
C(4)	11136(6)	9155(6)	4720(3)	46(2)
C(5)	10182(6)	8473(5)	4467(3)	41(1)
C(6)	9658(6)	8798(6)	3877(3)	46(2)
C(7)	7886(6)	8168(6)	3272(3)	44(1)
C(8)	7986(7)	9025(8)	2821(3)	65(2)
C(9)	7123(8)	8969(8)	2368(3)	70(2)
C(10)	6218(7)	8079(8)	2347(3)	70(2)
C(11)	6121(6)	7215(7)	2793(3)	51(2)
C(12)	6956(5)	7266(6)	3259(2)	40(1)
C(13)	6179(5)	5529(5)	3858(2)	39(1)
C(14)	6504(5)	4925(5)	4425(2)	37(1)
C(15)	5819(6)	3972(6)	4652(3)	46(2)
C(16)	6148(6)	3444(6)	5178(3)	47(2)
C(17)	7187(6)	3893(6)	5452(3)	48(2)
C(18)	7851(6)	4853(5)	5204(3)	43(1)
N(5)	3830(5)	1323(5)	3185(3)	56(1)
C(51)	4872(11)	1853(12)	3560(5)	74(3)
C(52)	6156(17)	1373(19)	3469(8)	113(6)
C(53)	4047(15)	1913(15)	2575(7)	109(5)
C(54)	3097(17)	1811(18)	2136(8)	117(5)
C(55)	2619(11)	1714(11)	3443(5)	72(3)
C(56)	2389(13)	3095(12)	3493(6)	74(3)
C(57)	3947(15)	-48(14)	3112(7)	102(4)
C(58)	3872(17)	-777(18)	3610(8)	116(6)
C(61)	2930(4)	750(4)	2743(17)	119(13)
C(62)	2440(3)	1110(3)	2257(14)	89(9)
C(63)	5070(3)	1310(4)	2946(16)	109(11)
C(64)	6110(3)	1790(3)	3212(15)	89(10)
C(65)	3360(3)	2640(3)	3308(13)	79(8)
C(66)	1960(3)	2620(3)	3513(14)	80(9)
C(67)	3720(4)	550(4)	3723(19)	130(14)
C(68)	4300(3)	-530(3)	3915(13)	77(8)
O(3)	3973(10)	4715(12)	2517(5)	195(5)

least-square fit to 25 reflections in the range $9.35 \leq \theta \leq 13.94^\circ$. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The crystal and experimental data are given in Table 1. The crystal structure was determined by a direct method and Fourier techniques. All of the calculations were performed on an IBM Pentium computer using SHELXS-97³ and SHELXL-97.⁴ The atomic-scattering factors for all non-hydrogen atoms were supplied by SHELXS-97. The atomic coordinates for non-hydrogen atoms are listed in Table 2, and the bond distances and angles are listed in Table 3. All non-H atoms, except for carbon atoms of the disordered four ethyl groups in a cation, were refined anisotropically; H-atoms, except the water hydrogen atoms, were located geometrically and were refined isotropically with fixed displacement parameters. The molecular structure was drawn by the Ortep-3 for Windows program.⁵ The chemical diagram is shown in Fig. 1 and the structure is shown in Fig. 2.

Table 3 Selected bond lengths [$\text{\AA}$], angles [$^\circ$], and torsion angles [$^\circ$]

Co(1)-N(3)	1.868(4)	Co(1)-Cl(2)	2.2586(17)
Co(1)-N(2)	1.876(5)	Co(1)-Cl(1)	2.2631(17)
Co(1)-N(4)	1.981(4)	O(1)-C(6)	1.217(7)
Co(1)-N(1)	1.976(5)	O(2)-C(13)	1.227(7)
N(3)-Co(1)-N(2)	84.7(2)	N(4)-Co(1)-Cl(2)	89.23(14)
N(3)-Co(1)-N(4)	82.69(19)	N(1)-Co(1)-Cl(2)	90.00(14)
N(2)-Co(1)-N(4)	167.39(19)	N(3)-Co(1)-Cl(1)	91.79(15)
N(3)-Co(1)-N(1)	167.53(19)	N(2)-Co(1)-Cl(1)	92.46(16)
N(2)-Co(1)-N(1)	82.84(19)	N(4)-Co(1)-Cl(1)	88.57(14)
N(4)-Co(1)-N(1)	109.75(18)	N(1)-Co(1)-Cl(1)	87.77(14)
N(3)-Co(1)-Cl(2)	91.07(15)	Cl(2)-Co(1)-Cl(1)	176.15(7)
N(2)-Co(1)-Cl(2)	90.37(16)		
N(3)-Co(1)-N(1)-C(1)	169.5(8)		
N(2)-Co(1)-N(1)-C(1)	174.1(6)		
N(4)-Co(1)-N(1)-C(5)	178.1(4)		
Cl(1)-Co(1)-N(1)-C(1)	81.3(5)		
Cl(1)-Co(1)-N(2)-C(6)	92.6(5)		
Cl(1)-Co(1)-N(3)-C(12)	92.3(4)		
Cl(2)-Co(1)-N(1)-C(5)	88.9(4)		
Cl(2)-Co(1)-N(2)-C(7)	91.0(4)		
Cl(2)-Co(1)-N(3)-C(13)	90.9(4)		

The asymmetric unit contains a tetraethylammonium cation $[\text{Et}_4\text{N}]^+$, a $[\text{Co}(\text{bpb})\text{Cl}_2]^-$ anion, and one water solvent molecule in $P2_1/n$ with $Z = 4$. Four N atoms of the bpb²⁻ ligand and two chloro ligands are coordinated to the Co(III) atom. The two inner Co-N distances, 1.868(4) and 1.876(5) $\text{\AA}$, are somewhat shorter than the outer Co-N distances, 1.981(4) and 1.976(5) $\text{\AA}$. The Co-Cl distances are 2.2586(18) and 2.2631(17) $\text{\AA}$, and the Cl-Co-Cl angle is 176.15(7)°. The C-O distances of the bpb²⁻ ligand are 1.217(7) and 1.227(7) $\text{\AA}$. There are two disordered sets of ethyl groups in a tetraethylammonium cation with 70% and 30% occupancies for each set. The angles between the pyridine ring and the N1/N2/N3/N4 plane are 5.19(3) and 4.17(3)°. The coordination geometry of the Co atom is a distorted octahedral with long chloro axial ligands.

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