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Aqua(*n*-pentyl)[3,3′-(propane-1,3-diyldinitrilo)bis-(butan-2-one) dioximato-κ^4N]cobalt(III) perchlorate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
Disorder in solvent or counterion
R factor = 0.066
wR factor = 0.189
Data-to-parameter ratio = 12.6

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

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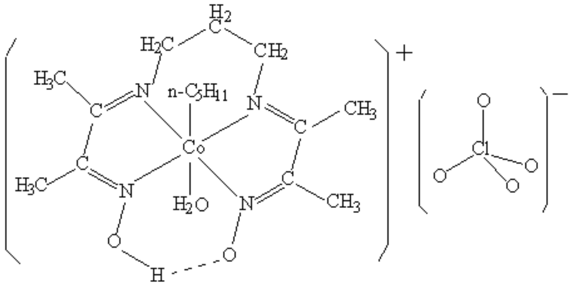
The title compound, $[Co(C_{11}H_{19}N_4O_2)(C_5H_{11})(H_2O)]ClO_4$, is one of the coenzyme B_{12} models with the equatorial ligand having the same −1 formal charge as B_{12} corrin. In the complex, the Co atom has a distorted octahedral coordination, with the *n*-pentyl and water ligands in axial positions.

Comment

As important coenzyme B_{12} models, several Costa-type organocobalt complexes, [LCo(DO–DOH-pn)R]X, where L = neutral base, DO–DOH-pn = 3,3′-(propane-1,3-diyldinitrilo)-bis(butan-2-one)dioximato, R = alkyl and X = anion group (PF_6^- or ClO_4^- *etc.*), have been reported (Finke *et al.*, 1983). However, only a few structures are available, especially with aqua as the axial ligand (Randaccio *et al.*, 1989). In this report, we describe the structure of the title compound, (I), with L = H_2O, R = pentyl and X = perchlorate.



(I)

The Co atom has a distorted octahedral coordination with the R and H_2O ligands in axial positions (Fig. 1). The four equatorial N atoms of the DO–DOH-pn ligand are coplanar within 0.004 Å, and the Co atom is displaced by 0.025 (6) Å from this mean plane towards the axial alkyl group. The two chemically equivalent halves of the equatorial macrocycle, with the exclusion of C6, have a dihedral angle of 6.3 (7)° and bend toward the aqua ligand. Compared with the complex having R = hexyl, which we have previously reported (Xiang *et al.*, 2000), the Co—C bond length is slightly shorter. The Co—C bond lengths are 1.993 (5) and 2.022 (5) Å for R = pentyl and hexyl, respectively. Other bond lengths and angles agree with those in related compounds (Zagrando *et al.*, 1987; Parker *et al.*, 1985; Marzilli *et al.*, 1985).

Experimental

The title compound was synthesized as described by Parker *et al.* (1985). A crystal suitable for X-ray diffraction was grown from an acetone–water solution in the dark under aerobic conditions.

Crystal data

$[Co(C_5H_{11})(C_{11}H_{19}N_4O_2)(H_2O)]ClO_4$
$M_r = 486.84$
Monoclinic, $P2_1/n$
$a = 17.761$ (4) Å
$b = 6.6774$ (13) Å
$c = 19.173$ (4) Å
$\beta = 96.91$ (2)°
$V = 2257.3$ (8) Å^3
$Z = 4$
$D_x = 1.433$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 60 reflections
$\theta = 5.3$–10.0°
$\mu = 0.92$ mm^{-1}
$T = 293$ (2) K
Prism, red
0.55 × 0.30 × 0.30 mm

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.641$, $T_{max} = 0.759$
5163 measured reflections
3956 independent reflections
2709 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 21$
$k = -1 \rightarrow 7$
$l = -22 \rightarrow 22$
3 standard reflections every 97 reflections intensity decay: 9.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.189$
$S = 1.04$
3956 reflections
313 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1023P)^2 + 2.2665P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N1	1.876 (4)	N2—C3	1.276 (7)
Co1—N4	1.880 (4)	N2—C5	1.461 (7)
Co1—N2	1.905 (4)	N3—C9	1.284 (7)
Co1—N3	1.908 (4)	N3—C7	1.464 (8)
Co1—C12	1.993 (5)	N4—C10	1.280 (7)
Co1—O1*W*	2.100 (3)	N4—O2	1.332 (6)
N1—C2	1.281 (7)	C5—C6	1.496 (9)
N1—O1	1.327 (5)	C6—C7	1.498 (9)
N1—Co1—N4	97.0 (2)	N3—Co1—C12	89.4 (2)
N1—Co1—N2	81.86 (19)	N1—Co1—O1*W*	87.62 (16)
N4—Co1—N2	178.32 (19)	N4—Co1—O1*W*	88.50 (17)
N1—Co1—N3	177.65 (18)	N2—Co1—O1*W*	90.19 (17)
N4—Co1—N3	81.4 (2)	N3—Co1—O1*W*	90.56 (17)
N2—Co1—N3	99.6 (2)	C12—Co1—O1*W*	179.6 (2)
N1—Co1—C12	92.4 (2)	N2—C5—C6	111.2 (5)
N4—Co1—C12	91.1 (2)	C5—C6—C7	115.0 (5)
N2—Co1—C12	90.2 (2)	N3—C7—C6	111.8 (5)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
O1*W*—H1*WA*$\cdots$O11^{i}	0.850 (10)	2.01 (2)	2.830 (13)	160 (4)
O2—H2$\cdots$O1	0.87 (17)	1.57 (7)	2.441 (12)	170 (6)
O1*W*—H1*WB*$\cdots$O14	0.849 (10)	1.95 (18)	2.788 (14)	168 (6)

Symmetry code: (i) $-x, 3 - y, 1 - z$.

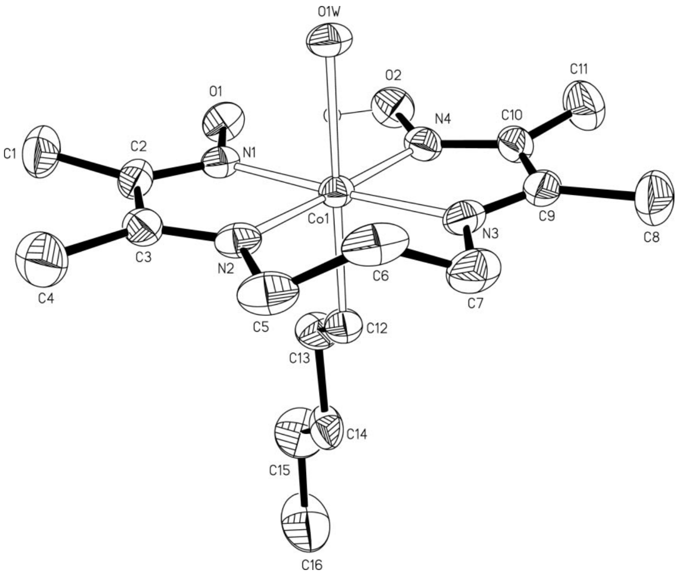


Figure 1
ORTEP drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The perchlorate anion shows an orientational disorder. The positional parameters of the O atoms were refined with Cl—O constrained to 1.43 (1) Å and O$\cdots$O to 2.32 (2) Å. The site-occupation factor of the O11—O14 atoms was refined using a free variable as 0.729 (11) and that of the O11′—O14′ atoms as 0.271 (11). The hydroxy and aqua H atoms were located from difference Fourier maps and were refined isotropically. The positional parameters of the other H atoms were calculated geometrically and were refined using a riding model.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1995); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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