

Aqua(*n*-hexyl)[3,3'-(propane-1,3-diyl-dinitrilo)bis(butan-2-one) dioximato- κ^4N]cobalt(III) perchlorate

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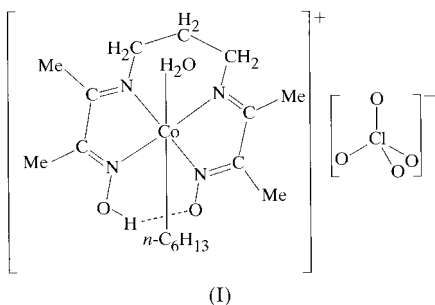
Received 22 July 1999

Accepted 22 December 1999

The title compound, $[\text{Co}(\text{C}_6\text{H}_{13})(\text{C}_{11}\text{H}_{19}\text{N}_4\text{O}_2)(\text{H}_2\text{O})]\text{ClO}_4$, is in the general class of coenzyme B₁₂ models which contain a ClO_4^- anion and a $[\text{Co}(\text{C}_6\text{H}_{13})(\text{C}_{11}\text{H}_{19}\text{N}_4\text{O}_2)(\text{H}_2\text{O})]^+$ cation. In the cation, the Co atom has a distorted octahedral coordination, with the *n*-hexyl and H_2O ligands in axial positions. The crystal data reveal some degree of flexibility in the Costa-type system, which is similar to the coenzyme B₁₂.

Comment

Costa-type organocobalt complexes, $[\text{LCo}\{(\text{DO})(\text{DOH})\text{pn}\}R]X$, where *L* is a neutral base, (DO)(DOH)pn is 3,3'-(propane-1,3-diyl)dinitrilo)bis(butan-2-one)dioximato, *R* is an alkyl group and *X* is an anion (PF_6^- , ClO_4^- etc.), exhibit many interesting properties and have been examined in detail as coenzyme B₁₂ models (Randaccio *et al.*, 1989). However, only a few structures of (aqua)alkyl Costa-type complexes (*R* = CH_3 , *X* = PF_6^- , etc.) are available (Marzilli *et al.*, 1985), and we report here the structural data for a new compound with *R* = *n*- C_6H_{13} , (I).



An ORTEP plot (Johnson, 1965) of the cation in (I), with the atom-numbering scheme, is shown in Fig. 1. The Co atom exhibits a distorted octahedral stereochemistry and the (DH)(DOH)pn ligand occupies four equatorial positions. The four equatorial N atoms are coplanar within 0.01 (4) Å, and

the Co atom is displaced by 0.033 (1) Å from this mean plane towards the axial alkyl group. The two chemically equivalent halves of the equatorial macrocycle, with the exclusion of C6, are approximately planar. These planes have a dihedral angle of 8.5 (2)° and bend towards the axial water group. The position of the central atom of the propylene bridge appears to be determined mainly by interaction with the axial ligands (Parker *et al.*, 1985). Other bond lengths and angles are in agreement with those in related compounds (Zangrando, Parker, Bresciani-Pahor *et al.*, 1987; Zangrando, Parker & Mezzetti, 1987; Parker *et al.*, 1985).

The oxime H atom takes part in a short intramolecular hydrogen bond linking the oxime O1 and O2 atoms. The H atoms of the water molecule form O—H...O hydrogen bonds with perchlorate O atoms. Details of the hydrogen bonding are given in Table 2.

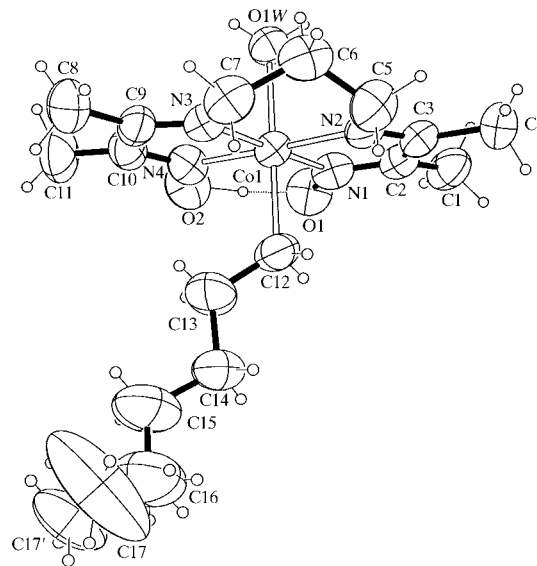


Figure 1

The molecular structure of the cation of (I) showing 30% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

Experimental

Compound (I) was prepared according to the method of 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

$[\text{Co}(\text{C}_6\text{H}_{13})(\text{C}_{11}\text{H}_{19}\text{N}_4\text{O}_2)(\text{H}_2\text{O})]\text{ClO}_4$
 $M_r = 500.86$
 Trigonal, $R\bar{3}$
 $a = 42.064$ (6) Å
 $b = 42.064$ (6) Å
 $c = 7.052$ (3) Å
 $V = 10\,806$ (5) Å³
 $Z = 18$

$D_x = 1.385$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 34 reflections
 $\theta = 5.25$ – 14.77°
 $\mu = 0.87$ mm⁻¹
 $T = 293$ (2) K
 Prism, red
 $0.8 \times 0.4 \times 0.4$ mm

Data collection

Siemens P4 diffractometer	$R_{\text{int}} = 0.032$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: empirical via ψ scan (North <i>et al.</i> , 1968)	$h = -1 \rightarrow 47$
$T_{\text{min}} = 0.687$, $T_{\text{max}} = 0.707$	$k = -50 \rightarrow 1$
4691 measured reflections	$l = 0 \rightarrow 8$
4077 independent reflections	3 standard reflections
2891 reflections with $I > 2\sigma(I)$	every 97 reflections intensity decay: 6.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2 + 52.947P]$
$R[F^2 > 2\sigma(F^2)] = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.183$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.025$	$\Delta\rho_{\text{max}} = 0.69 \text{ e } \text{\AA}^{-3}$
4077 reflections	$\Delta\rho_{\text{min}} = -0.41 \text{ e } \text{\AA}^{-3}$
298 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Co1—N1	1.882 (4)	N1—C2	1.299 (7)
Co1—N2	1.919 (4)	N2—C3	1.291 (6)
Co1—N3	1.914 (4)	N2—C5	1.464 (7)
Co1—N4	1.876 (4)	N3—C7	1.455 (7)
Co1—C12	2.023 (5)	N3—C9	1.289 (7)
Co1—O1W	2.116 (4)	N4—O2	1.330 (5)
N1—O1	1.337 (5)	N4—C10	1.298 (7)
N4—Co1—N1	97.5 (2)	N3—Co1—C12	90.8 (2)
N4—Co1—N3	81.31 (19)	N2—Co1—C12	89.3 (2)
N1—Co1—N3	177.83 (17)	N4—Co1—O1W	86.7 (2)
N4—Co1—N2	177.75 (18)	N1—Co1—O1W	87.86 (19)
N1—Co1—N2	81.39 (19)	N3—Co1—O1W	90.23 (18)
N3—Co1—N2	99.68 (18)	N2—Co1—O1W	91.29 (19)
N4—Co1—C12	92.7 (2)	C12—Co1—O1W	178.7 (2)
N1—Co1—C12	91.1 (2)		

The hydrogen-bonding H atoms H1, H1WA and H1WB were located from a difference Fourier map and refined isotropically. The remaining H atoms were treated as riding. The terminal methyl group of the hexyl ligand was found to be disordered over two positions,

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O2	1.15 (9)	1.31 (9)	2.443 (8)	167 (8)
O1W—H1WA \cdots O12	0.79 (7)	2.04 (7)	2.819 (8)	171 (8)
O1W—H1WB \cdots O14 ⁱ	0.75 (9)	2.20 (9)	2.940 (10)	166 (8)

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

C17 and C17'. These two atoms refined to occupancies of 0.31 (5) and 0.69 (5), respectively.

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: SHELXTL (Sheldrick, 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.

This research was supported by the National Nature Science Foundation of China (No. 29823001).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1502). Services for accessing these data are described at the back of the journal.

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