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[*N*,*N*′-Bis(1-benzoylethylidene)propylenediiminato(2−)]dipyrrolidinecobalt(III) perchlorate

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Key indicators

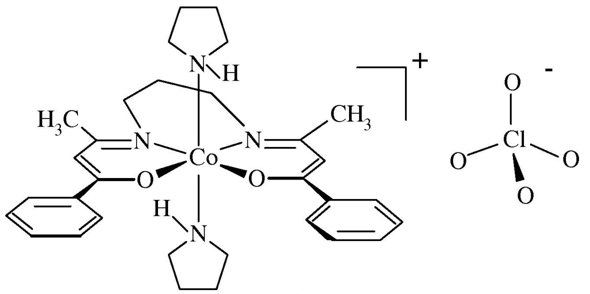
Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.005 Å
R factor = 0.050
wR factor = 0.120
Data-to-parameter ratio = 15.3

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

In the title compound, $[Co(C_{23}H_{24}N_2O_2)(C_4H_9N)_2]ClO_4$, the *N*,*N*′-bis(1-benzoylethylidene)propylenediimine dianion, $(BA)_2pn$, coordinates the Co^{III} ion in four equatorial positions and the two amine (pyrrolidine, prldn) molecules occupy the two axial positions. The Co^{III} ion has a slightly distorted octahedral coordination geometry. The N atoms of the pyrrolidine axial ligands are involved in hydrogen bonds with the O atoms of the perchlorate anions, forming chains along the *a* axis.

Comment

Quadridentate Schiff base cobalt complexes have been extensively used to mimic the cobalamine (B_{12}) coenzyme (Hirota *et al.*, 1998), as dioxygen carriers and oxygen activators (Yamada, 1999; Henson *et al.*, 1999), and in enantioselective reduction (Nagata *et al.*, 1995). Co^{III} Schiff base complexes with two amines in the axial positions have also been used as antimicrobial agents (Böttcher *et al.*, 1997). More recently the interest in the influence of steric and electronic factors of both the equatorial chelating Schiff base ligand and the axial amines on the stability and reaction kinetics of these complexes have been renewed (Dreos *et al.*, 2003; Amirnasr *et al.*, 2006). In continuation of our work in this field, here we report the X-ray structure of *trans*-$[Co\{(BA)_2pn\}(prldn)_2]ClO_4$, (I).



(I)

As shown in Fig. 1, the structure exhibits a distorted octahedral environment around cobalt, with the $(BA)_2pn$ ligand occupying the four equatorial positions. The Co—O1 and Co—O2 bond lengths of the $(BA)_2pn$ (Table 1) are nearly the same and are in agreement with those reported for *trans*-$[Co^{III}\{(BA)_2en\}(ta)_2]PF_6$, (II), [1.9004 (9) Å] (Amirnasr *et al.*, 2005). The Co—N1 and Co—N2 bonds of the $(BA)_2pn$, however, are considerably longer than the corresponding ones [1.901 (1) Å] in (II) (Amirnasr *et al.*, 2006), implying the existence of a greater steric hindrance in the $N(CH_2)_3N$ chelate ring relative to $N(CH_2)_2N$. The axial Co—N3 and Co—N4 bond lengths are in agreement with those reported for

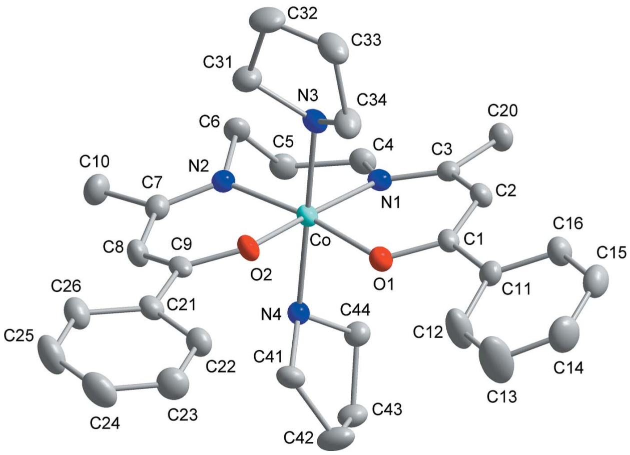


Figure 1
The molecular structure of the title compound, (I), with displacement ellipsoids drawn at 40% probability level. H atoms and perchlorate groups have been omitted for clarity.

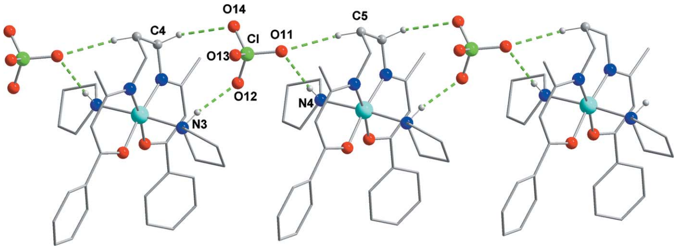


Figure 2
The extended chain structure of (I). The dashed lines denote hydrogen bonds.

trans-[Co^{III}(salophen)(prldn)$_2$]ClO_4 [salophen is the *N*,*N*′-disalicylidene-1,2-phenylenediamine dianion; 2.006 (2) and 2.004 (2) Å] (Amirnasr *et al.*, 2001).

The N—Co—O *trans* angles are indicative of a slight tetrahedral distortion of the equatorial coordination of Co^{III}; in the case of perfect planarity, they would have values of 180°. This distortion is also reflected by selected torsion angles of the coordinating ligand (Table 1) and the angle [2.90 (11)°] between the least-squares planes of Co/O1/C1—C3/N1 and Co/N2/C7—C9/O2.

The N atoms of both pyrrolidine axial ligands are involved in hydrogen bonds with the O atoms of the perchlorate anions, forming chains along the *a* axis (Table 2, Fig. 2). This behaviour has also been evidenced in the IR spectrum of the complex. The fairly broad band of medium intensity appearing at 1278 cm^{-1}, which corresponds to the intramolecular hydrogen bonding in the free ligand (Yamazaki & Hohokabe, 1971), is absent in the complex. The bands corresponding to the axial amine N—H stretching vibrations appear in the range 3200–3300 cm^{-1}. These bands, as expected, are shifted to lower frequencies by 150 cm^{-1} relative to the uncoordinated amine.

Experimental

Equimolar (0.5 mmol) quantities of cobalt(II) acetate tetrahydrate and the ligand $H_2(BA)_2pn$ [prepared according to the method of McCarthy *et al.* (1955)] were dissolved in methanol, pyrrolidine (1.5 mmol) was added to the solution and air was bubbled slowly through the reaction mixture for 3 h. Solid $NaClO_4$ (0.5 mmol) was then added to the resulting clear red solution, which was stirred for 5 min. The solution was filtered and the filtrate was left undisturbed to give dark red-brown crystals of the complex (yield 0.250 g, 76%, m.p. 443 K) suitable for X-ray crystallography.

Crystal data

[$Co(C_{23}H_{24}N_2O_2)(C_4H_9N)_2$]$ClO_4$
M_r = 661.07
Monoclinic, $P2_1/c$
a = 9.323 (2) Å
b = 13.355 (1) Å
c = 25.701 (1) Å
β = 101.030 (2)°
V = 3140.9 (7) Å^3
Z = 4

D_x = 1.398 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7739 reflections
θ = 1–25°
μ = 0.68 mm^{-1}
T = 183 (2) K
Rectangular prism, dark red-brown
0.34 × 0.08 × 0.04 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.855, T_{max} = 0.977
30114 measured reflections

5948 independent reflections
3975 reflections with $I > 2\sigma(I)$
R_{int} = 0.119
θ_{max} = 25.8°
$h = -11 \rightarrow 11$
$k = -16 \rightarrow 16$
$l = -31 \rightarrow 31$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.120
S = 1.03
5948 reflections
390 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 2.0135P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co—O1	1.897 (2)	Co—N1	1.991 (2)
Co—O2	1.903 (2)	Co—N4	2.006 (3)
Co—N2	1.937 (3)	Co—N3	2.007 (3)
O1—Co—O2	81.48 (9)	N2—Co—N4	90.33 (11)
O1—Co—N2	172.06 (10)	N1—Co—N4	93.11 (10)
O2—Co—N2	91.66 (10)	O1—Co—N3	92.32 (10)
O1—Co—N1	91.83 (9)	O2—Co—N3	86.44 (10)
O2—Co—N1	172.16 (10)	N2—Co—N3	91.23 (11)
N2—Co—N1	95.28 (10)	N1—Co—N3	89.77 (10)
O1—Co—N4	85.76 (10)	N4—Co—N3	176.59 (10)
O2—Co—N4	90.48 (10)		
N1—C3—C2—C1	10.0 (5)	N1—C4—C5—C6	46.6 (4)
O1—C1—C2—C3	−9.1 (5)	N2—C6—C5—C4	−83.8 (3)
N2—C7—C8—C9	9.8 (5)	O1—C1—C11—C16	−169.2 (3)
O2—C9—C8—C7	−10.1 (5)	O2—C8—C21—C26	163.2 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O12^i	0.93	2.08	2.975 (3)	161
N4—H4···O11	0.93	2.16	3.058 (3)	161
C4—H4*B*···O14^i	0.99	2.53	3.466 (4)	158
C5—H5*A*···O11	0.99	2.51	3.422 (4)	153

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

An attempt to determine the structure from room-temperature data was unsuccessful because of dynamic disorder, reflected in high displacement parameters. Cooling at and below 173 K results in cracking of crystals. By careful examination in the range 173–223 K, a more satisfactory result was obtained at 183 K.

H atoms were positioned geometrically [0.93 (NH), 0.95 (CH), 0.99 (CH_2) and 0.98 Å (CH_3)] and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2 (1.5 methyl) U_{eq}(C/N).

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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