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

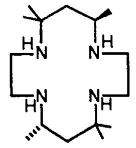
(*Received* 9 *December* 1992; *accepted* 29 *April* 1993)

Abstract

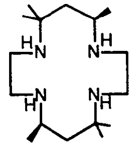
The product of the reaction of silver(II) perchlorate with the racemic form of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet *b*) contains discrete $[\mathrm{Ag(tet}\ b)]^{2+}$ and $\mathrm{ClO_4^-}$ ions with no axial Ag—O bond. The cation has crystallographic twofold symmetry and 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

Three structures of tetraaza macrocyclic complexes of silver(II) have been reported. In [Ag(tet *a*)]$(NO_3)_2$ (Mertes, 1978), [Ag(tmc)]$(ClO_4)_2$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) (Po, Brinkman & Doedens, 1991) and one isomer of [Ag(cyclam)]$(ClO_4)_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) (Ito, Ito & Toriumi, 1981), the Ag atom is located on a center of inversion and is bound to the N atoms of the macrocycle in a square-planar configuration. Each of these compounds shows axial interactions of Ag and O atoms. In a second isomer of [Ag(cyclam)]$(ClO_4)_2$, however, the Ag atom is situated on a mirror plane which bisects the two six-membered chelate rings. In this isomer, the metal atom is displaced 0.24 Å from the plane of the four N atoms and thus shows no axial Ag—O interactions.

[Ag(tet *b*)]$(ClO_4)_2$ was prepared according to the literature procedure (Clark & Harrowfield, 1984; Trismitro & Po, 1988) by adding 10 mmol of the macrocycle to 5 mmol of silver perchlorate in 60 ml of water and stirring for 2 h. The solution was then filtered and the filtrate cooled to 278 K with 0.5 ml of concentrated $HClO_4$. The orange–yellow crystals were collected by vacuum filtration and washed with cold ethanol–water (1/1 *v*/*v*). The crystals were dissolved and recrystallized from pH 2 perchloric acid solution.

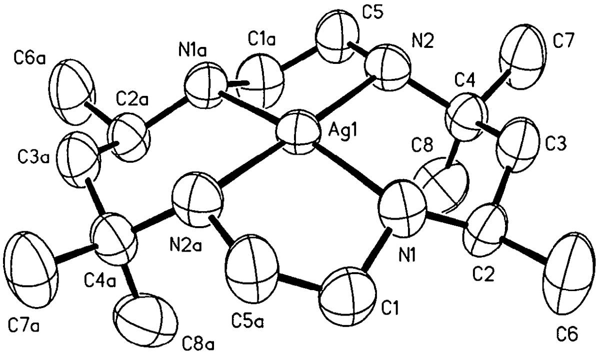


Fig. 1. View of the [Ag(tet *b*)]$^{2+}$ cation. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Under these conditions a dihydrate was obtained. The structure of the cation, shown in Fig. 1, has twofold crystallographic symmetry. The four N atoms of the macrocycle deviate significantly from planarity, with a mean deviation of 0.124 Å from the 'best' N_4 plane. The mean Ag—N bond distance is 2.162 (5) Å, close to the values of 2.160 (3) Å in [Ag(tet *a*)]$(NO_3)_2$ (Mertes, 1978) and 2.158 (2) Å in [Ag(cyclam)]$(ClO_4)_2$ (Ito, Ito & Toriumi, 1981). A longer mean distance of 2.195 (3) Å is observed in [Ag(tmc)]$(ClO_4)_2$ (Po, Brinkman & Doedens, 1991). The near linearity of the N(2)—Ag—N(2*a*) angle is probably a consequence of the steric demands of the axial methyl groups on C(4) and its symmetry equivalent. The six-membered chelate rings have chair conformations with C(3) and C(3*a*) on the same side of the macrocycle plane. The five-membered chelate rings are in slightly flattened *gauche* conformations. There is no axial bond to a perchlorate group; the closest Ag—O interaction is 4.086 Å.

Experimental

Crystal data

[Ag($C_{16}H_{36}N_4$)]$(ClO_4)_2$.-$2H_2O$
M_r = 627.29
Orthorhombic
Pbcn
a = 16.012 (2) Å
b = 8.7156 (11) Å
c = 19.130 (3) Å
V = 2669.7 (6) Å^3
Z = 4
D_x = 1.561 Mg m^{-3}
Mo *Kα* radiation
λ = 0.71073 Å

Cell parameters from 32 reflections
θ = 13.7–15.0°
μ = 1.01 mm^{-1}
T = 296 K
Rhombus
0.60 × 0.53 × 0.20 mm
Orange-yellow
Crystal source: prepared from macrocycle and $AgClO_4$ in aqueous solution

Data collection

Nicolet *R3m/V* diffractometer
ω/2θ scans
Absorption correction: empirical
T_{min} = 0.232, T_{max} = 0.301
3505 measured reflections
3505 independent reflections

1863 observed reflections [$I \geq 3\sigma(I)$]
θ_{max} = 27.5°
h = 0 → 11
k = 0 → 20
l = 0 → 24
3 standard reflections monitored every 97 reflections
intensity variation: ±1%

Refinement

Refinement on *F*
Final *R* = 0.0535
wR = 0.0729
S = 2.51
1863 reflections
150 parameters
H-atom parameters not refined
$w = [\sigma^2(F) + 0.00038F^2]^{-1}$

$(\Delta/\sigma)_{max}$ = 0.019
$\Delta\rho_{max}$ = 1.80 e Å^{-3} (near Ag)
$\Delta\rho_{min}$ = −0.59 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Difference Fourier maps showed evidence for disorder of the perchlorate anion. However, no alternative set of O-atom positions that were chemically reasonable and refinable could be found. Computer programs included the Siemens *R3m/V* system *SHELXTL-Plus* (Sheldrick, 1991), as well as *CARESS* (Broach, 1978) for data reduction.

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

U_{eq} = 1/3(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
Ag(1)	0.0	0.3664 (1)	0.7500	0.0443 (2)
N(1)	0.0849 (3)	0.3444 (7)	0.6626 (3)	0.0531 (19)
N(2)	−0.1144 (3)	0.3728 (7)	0.6902 (3)	0.0536 (19)
C(1)	0.1588 (4)	0.2704 (11)	0.6960 (4)	0.0687 (29)
C(2)	0.0499 (4)	0.2631 (9)	0.6014 (3)	0.0533 (23)
C(3)	−0.0363 (5)	0.3252 (9)	0.5813 (4)	0.0608 (25)
C(4)	−0.1141 (4)	0.2783 (8)	0.6238 (4)	0.0534 (23)
C(5)	−0.1844 (5)	0.3510 (10)	0.7399 (3)	0.0670 (29)
C(6)	0.1101 (5)	0.2780 (14)	0.5402 (4)	0.0940 (40)
C(7)	−0.1918 (4)	0.3242 (12)	0.5811 (4)	0.0849 (34)
C(8)	−0.1173 (6)	0.1125 (9)	0.6424 (5)	0.0828 (35)
Cl(1)	0.1055 (2)	−0.1977 (3)	0.6310 (2)	0.0860 (9)
O(1)	0.0336 (8)	−0.2028 (18)	0.5952 (5)	0.1994 (63)
O(2)	0.0955 (7)	−0.1189 (10)	0.6910 (5)	0.1640 (52)
O(3)	0.1398 (7)	−0.3317 (10)	0.6359 (10)	0.2390 (85)
O(4)	0.1597 (11)	−0.1004 (13)	0.5909 (7)	0.2267 (74)
O(5)	−0.1150 (5)	−0.2907 (8)	0.6769 (4)	0.1160 (32)

Table 2. *Selected geometric parameters* (Å, °)

Ag(1)—N(1)	2.164 (5)	Ag(1)—N(2)	2.160 (5)
N(1)—C(1)	1.492 (9)	N(1)—C(2)	1.478 (9)
N(2)—C(4)	1.513 (9)	N(2)—C(5)	1.482 (9)
C(1)—C(5*a*)*	1.472 (11)	C(2)—C(3)	1.532 (10)
C(3)—C(4)	1.544 (10)		
N(1)—Ag(1)—N(2)	97.2 (2)	N(1)—Ag(1)—N(1*a*)	169.8 (3)
N(2)—Ag(1)—N(1*a*)	83.0 (2)	N(2)—Ag(1)—N(2*a*)	177.0 (3)
Ag(1)—N(1)—C(1)	101.8 (4)	Ag(1)—N(1)—C(2)	114.6 (4)
C(1)—N(1)—C(2)	115.6 (6)	Ag(1)—N(2)—C(4)	115.3 (4)
Ag(1)—N(2)—C(5)	107.4 (4)	C(4)—N(2)—C(5)	118.0 (5)
N(1)—C(1)—C(5*a*)	111.9 (7)	N(1)—C(2)—C(3)	111.8 (6)
C(2)—C(3)—C(4)	120.1 (6)	N(2)—C(4)—C(3)	107.5 (5)
N(2)—C(5)—C(1*a*)	112.6 (6)		

* Atoms related to those in the crystallographic asymmetric unit by the molecular twofold axis ($-x, y, \frac{1}{2} - z$) are designated by the letter *a* following the atom number.

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 71293 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1059]

References

Broach, R. W. (1978). *CARESS*. Argonne National Laboratory, Illinois, USA.

Clark, I. J. & Harrowfield, J. M. (1984). *Inorg. Chem.* **23**, 3740–3745.

Ito, T., Ito, H. & Toriumi, K. (1981). *Chem. Lett.* pp. 1101–1104.

Mertes, K. B. (1978). *Inorg. Chem.* **17**, 49–52.

Po, H. N., Brinkman, E. & Doedens, R. J. (1991). *Acta Cryst.* C**47**, 2310–2312.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Trismitro, R. & Po, H. N. (1988). *J. Coord. Chem.* **17**, 1–14.

Acta Cryst. (1993). C**49**, 1916–1918

Structure d'un Produit de Mercuration de la 2,4-Pentanedione, $Hg(C_5H_7O_2)Cl$

PAUL TOLEDANO, CHRISTIAN BONHOMME,*
MARC HENRY ET JACQUES LIVAGE

Laboratoire de Chimie de la Matière Condensée,
Université P. et M. Curie, 4 Place Jussieu, Tour 54,
75230 Paris CEDEX 05, France

(*Reçu le* 12 *janvier* 1993, *accepté le* 4 *mai* 1993)

Abstract

The structure of chloro(diacetylmethyl)mercury(II), [$Hg(C_5H_7O_2)Cl$], contains discrete molecules. Each molecule is related to another one by a centre of symmetry, leading to two groups of two molecules in the cell. Each Hg atom is coordinated to a Cl atom and to the γ-C atom, C(4), of a 2,4-pentanedione moiety [Hg—Cl = 2.329 (3), Hg—C = 2.11 (1) Å] with the angle Cl—Hg—C(4) = 161.1 (3)°. Each Hg atom is also connected to the O atoms of the centrosymmetrically related molecule [Hg—O(1^{i}) = 2.57 (1) and Hg—O(2^{i}) = 2.69 (1) Å; (i) $1 - x$, $-y$, $1 - z$].

Commentaire

Les dérivés mono- et polymercurés de la 2,4-pentanedione ont été largement étudiés, essentiellement par des techniques spectroscopiques locales (IR, Raman, RMN ^{1}H et ^{13}C en solution) (Allmann, Flatau & Musso, 1972; Macklin, 1976). Certaines structures faisant intervenir la 2,4-pentanedione ou d'autres β-dicétones ont pu être résolues par diffraction des rayons X (Allmann, Flatau & Musso, 1972; Allmann & Musso, 1973; McCandlish & Macklin, 1975). Toutes font état d'une mercuration *via* l'atome de carbone en γ des molécules de 2,4-pentanedione. Plus rarement, la mercuration peut avoir lieu *via* les atomes de carbone des groupements méthyles, à condition d'imposer un encombrement stérique de la position en γ des molécules considérées (Depmeier, Dietrich, König, Musso & Weiss, 1986). L'étude de sols et de gels à base de dérivés organomercurés nous a conduit à la synthèse et à la caractérisation de références dont certaines ont pu être obtenues sous forme de monocristaux.

Le Tableau 1 rassemble les valeurs finales des coordonnées des atomes autres que le atomes d'hydrogène, avec leurs écarts types et leurs facteurs de température isotropes équivalents $U_{éq}$. Quelques distances et angles interatomiques sont reportés dans le Tableau 2. La structure est formée d'ensembles

Acta Crystallographica Section C
ISSN 0108-2701 ©1993