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]

References

Bencini, A., Fabbrizzi, L. & Poggi, A. (1981). *Inorg. Chem.* **20**, 2544–2549.

Eigenbrot, C., Osvath, P., Lappin, A. G., Curtis, N. F. & Weatherburn, D. C. (1988). *Acta Cryst.* C**44**, 2085–2087.

Gabe, E. J., Le Page, Y., White, P. S. & Lee, F. L. (1987). *Acta Cryst.* A**43**, C-294.

Hay, R. W., Bembi, R., McLaren, F. & Moodie, W. F. (1984). *Inorg. Chem.* **85**, 23–31.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1993). C**49**, 1912–1914

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

TIAN-HUEY LU*

Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300

BOR-HANN CHEN AND CHUNG-SUN CHUNG

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300

(*Received* 8 *September* 1992; *accepted* 23 *April* 1993)

Abstract

The complex ion has a twofold axis passing through the Co^{III} ion and the carbonate ion. The Co^{III} 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^{III} 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_2](ClO_4) was obtained by the procedures reported by Whimp & Curtis (1966). Slow evaporation of its aqueous solution containing excess

Acta Crystallographica Section C
ISSN 0108-2701 ©1993

Na_2CO_3 resulted in transparent purple crystals of the title complex.

The complex ion has a twofold symmetry axis passing through Co^{III} and the C—O(2) bond of the carbonate ion. The perchlorate ion, seriously disordered, also possesses a twofold axis. The Co^{III} ion is hexacoordinated in a distorted octahedral geometry with tetraamine N(1) and N(1*a*) atoms and carbonate O(1) and O(1*a*) atoms in equatorial positions, and N(2) and N(2*a*) at the fifth and sixth ligand sites. The atoms in the equatorial plane are coplanar within 0.025 (6) Å, and the Co^{III}, O(2) and C atoms are on the best plane. Of the macrocyclic ligand, each five-membered ring is in a skew form and each of the two six-membered rings is in a chair form. Thus, the macrocyclic ligand is in its most stable folded form, with N(2) and N(2*a*) *trans* to each other. This conformation is also found in the Cr^{III} (Bang & Monsted, 1984), Co^{II} (Toby, Hughey, Fawcett, Potenza & Schugar, 1981), Ni^{II} (Whimp, Bailey & Curtis, 1970) and Hg^{II} (Burke & Richardson, 1983) complexes. However, in the blue complex of [Cu(tet *b*)(H_2O)](ClO_4)$_2$ (Sheu, Lee, Lu, Liang & Chung, 1983), N(1) and N(1*a*) are *trans* to each other. As pointed out by Whimp, Bailey & Curtis (1970), the conformation of tet *b* within these Cu^{II} complexes is less stable than that of the title complex.

The high temperature factors of the perchlorate O atoms reveal the presence of a disordered structure. The O atoms of the disordered perchlorate ion are too removed to allow coordination with the Co^{III} ion.

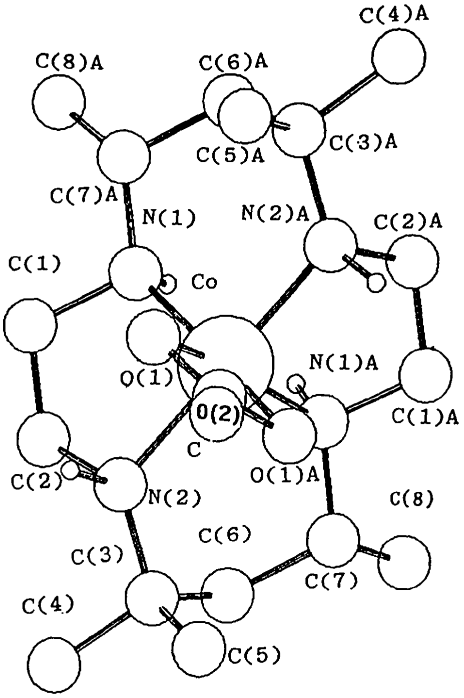


Fig. 1. A perspective view of the numbering scheme of the complex molecule without the H atoms attached to C atoms.

Experimental

Crystal data

[Co(CO_3)($C_{16}H_{36}N_4$)]ClO_4
$M_r = 502.88$
Orthorhombic
$P22_12_1$
$a = 7.185$ (5) Å
$b = 9.552$ (3) Å
$c = 16.742$ (3) Å
$V = 1148.9$ (8) Å^3
$Z = 2$
$D_x = 1.454$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7093$ Å
Cell parameters from 25 reflections
$\theta = 10.0$–$21.0°$
$\mu = 0.90$ mm^{-1}
$T = 298$ (3) K
Rectangular pillar
0.44 × 0.25 × 0.16 mm
Purple

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{min} = 0.815$, $T_{max} = 0.921$
4191 measured reflections
2034 independent reflections

1120 observed reflections [$I \geq 2.5(I)$]
$R_{int} = 0.032$
$\theta_{max} = 24.9°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity variation: ±2%

Refinement

Refinement on F
Final $R = 0.064$
$wR = 0.081$
$S = 1.04$
1120 reflections
166 parameters
Only H-atom U's refined
$w = 1.0/[\sigma^2(F_o) + 0.01|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.016$
$\Delta\rho_{max} = 0.89$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}

Secondary-extinction correction: *NCRVAX* (Gabe, Le Page, White & Lee, 1987)
Extinction coefficient: 0.016 (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

The easily disordered perchlorate group gives a high R factor. Non-H atoms were solved by heavy-atom and Fourier methods and refined by full-matrix least squares. H atoms were solved by difference Fourier method and theoretical calculation. Program used: *NRCVAX* (Gabe, Le Page, White & Lee, 1987).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (32\pi^2/3)\Sigma_i\Sigma_j U_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co	0.40141 (11)	0.0	0.0	1.95 (4)
Cl	0.7923 (5)	0.5	0.0	18.5 (6)
O(1)	0.6211 (5)	−0.0570 (4)	0.0552 (2)	2.81 (15)
O(2)	0.8961 (6)	0.0	0.0	4.7 (3)
O(3)*	0.9231 (15)	0.5094 (3)	0.0670 (9)	15.4 (16)
O(4)†	0.626 (2)	0.434 (2)	−0.029 (2)	21 (2)
O(5)*	0.780 (2)	0.3667 (18)	0.0286 (18)	18.0 (17)
N(1)	0.2240 (7)	0.0754 (5)	−0.0798 (3)	2.77 (19)
N(2)	0.4020 (7)	0.1927 (5)	0.0497 (3)	2.75 (18)

C	0.7214 (10)	0	0.0	3.0 (3)
C(1)	0.2517 (9)	0.2300 (7)	−0.0780 (4)	4.0 (3)
C(2)	0.2529 (8)	0.2758 (7)	0.0036 (6)	4.7 (3)
C(3)	0.3870 (9)	0.2131 (9)	0.1393 (4)	4.3 (3)
C(4)	0.3550 (14)	0.3729 (9)	0.1572 (5)	5.8 (4)
C(5)	0.5704 (11)	0.1718 (10)	0.1760 (4)	4.9 (3)
C(6)	0.2234 (12)	−0.1297 (10)	−0.1710 (4)	4.8 (3)
C(7)	0.2328 (9)	0.0256 (9)	−0.1657 (4)	3.9 (3)
C(8)	0.0723 (14)	0.0896 (13)	−0.2130 (5)	6.9 (6)

* Perchlorate O-atom occupancy factor of 0.7.
† Perchlorate O-atom occupancy factor of 0.6.

Table 2. *Selected bond distances* (Å) *and angles* (°)

Co—O(1)	1.908 (4)	N(1)—C(7)	1.516 (8)
Co—N(1)	1.982 (5)	N(2)—C(2)	1.540 (8)
Co—N(2)	2.020 (5)	N(2)—C(3)	1.517 (9)
Cl—O(3)	1.467 (14)	C(1)—C(2)	1.433 (13)
Cl—O(4)	1.43 (2)	C(3)—C(4)	1.572 (11)
Cl—O(5)	1.363 (18)	C(3)—C(5)	1.507 (10)
O(1)—C	1.292 (6)	C(3)—C(6*a*)*	1.516 (12)
O(2)—C	1.255 (9)	C(6)—C(7)	1.487 (13)
N(1)—C(1)	1.491 (8)	C(7)—C(8)	1.527 (11)
O(1)—Co—O(1*a*)	68.41 (17)	C(4)—C(3)—C(6*a*)	109.3 (6)
O(1)—Co—N	164.17 (18)	C(5)—C(3)—C(6*a*)	113.4 (7)
O(1)—Co—N(1*a*)	95.84 (18)	Co—O(1)—C	89.7 (3)
O(1)—Co—N(2*a*)	86.44 (19)	C(3*a*)—C(6)—C(7)	117.9 (6)
O(1)—Co—N(2)	93.37 (19)	Co—N(1)—C(1)	105.1 (4)
N(1)—Co—N(1*a*)	99.94 (19)	Co—N(1)—C(7)	119.9 (4)
N(1)—Co—N(2)	87.0 (2)	N(1)—C(7)—C(6)	111.6 (6)
N(1)—Co—N(2*a*)	93.1 (2)	N(1)—C(7)—C(8)	109.6 (6)
N(1)—C(1)—C(2)	108.8 (5)	C(1)—N(1)—C(7)	109.0 (5)
N(2)—Co—N(2*a*)	179.8 (2)	C(6)—C(7)—C(8)	109.5 (7)
N(2)—C(2)—C(1)	108.9 (5)	Co—N(2)—C(2)	105.2 (4)
N(2)—C(3)—C(4)	108.9 (6)	Co—N(2)—C(3)	121.6 (4)
N(2)—C(3)—C(5)	107.9 (5)	C(2)—N(2)—C(3)	112.3 (5)
N(2)—C(3)—C(6*a*)	109.5 (5)	O(1)—C—O(1*a*)	112.2 (6)
C(4)—C(3)—C(5)	107.7 (6)	O(1)—C—O(2)	123.9 (3)

* Atoms related to those in the crystallographic asymmetric unit by the molecular twofold axis ($-x$, $-y$, $-z$) are designated by the letter *a* following the atom number.

The authors thank the National Science Council for support under grants NSC81-0208-M007-110 and NSC81-0208-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 and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71280 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1029]

References

Bang, E. & Monsted, O. (1984). *Acta Chem. Scand. Ser. A*, **38** 281–287.

Burke, M. R. & Richardson, M. F. (1983). *Inorg. Chim. Acta*, **69**, 29–35.

Curtis, N. F. & Curtis, Y. M. (1965). *Inorg. Chem.* **4**, 804–809.

Gabe, E. J., Le Page, Y., White, P. S. & Lee, F. L. (1987). *Acta Cryst.* A**43**, C-294.

Kenohan, J. A. & Endicott, J. F. (1969). *J. Am. Chem. Soc.* **91**, 6977–6983.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheu, H.-R., Lee, T.-J., Lu, T.-H., Liang, B.-F. & Chung, C.-S. (1983). *Proc. Natl Sci. Counc. ROC*, **7**, 113–118.

Toby, B. H., Hughey, J. L. IV, Fawcett, T. G., Potenza, J. A. & Schugar, H. J. (1981). *Acta Cryst.* B**37**, 1737–1738.

Whimp, P. O., Bailey, M. F. & Curtis, N. F. (1970). *J. Chem. Soc. A*, pp. 1956–1963.

Whimp, P. O. & Curtis, N. F. (1966). *J. Chem. Soc. A*, pp. 1827–1830.

Acta Cryst. (1993). C**49**, 1914–1916

Structure of (*rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane)silver(II) Diperchlorate Dihydrate

Henry N. Po and Shu-Chin Shen

Department of Chemistry, California State University, Long Beach, CA 90840, USA

Robert J. Doedens*

Department of Chemistry, University of California, Irvine, CA 92717, USA

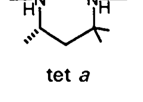
(*Received* 9 *December* 1992; *accepted* 29 *April* 1993)

Abstract

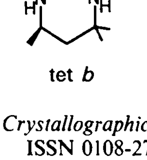
The product of the reaction of silver(II) perchlorate with the racemic form of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet *b*) contains discrete $[Ag(tet\ b)]^{2+}$ and ClO_4^- ions with no axial Ag—O bond. The cation has crystallographic twofold symmetry and a nonplanar coordination environment about the metal ion. The mean Ag—N distance is 2.162 (5) Å.

Comment

The tetraaza macrocycle 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane can exist in two diastereoisomeric forms, based on the relative configurations of the C atoms at ring positions 7 and 14. In the *C-meso* form (tet *a*), these two C atoms are of opposite configurations, *R* and *S*, while in the *C*-racemic form (tet *b*) they are of the same configuration. Both tet *a* and tet *b* form stable complexes with silver(II).



tet *a*



tet *b*

Acta Crystallographica Section C
ISSN 0108-2701 ©1993