

Tris(8-quinolinolato-*N,O*)cobalt(III) ethanol solvate

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Received 21 February 2000

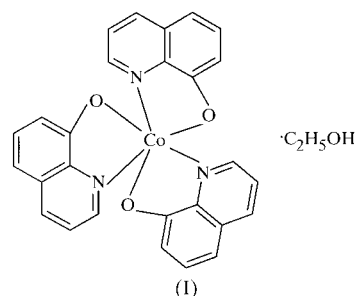
Accepted 3 March 2000

Data validation number: IUC0000064

In the crystal of the title complex, $[\text{Co}(\text{C}_9\text{H}_6\text{NO})_3] \cdot \text{C}_2\text{H}_5\text{OH}$, the central Co atom has a distorted octahedral coordination comprised of three N atoms and three O atoms from the three 8-quinolinolato ligands. The three Co—O bond distances are in the range 1.887 (2)–1.910 (2) Å, while the three Co—N bond distances range from 1.919 (2) to 1.934 (2) Å. The solvent ethanol molecule forms an intermolecular O—H...O hydrogen bonding with a quinolinolato ligand.

Comment

8-Quinolinol has been used widely as an extracting agent for transition metals and for the fluorescence analysis of group 3A elements as well as in the preparation of non-linear optical materials with second harmonic generation at high intensity and stability at room temperature (Sanz-Medel *et al.*, 1987; Sugiyama *et al.*, 1991; Kato *et al.*, 1988). Its complexes with transition metals have also found extensive applications. For example, bis(8-quinolinolato-*N,O*)nickel(II) $[\text{NiQ}_2]$ has been used as a free-resistant additive for olefin polymers and as a fungicide for leather (Uma & Krishnamurthi, 1984). Also, tris(8-quinolinolato)cobalt(III) has been synthesized and used to assist in the metal–ligand assignments which are further based on Zn labeling of the Zn complex and on the effects of metal ion substitution in relation to expectations based on crystal field theory (Nakamoto & Ohkahu, 1971). Although the synthesis and characterization of the title complex, (I), have been discussed previously (Hollingshead, 1954; Engelter *et al.*, 1989; Cheng, 1983), its crystal structure, to our knowledge, has not been reported.



In the 8-quinolinolato ligands, the absence of any unusually long bonds and the marginally longer carbonyl bonds (C1—O1 = 1.325 (4) Å, C10—O2 = 1.337 (3) Å and C19—O3 = 1.313 (4) Å *versus* 1.28 Å), shorter than the normal single bond in ether and alcohols (>1.4 Å), suggest that the delocalization extends over the entire molecule and will therefore withdraw more negative charge from the cation (Barton *et al.*, 1983). The three 8-quinolinol ligands are coordinated to the central Co atom by their O and N atoms, forming five-membered chelate rings. The Co^{III} atom has a slightly distorted octahedral coordination.

The structure of the title complex is very similar to that of tris(8-quinolinolato)chromium(III) (CrQ₃; Folting *et al.*, 1968) and tris(8-quinolinolato)manganese(III) (MnQ₃; Xiong & You, 1995). The Co—O bond distances in CoQ₃ [1.887 (2), 1.903 (2) and 1.910 (2) Å] are normal, slightly shorter than those in $[\text{Co}(\text{C}_5\text{H}_4\text{NOS})_3]$ [1.943 (7) Å; Xu *et al.*, 1995], and are in agreement with those of $[\text{Co}(\text{salpron})(\text{py})_3]$ [1.890 (4) Å; Zhu *et al.*, 1996]. Similarly, the Co—N bond distances [1.919 (2), 1.931 (2) and 1.934 (2) Å] are somewhat shorter than those in $[\text{Co}(\text{phen})(\text{pro})_2]^+$ [1.948 (3) Å; Ye *et al.*, 1994] and $[\text{Co}(\text{C}_4\text{H}_9(\text{salen})(\text{py}))]$ [1.967 (5) Å; Zhu *et al.*, 1996].

The mean chelate angles Co—O—C and Co—N—C [111.5 (2) and 110.3 (2)°, respectively] and the mean bite angle O—Co—N of 85.7 (1)° are close to those metal complexes of 8-hydroxyquinoline reported (Xiong & You, 1995; Xiong *et al.*, 1995; Folting *et al.*, 1968). The three chelate rings, Co1/O1/C1/C9/N1, Co1/O2/C10/C18/N2 and Co1/O3/C19/C27/N3 make dihedral angles of 87.1 (1), 86.9 (1) and 88.1 (1)°, respectively, with each other. Stereochemistry explains that this *cis* geometry of the ligands minimizes the stereochemical interference between the H atoms in the 2 and 4 positions of different ring systems.

The ethanol molecules do not take part in the coordination but involves in an O—H...O intermolecular hydrogen bond with one of the ligands; the donor and acceptor distance, O4...O2, is 2.777 (4) Å. The molecular packing is stabilized by C—H...O and C—H... π (Cg) interactions (Table 2).

Experimental

The title complex was prepared by mixing an aqueous solution of cobalt(II) acetate and 8-hydroxyquinoline with heating. The complex was collected by filtration, washed with water and dried over a night.

The deep red single crystals suitable for X-ray analysis were obtained by recrystallization from anhydrous ethanol solution.

Crystal data

[Co(C₉H₆NO)₃]₂·C₂H₆O
M_r = 537.44
 Monoclinic, *P*2₁/*n*
a = 11.2649 (1) Å
b = 13.1101 (2) Å
c = 16.6181 (3) Å
 β = 94.2249 (3)°
V = 2447.56 (6) Å³
Z = 4
D_x = 1.459 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 6862 reflections
 θ = 1.98–28.31°
 μ = 0.743 mm⁻¹
T = 293 (2) K
 Slab, black
 0.38 × 0.22 × 0.12 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
T_{min} = 0.765, *T_{max}* = 0.916
 16 823 measured reflections
 5957 independent reflections
 3727 reflections with *I* > 2σ(*I*)
R_{int} = 0.069
 θ_{max} = 28.27°
h = -14 → 9
k = -17 → 17
l = -22 → 21

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.055
wR (*F*²) = 0.147
S = 0.973
 5957 reflections
 334 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0709P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 $\Delta\rho_{max} = 0.56 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.77 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (°).

O1—C1—C9	117.2 (3)	N2—C18—C10	115.5 (3)
N1—C9—C1	114.8 (3)	O3—C19—C27	117.4 (3)
O2—C10—C18	116.7 (3)	N3—C27—C19	114.9 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

Cg1 is the centroid of the Co1/O3/C19/C27/N3 ring.

<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>
O4—H4B...O2	0.82	2.20	2.777 (4)	128
C4—H4A...O1 ⁱ	0.93	2.54	3.380 (4)	150
C24—H24A...O1 ⁱⁱ	0.93	2.59	3.390 (4)	145
C15—H15A...Cg1 ⁱⁱⁱ	0.93	2.58	3.496 (4)	168

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, -z$; (iii) $1 - x, 1 - y, 1 - z$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 1990).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 305/pfizik/622004. SSSR thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

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