

(1,4,7,10,13-Pentamethyl-1,4,7,10,13-pentaazacyclopentadecane- κ^5N)cobalt(II) perchlorate**Feng Zhang,^a Jian-Rong Zhang,^a Dao-Li Deng^{a*} and Ronald Hage^b**^aUnilever Research China, 99 Tianzhou Road, Shanghai 200233, People's Republic of China, and ^bUnilever R&D Vlaardingen, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands

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Key indicators

Single-crystal X-ray study

 $T = 293\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.011\text{ \AA}$ R factor = 0.052 wR factor = 0.061

Data-to-parameter ratio = 8.2

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

The title compound, $[\text{Co}(\text{C}_{15}\text{H}_{35}\text{N}_5)](\text{ClO}_4)_2$, conventionally abbreviated $[\text{Co}(\text{Me}_5\text{PACP})](\text{ClO}_4)_2$, where Me_5PACP is 1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane, displays a significantly distorted trigonal-bipyramidal coordination geometry. The bond lengths and distances are comparable to those previously reported for cobalt(II) complexes with macrocyclic polyamine ligands. The $\text{N}-\text{Co}-\text{N}$ angle for the axial sites is $160.4(2)^\circ$. The perchlorate anions are not coordinated.

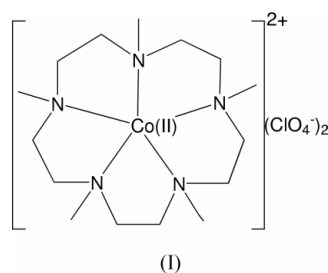
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Comment

Transition metal complexes with macrocyclic ligands are of significant interest for oxidation catalysis. Manganese and iron complexes with macrocyclic ligands have received considerable attention (Hage *et al.*, 1994; Hubin *et al.*, 2000). Manganese complexes with pentaazamacrocyclic ligands show very high superoxide dismutase activity, as discovered by Riley & Weiss (1994). However, less attention has been paid to Co^{II} complexes with polyamine macrocyclic ligands as oxidation catalysts. The report that $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was found to have significant bleaching/oxidation activity with hydrogen peroxide (Diakun & Wright, 1989) aroused our interest in the study of other Co-polyamine complexes as oxidation catalysts. The macrocyclic ligand 1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane has five potential donor N atoms, which can afford stable Co^{II} complexes.



The molecular structure of (I) is illustrated in Fig. 1. Three N atoms (N2, N4 and N5) of Me_5PACP form a trigonal plane, with the Co^{II} atom at its center, while the other two N atoms (N1 and N3) occupy the axial positions, completing the trigonal-bipyramidal coordination geometry around the Co^{II} atom. The $\text{Co}-\text{N}$ distances of 2.220 (5) and 2.228 (5) Å in the axial directions are significantly longer than the $\text{Co}-\text{N}$ distances in the equatorial plane, which are 2.095 (5), 2.101 (5) and 2.151 (5) Å (Table 1). The bond lengths and distances are comparable to those previously reported for cobalt(II) complexes with macrocyclic polyamine ligands (Kueppers *et al.*, 1986; Hubin *et al.*, 2002). The $\text{N}-\text{Co}-\text{N}$ angles in the

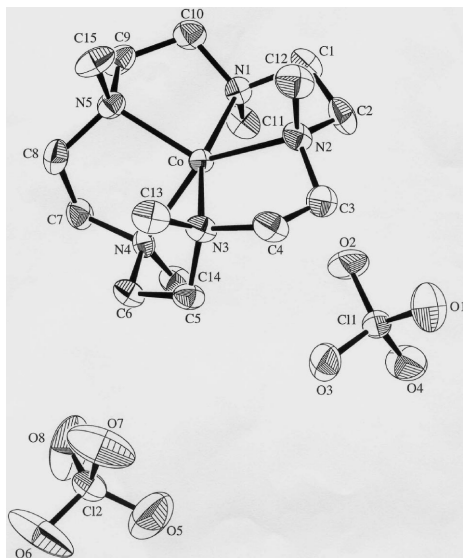


Figure 1
The asymmetric unit of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms have been omitted for clarity.

equatorial plane are 142.1 (2), 133.4 (2) and 84.6 (2)°, indicating a highly distorted trigonal-bipyramidal coordination geometry (Bhattacharyya *et al.*, 2000; Hubin *et al.*, 2002). The N1–Co–N3 angle for the axial positions is 160.4 (2)°, deviating significantly from the ideal 180°. A similar deviation was reported for another cobalt(II) complex having a trigonal-bipyramidal coordination geometry with two apical N atoms linked to the same equatorial N atom (Britovsek *et al.*, 1999). This observed distortion might be due to the CH₂CH₂ link between the neighboring N atoms, which form five-membered chelate rings. The N–Co–N angles in the five-membered rings [80.1 (2)–84.6 (2)°] are similar to those previously reported (Kueppers *et al.*, 1986; Hubin *et al.*, 2002). Of the angles not in the five-membered rings, those in the equatorial plane [142.1 (2) and 133.4 (2)°] are much larger than those between the axial N atoms and equatorial N atoms [110.9 (2) and 114.1 (2)°].

This single-crystal structure analysis confirms that (I) is an ionic compound, with [Co(Me₅PACP)]²⁺ cations and uncoordinated ClO₄[−] anions. The shortest Co···Co distance is 9.14 (1) Å.

Experimental

1,4,7,10,13-Pentamethyl-1,4,7,10,13-pentaazacyclopentadecane was prepared according to a reported procedure (Barefield & Wagner, 1973; Coates & Lincoln, 1982). The title compound, (I), was obtained when Co(ClO₄)₂·6H₂O (900 mg, 2.46 mmol), dissolved in water (3 ml), was added to a solution of 1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane (420 mg, 1.47 mmol) in water (4 ml). The resulting red solid was filtered off, washed with a little water, and vacuum dried (yield: 60%, 480 mg). Analysis calculated for C₁₅H₃₅Cl₂CoN₅O₈: C 33.20, H 6.50, N 12.90%; found: C 33.11, H 6.60, N 12.98%. Red crystals suitable for X-ray diffraction analysis were obtained from the filtrate after standing at 277 K for several days. Crystals can also be obtained by recrystallization from water.

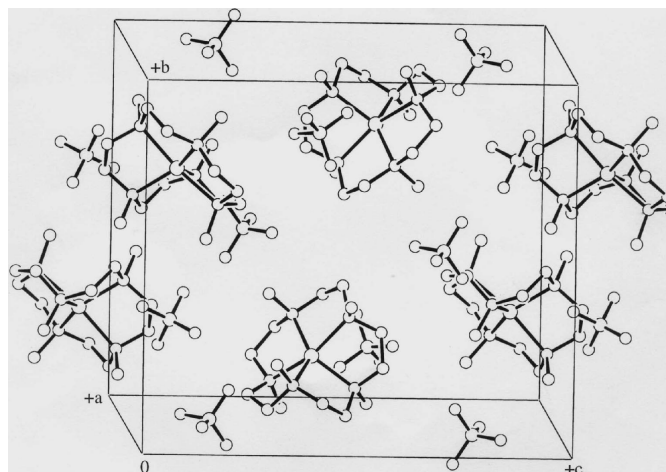


Figure 2
A packing view of the title complex.

Crystal data

[Co(C₁₅H₃₅N₅)](ClO₄)₂
M_r = 543.31
 Monoclinic, *P*2₁/*n*
a = 9.451 (2) Å
b = 15.294 (4) Å
c = 17.049 (4) Å
 β = 98.47 (2)°
V = 2437.0 (10) Å³
Z = 4

D_x = 1.480 Mg m^{−3}
 Mo Kα radiation
 Cell parameters from 20 reflections
 θ = 13.7–21.1°
 μ = 0.97 mm^{−1}
T = 293 K
 Prism, red
 0.30 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-7R diffractometer
 ω/2θ scans
 Absorption correction: ψ scan
 (TEXSAN; Molecular Structure Corporation, 1989)
T_{min} = 0.79, *T_{max}* = 0.82
 4450 measured reflections
 4165 independent reflections
 2297 reflections with *I* > 3σ(*I*)

R_{int} = 0.031
 θ_{max} = 25.0°
h = 0 → 10
k = 0 → 18
l = −20 → 20
 3 standard reflections every 200 reflections
 intensity decay: 2.9%

Refinement

Refinement on *F*²
R = 0.052
wR = 0.061
S = 1.75
 2297 reflections
 280 parameters

H-atom parameters not refined
w = 1/[σ²(*F_o*)]
 (Δ/σ)_{max} = 0.005
 Δρ_{max} = 0.70 e Å^{−3}
 Δρ_{min} = −0.37 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Co–N1	2.220 (5)	N2–C12	1.476 (10)
Co–N2	2.101 (5)	N3–C4	1.495 (9)
Co–N3	2.228 (5)	N3–C5	1.477 (8)
Co–N4	2.151 (5)	N3–C13	1.464 (9)
Co–N5	2.095 (5)	N4–C6	1.483 (8)
N1–C1	1.493 (9)	N4–C7	1.470 (8)
N1–C10	1.464 (9)	N4–C14	1.479 (8)
N1–C11	1.474 (8)	N5–C8	1.489 (9)
N2–C2	1.494 (9)	N5–C9	1.497 (9)
N2–C3	1.486 (9)	N5–C15	1.482 (9)
N1–Co–N2	80.1 (2)	N2–Co–N4	142.1 (2)
N1–Co–N3	160.4 (2)	N2–Co–N5	133.4 (2)
N1–Co–N4	110.9 (2)	N3–Co–N4	82.2 (2)
N1–Co–N5	82.6 (2)	N3–Co–N5	114.1 (2)
N2–Co–N3	80.7 (2)	N4–Co–N5	84.6 (2)

H atoms were positioned geometrically, with C–H = 0.93–1.01 Å, and were not refined; $U_{\text{iso}}(\text{H})$ values were set at 0.0715 Å².

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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