

N(5)	0.3331 (7)	0.9725 (4)	0.20088 (25)	5.1 (3)
N(6)	0.6161 (6)	0.4568 (4)	0.10608 (21)	4.2 (3)
N(7)	0.9095 (5)	0.4062 (4)	0.09751 (20)	3.79 (24)
N(8)	0.8139 (6)	0.2169 (4)	0.13201 (21)	4.2 (3)
N(9)	0.5486 (6)	0.2725 (4)	0.11643 (21)	4.3 (3)
N(10)	0.7063 (6)	0.3018 (5)	0.01845 (21)	5.0 (3)
N(11)	0.8189 (7)	0.3542 (5)	0.22486 (23)	5.4 (3)
N(12)	0.0933 (7)	0.1720 (6)	-0.0194 (3)	5.3 (4)
C(1)	0.4343 (8)	0.9465 (5)	0.0690 (3)	4.8 (3)
C(2)	0.2919 (8)	0.9536 (5)	0.0389 (3)	4.7 (3)
C(3)	0.1762 (7)	0.9727 (5)	0.0745 (3)	4.2 (3)
C(4)	0.0219 (7)	0.9128 (6)	0.1365 (3)	4.4 (3)
C(5)	-0.0340 (7)	0.8290 (6)	0.1640 (3)	4.9 (4)
C(6)	0.0539 (7)	0.7977 (6)	0.2123 (3)	4.9 (4)
C(7)	0.2763 (7)	0.7289 (5)	0.2454 (3)	4.1 (3)
C(8)	0.4122 (7)	0.6985 (5)	0.2260 (3)	4.2 (3)
C(9)	0.5748 (7)	0.7574 (6)	0.1616 (3)	4.5 (3)
C(10)	0.5842 (6)	0.8433 (6)	0.1272 (3)	4.8 (4)
C(11)	0.3416 (7)	0.9865 (5)	0.2458 (3)	4.1 (3)
C(12)	0.6489 (10)	0.5334 (6)	0.0706 (3)	5.5 (4)
C(13)	0.7932 (11)	0.5650 (6)	0.0806 (3)	6.1 (5)
C(14)	0.8992 (9)	0.4934 (6)	0.0652 (3)	5.4 (4)
C(15)	1.0223 (7)	0.3456 (7)	0.0802 (3)	5.5 (4)
C(16)	1.0516 (8)	0.2606 (7)	0.1138 (3)	5.9 (4)
C(17)	0.9435 (9)	0.1841 (6)	0.1109 (3)	5.8 (4)
C(18)	0.7066 (10)	0.1447 (5)	0.1311 (3)	5.4 (4)
C(19)	0.5790 (9)	0.1900 (6)	0.1493 (3)	5.5 (4)
C(20)	0.4547 (8)	0.3416 (7)	0.1357 (3)	5.7 (4)
C(21)	0.4684 (8)	0.4286 (7)	0.1037 (3)	5.7 (4)
C(22)	0.7281 (6)	0.3238 (4)	-0.02313 (23)	3.1 (3)
C(23)	0.7651 (7)	0.4240 (6)	0.23091 (24)	4.1 (3)
C(24)	0.1829 (13)	0.1918 (6)	-0.0093 (3)	6.3 (6)

Table 2. Selected geometric parameters (Å, °)

Cu(1)—N(1)	2.041 (5)	N(2)—C(4)	1.494 (8)
Cu(1)—N(2)	2.011 (5)	N(3)—C(6)	1.473 (9)
Cu(1)—N(3)	2.050 (5)	N(3)—C(7)	1.480 (8)
Cu(1)—N(4)	2.025 (5)	N(4)—C(8)	1.467 (9)
Cu(1)—N(5)	2.292 (6)	N(4)—C(9)	1.481 (8)
Cu(2)—N(6)	2.016 (6)	N(5)—C(11)	1.16 (1)
Cu(2)—N(7)	2.010 (5)	N(6)—C(12)	1.47 (1)
Cu(2)—N(8)	2.023 (6)	N(6)—C(21)	1.48 (1)
Cu(2)—N(9)	2.038 (6)	N(7)—C(14)	1.48 (1)
Cu(2)—N(10)	2.182 (5)	N(7)—C(15)	1.49 (1)
S(1)—C(11)	1.641 (8)	N(8)—C(17)	1.48 (1)
S(2)—C(22)	1.631 (6)	N(8)—C(18)	1.46 (1)
S(3)—C(23)	1.615 (8)	N(9)—C(19)	1.45 (1)
S(4)—C(24)	1.73 (1)	N(9)—C(20)	1.45 (1)
N(1)—C(1)	1.467 (9)	N(10)—C(22)	1.142 (8)
N(1)—C(10)	1.488 (8)	N(11)—C(23)	1.13 (1)
N(2)—C(3)	1.483 (8)	N(12)—C(24)	0.93 (2)
N(1)—Cu(1)—N(2)	95.3 (2)	C(3)—N(2)—C(4)	108.6 (5)
N(1)—Cu(1)—N(3)	154.5 (2)	Cu(1)—N(3)—C(6)	117.1 (4)
N(1)—Cu(1)—N(4)	84.4 (2)	Cu(1)—N(3)—C(7)	107.3 (4)
N(1)—Cu(1)—N(5)	100.6 (2)	C(6)—N(3)—C(7)	112.2 (5)
N(2)—Cu(1)—N(3)	95.8 (2)	Cu(1)—N(4)—C(8)	109.2 (4)
N(2)—Cu(1)—N(4)	176.9 (2)	Cu(1)—N(4)—C(9)	108.0 (4)
N(2)—Cu(1)—N(5)	94.0 (2)	C(8)—N(4)—C(9)	116.8 (5)
N(3)—Cu(1)—N(4)	83.4 (2)	Cu(1)—N(5)—C(11)	132.6 (6)
N(3)—Cu(1)—N(5)	101.5 (2)	Cu(2)—N(6)—C(12)	116.1 (5)
N(4)—Cu(1)—N(5)	89.1 (2)	Cu(2)—N(6)—C(21)	107.4 (5)
N(6)—Cu(2)—N(7)	94.5 (2)	C(12)—N(6)—C(21)	115.6 (6)
N(6)—Cu(2)—N(8)	153.1 (2)	Cu(2)—N(7)—C(14)	114.4 (4)
N(6)—Cu(2)—N(9)	83.8 (3)	Cu(2)—N(7)—C(15)	113.8 (5)
N(6)—Cu(2)—N(10)	103.7 (2)	C(14)—N(7)—C(15)	109.4 (6)
N(7)—Cu(2)—N(8)	95.8 (2)	Cu(2)—N(8)—C(17)	117.2 (5)
N(7)—Cu(2)—N(9)	172.6 (2)	Cu(2)—N(8)—C(18)	108.7 (5)
N(7)—Cu(2)—N(10)	94.4 (2)	C(17)—N(8)—C(18)	113.5 (6)
N(8)—Cu(2)—N(9)	82.8 (3)	Cu(2)—N(9)—C(19)	109.5 (5)
N(8)—Cu(2)—N(10)	100.3 (2)	Cu(2)—N(9)—C(20)	109.1 (5)
N(9)—Cu(2)—N(10)	93.0 (2)	C(19)—N(9)—C(20)	116.7 (6)
Cu(1)—N(1)—C(1)	116.0 (4)	Cu(2)—N(10)—C(22)	146.2 (6)
Cu(1)—N(1)—C(10)	106.4 (4)	N(6)—C(12)—C(13)	111.7 (6)
C(1)—N(1)—C(10)	113.4 (5)	S(2)—C(22)—N(10)	179.4 (6)
Cu(1)—N(2)—C(3)	114.5 (4)	S(3)—C(23)—N(11)	178.0 (7)
Cu(1)—N(2)—C(4)	112.3 (4)	S(4)—C(24)—N(12)	175.4 (9)

The authors thank the National Science Council for support under grants NSC82-0208-M007-119 and NSC82-0208-M007-32. They are also indebted to Ms Shu-Fang Tung for collecting the X-ray diffraction data.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71313 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1033]

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*Acta Cryst.* (1993). **C49**, 1910–1912

## Structure of meso-Chloro(1,4,7,11,14-pentaazacycloheptadecane)cobalt(III) Chloride Perchlorate

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(Received 8 September 1992; accepted 23 April 1993)

## Abstract

The coordination geometry about the Co<sup>III</sup> ion in the title compound, chloro[(1*RS*,7*SR*,11*SR*,14*RS*)-1,4,7-,11,14-pentaazacycloheptadecane]cobalt(III) chloride perchlorate, is distorted square bipyramidal with four tetraamine N atoms equatorial and a Cl and an N atom axial. The equatorial N atoms are nearly coplanar with the largest deviation from the least-squares plane of 0.018 Å; the deviation of the Co<sup>III</sup> ion from the plane is 0.039 Å. Both six-membered

rings are in chair forms and all three five-membered rings in *gauche* forms. The configuration of the chiral N centres is (1*RS*, 7*SR*, 11*SR*, 14*RS*).

### Comment

The coordination of 1,4,7,11,14-pentaazacycloheptadecane to the cobalt(III) ion can result in a number of isomeric forms. The crystal structure of one of the two isolated isomers, *rac*-bromo(1,4,7,11,14-pentaazacycloheptadecane)cobalt(III) tetrabromozincate, has been reported (Eigenbrot, Osvath, Lappin, Curtis & Weatherburn, 1988). The crystal structure of the other isomer is reported in this paper.

The ligand 1,4,7,11,14-pentaazacycloheptadecane pentahydrochloride was prepared by the literature method (Bencini, Fabbri & Poggi, 1981). Cobalt chloride hexahydrate (0.50 g, 2.1 mmol), the ligand (0.85 g, 2.0 mmol) and sodium hydroxide (0.42 g, 10.5 mmol) were dissolved in water by warming and air was bubbled through the solution. 2 ml of concentrated hydrochloric acid was added to the solution. The reddish brown solution was treated with a saturated aqueous solution of sodium perchlorate and allowed to stand for several days whereupon brown crystals were formed.

The Co<sup>III</sup> ion is in a nearly octahedral environment formed by one Cl<sup>-</sup> ion and five N atoms of the macrocyclic ligand. The macrocyclic ligand is coordinated in a configuration with six-, five- and six-membered chelate rings in the equatorial plane; according to Hay's scheme (Hay, Bembi, McLaren & Moodie, 1984), this is a 3,2,3 configuration. The N(1)

and N(5) atoms have opposite chirality giving the *meso-anti* diastereoisomer. The configurations of the four chiral amine N centres are 1*RS*, 7*SR*, 11*SR* and 14*RS*. The conformation of the ligand is the most stable; both six-membered rings are in chair forms and all three five-membered rings in *gauche* forms.

### Experimental

#### Crystal data

[CoCl(C<sub>12</sub>H<sub>29</sub>N<sub>5</sub>)](ClO<sub>4</sub>)Cl

*M<sub>r</sub>* = 472.687

Monoclinic

*P*2<sub>1</sub>/*n*

*a* = 12.532 (2) Å

*b* = 13.000 (2) Å

*c* = 12.686 (4) Å

β = 110.91 (2)°

*V* = 1930.7 (7) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.626 Mg m<sup>-3</sup>

Mo Kα radiation

λ = 0.7093 Å

Cell parameters from 25 reflections

θ = 8.08–19.53°

μ = 1.33 mm<sup>-1</sup>

*T* = 298 (3) K

Parallelepiped

0.37 × 0.35 × 0.26 mm

Deep red-brown

#### Data collection

Enraf-Nonius CAD-4 diffractometer

θ/2θ scans

Absorption correction:

empirical based on ψ

scans (North, Phillips &

Mathews, 1968)

*T<sub>min</sub>* = 0.73876, *T<sub>max</sub>* =

0.74107

5851 measured reflections

5621 independent reflections

4132 observed reflections

[*I* ≥ 2.5σ(*I*)]

*R<sub>int</sub>* = 0.01

θ<sub>max</sub> = 29.9°

*h* = -17 → 16

*k* = 0 → 18

*l* = 0 → 17

3 standard reflections

frequency: 60 min

intensity variation: ±0.8%

#### Refinement

Refinement on *F*

Final *R* = 0.037

*wR* = 0.037

*S* = 0.99

4132 reflections

256 parameters

Only H-atom *U*'s refined

Unit weights applied

(Δ/σ)<sub>max</sub> = 0.217

Δρ<sub>max</sub> = 0.69 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.58 e Å<sup>-3</sup>

Secondary-extinction correc-

tion: Zachariasen (1968)

Extinction coefficient:

0.03 (1)

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Non-H atoms were solved by direct and Fourier methods and refined by full-matrix least squares. H atoms were solved by a difference Fourier method. Program used: *NRCVAX* (Gabe, Le Page, White & Lee, 1987).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

*B<sub>eq</sub>* is the mean of the principal axes of the thermal ellipsoid.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
Co	0.97594 (3)	0.79660 (3)	0.19474 (3)	1.857 (12)
Cl(1)	0.83698 (6)	0.87141 (6)	0.05031 (6)	3.16 (3)
Cl(2)	0.42849 (7)	0.83456 (7)	0.16874 (7)	3.81 (4)
Cl(3)	0.72557 (7)	0.59577 (6)	-0.00012 (6)	3.71 (3)

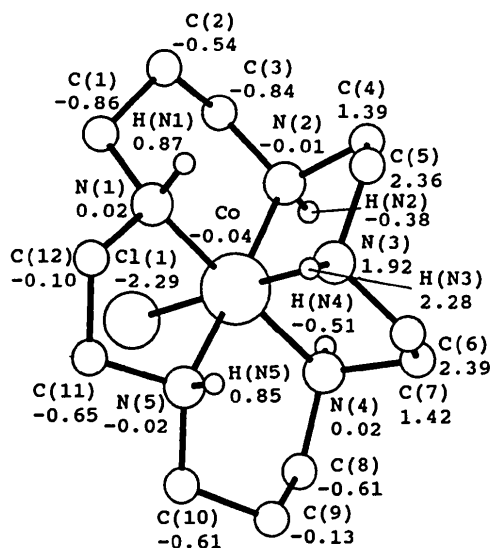


Fig. 1. A perspective view of the title molecule with the numbering scheme. The deviations of atoms from the least-squares plane of the four equatorial N atoms are shown.

O(1)	0.5304 (2)	0.8785 (3)	0.2441 (3)	6.58 (17)
O(2)	0.3785 (3)	0.8951 (4)	0.0729 (3)	9.7 (3)
O(3)	0.3536 (3)	0.8199 (5)	0.2236 (3)	13.4 (4)
O(4)	0.4612 (5)	0.7444 (3)	0.1297 (4)	12.4 (4)
N(1)	1.1017 (2)	0.8682 (2)	0.16232 (19)	2.88 (10)
N(2)	0.98244 (18)	0.67856 (18)	0.09676 (17)	2.43 (9)
N(3)	1.08888 (17)	0.72071 (17)	0.31866 (17)	2.19 (8)
N(4)	0.85698 (17)	0.72154 (19)	0.23436 (18)	2.45 (9)
N(5)	0.9799 (2)	0.91656 (18)	0.29255 (19)	2.73 (9)
C(1)	1.0973 (3)	0.8700 (3)	0.0445 (3)	3.78 (15)
C(2)	1.1012 (3)	0.7642 (3)	-0.0004 (3)	4.04 (16)
C(3)	0.9968 (3)	0.7010 (3)	-0.0124 (2)	3.50 (14)
C(4)	1.0638 (3)	0.5983 (2)	0.1638 (2)	3.05 (12)
C(5)	1.1477 (2)	0.6444 (2)	0.2714 (2)	2.88 (11)
C(6)	1.0309 (2)	0.6744 (2)	0.3916 (2)	2.82 (11)
C(7)	0.9131 (3)	0.6396 (3)	0.3198 (3)	3.15 (12)
C(8)	0.7705 (2)	0.7816 (3)	0.2639 (3)	3.63 (15)
C(9)	0.8214 (3)	0.8601 (3)	0.3547 (3)	4.11 (16)
C(10)	0.8763 (3)	0.9474 (3)	0.3161 (3)	4.02 (15)
C(11)	1.0216 (3)	1.0059 (2)	0.2446 (3)	3.85 (15)
C(12)	1.1217 (3)	0.9730 (3)	0.2157 (3)	3.76 (14)

Table 2. Selected bond lengths (Å) and angles (°)

Co—Cl(1)	2.249 (1)	N(4)—C(7)	1.504 (4)
Co—N(1)	1.995 (2)	N(4)—C(8)	1.488 (4)
Co—N(2)	1.995 (2)	N(5)—C(10)	1.488 (4)
Co—N(3)	1.965 (2)	N(5)—C(11)	1.489 (4)
Co—N(4)	1.991 (2)	C(1)—C(2)	1.496 (5)
Co—N(5)	1.982 (2)	C(2)—C(3)	1.505 (5)
N(1)—C(1)	1.476 (4)	C(4)—C(5)	1.518 (4)
N(1)—C(12)	1.502 (4)	C(6)—C(7)	1.502 (4)
N(2)—C(3)	1.488 (4)	C(8)—C(9)	1.501 (5)
N(2)—C(4)	1.494 (4)	C(9)—C(10)	1.497 (6)
N(3)—C(5)	1.484 (4)	C(11)—C(12)	1.490 (5)
N(3)—C(6)	1.492 (4)		
Cl(1)—Co—N(1)	93.96 (7)	Co—N(3)—C(5)	109.4 (2)
Cl(1)—Co—N(2)	90.97 (7)	Co—N(3)—C(6)	109.1 (2)
Cl(1)—Co—N(3)	175.06 (7)	C(5)—N(3)—C(6)	113.8 (2)
Cl(1)—Co—N(4)	89.18 (7)	Co—N(4)—C(7)	109.2 (2)
Cl(1)—Co—N(5)	90.51 (7)	Co—N(4)—C(8)	119.0 (2)
N(1)—Co—N(2)	91.1 (1)	C(7)—N(4)—C(8)	112.7 (2)
N(1)—Co—N(3)	90.2 (1)	Co—N(5)—C(10)	120.6 (2)
N(1)—Co—N(4)	176.85 (9)	Co—N(5)—C(11)	107.0 (2)
N(1)—Co—N(5)	85.2 (1)	C(10)—N(5)—C(11)	109.3 (3)
N(2)—Co—N(3)	86.24 (9)	N(1)—C(1)—C(2)	112.1 (3)
N(2)—Co—N(4)	88.91 (9)	C(1)—C(2)—C(3)	113.3 (3)
N(2)—Co—N(5)	176.2 (1)	N(2)—C(3)—C(2)	113.7 (2)
N(3)—Co—N(4)	86.70 (9)	N(2)—C(4)—C(5)	110.4 (2)
N(3)—Co—N(5)	92.54 (9)	N(3)—C(5)—C(4)	110.1 (2)
N(4)—Co—N(5)	94.7 (1)	N(3)—C(6)—C(7)	109.6 (2)
Co—N(1)—C(1)	118.0 (2)	N(4)—C(7)—C(6)	109.2 (2)
Co—N(1)—C(12)	110.3 (2)	N(4)—C(8)—C(9)	113.7 (2)
C(1)—N(1)—C(12)	112.5 (3)	C(8)—C(9)—C(10)	112.5 (3)
Co—N(2)—C(3)	118.4 (2)	N(5)—C(10)—C(9)	113.4 (3)
Co—N(2)—C(4)	110.7 (2)	N(5)—C(11)—C(12)	109.0 (3)
C(3)—N(2)—C(4)	112.4 (2)	N(1)—C(12)—C(11)	110.6 (2)

The authors thank the National Science Council for support under grants NSC81-0208-M007-110 and NCS81-0208-M007-86. They are also indebted to Ms Shu-Fang Tung for collecting the X-ray diffraction data.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71281 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1028]

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*Acta Cryst.* (1993). **C49**, 1912–1914

### Structure of Carbonato(*C-rac*-5,5,7,12,12,-14-hexamethyl-1,4,8,11-tetraazacyclo-tetradecane)cobalt(III) Perchlorate

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## Abstract

The complex ion has a twofold axis passing through the Co<sup>III</sup> ion and the carbonate ion. The Co<sup>III</sup> ion is hexacoordinated in a distorted octahedral geometry composed of the four N atoms of the macrocyclic tetraamine ligand and two O atoms of the carbonate ion. The macrocyclic ligand has a fold structure in which each of the two six-membered rings is in a chair form and each of the two five-membered rings is in a skew form. The perchlorate ion is too far from the Co<sup>III</sup> ion to allow coordination.

## Comment

*C-rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet *b*) reacts with transition-metal ions to form folded complexes which exhibit unusual spectral (Curtis & Curtis, 1965) and kinetic properties (Kenohan & Endicott, 1969).

[Co(tet *b*)Cl<sub>2</sub>](ClO<sub>4</sub>) was obtained by the procedures reported by Whimp & Curtis (1966). Slow evaporation of its aqueous solution containing excess