Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: FG1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Basu, A., Bhaduri, S., Sapre, N. Y. & Jones, P. G. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1724–1725.

Beyer, E. M. & Blomstrom, D. C. (1980). *Plant Growth Substances 1979*, edited by F. S. Koog, pp. 208–218. New York: Springer-Verlag.

Bhaduri, S., Sapre, N. Y. & Jones, P. G. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2539–2543.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1989). *XEMP. Empirical Absorption Correction Program.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1991). *XDISK. Data Reduction Program.* Version 3.11. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XP. Interactive Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Thomson, J. S., Harlow, R. L. & Whitney, J. F. (1983). *J. Am. Chem. Soc.* **105**, 3522–3527, and references therein.

Acta Cryst. (1996). C**52**, 806–807

Diperchlorato[(1*RS*,4*RS*,5*SR*,7*RS*,8*SR*,11*SR*,12*RS*,14*SR*)-(5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane)]copper(II)

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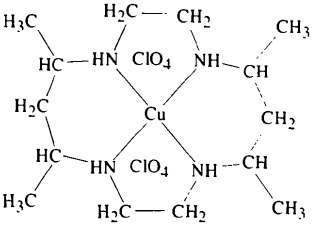
Abstract

The Cu^{II} ion of $[Cu(C_{14}H_{32}N_4)(ClO_4)_2]$ is sixfold coordinated in a distorted octahedral environment with the four N atoms of the macrocyclic ligand equatorial and the two O atoms of the perchlorate ion axial. The quadridentate ligand adopts its most stable conformation with the two six-membered rings in chair forms and the two five-membered rings in *gauche* forms. The complex has a 1*RS*,4*RS*,8*SR*,11*SR* configuration for the four chiral N-atom centres and a 5*SR*,7*RS*,12*RS*,14*SR* configuration for the four chiral C-atom centres.

Comment

There is a great deal of interest in transition metal complexes of 14-membered tetraaza macrocycles because of their particular stereochemistry (Boeyen & Dobson, 1987; Bosnich, Poon & Tobe, 1965). This paper reports the crystal structure of the copper(II) complex of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane, (I).



(I)

The coordination around the Cu^{II} ion is distorted octahedral with the four N atoms of the macrocyclic ligand equatorial and the two O atoms of the perchlorate ions axial. This structure is similar to that of diperchlorato(1,4,8,11-tetraazacyclotetradecane)copper(II) (Tasker & Sklar, 1975). The quadridentate ligand adopts its most stable conformation with the two six-membered rings in chair forms and the two five-membered rings in *gauche* forms. The Cu—N distances range from 2.023 (3) to 2.030 (3) Å. The long Cu—O bond of 2.539 (2) Å is the result of the Jahn–Teller effect. The four methyl groups occupy equatorial positions. The complex has a 1*RS*,4*RS*,8*SR*,11*SR* configuration for the four chiral N-atom centres and a 5*SR*,7*RS*,12*RS*,14*SR* configuration for the four chiral C-atom centres.

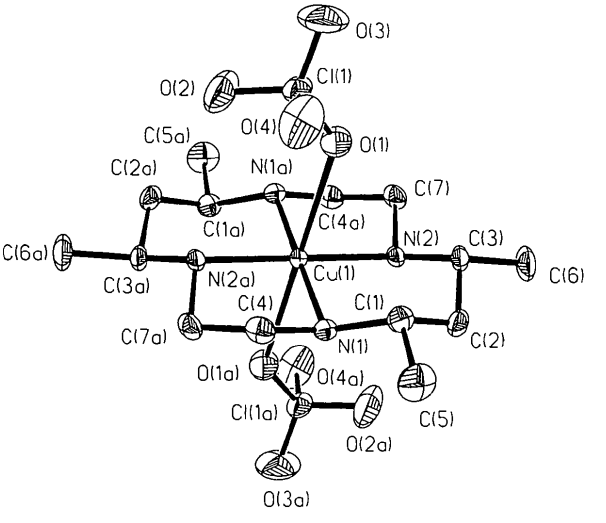


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of a single molecule with displacement ellipsoids scaled to 30% probability. H atoms are not shown.

Experimental

5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate was prepared according to the reported method (Kolinski & Korybut-Daszkiewicz, 1975). To a suspension of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate (10 g) in methanol (200 ml) was added $NaBH_4$ (5 g) in small portions at 273 K. Upon completion of the addition, the solution was refluxed for 2 h and cooled to room temperature. The white precipitate was filtered off, washed with diethyl ether and dried *in vacuo*. $CuCO_3.Cu(OH)_2$ (1.0 g) and (5*SR*,7*RS*,12*RS*,14*SR*)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane dihydroperchlorate (1 g) were dissolved in water (100 ml) and stirred for 4 h at 323 K. The blue crystals were recrystallized from water–methanol solution (*v*/*v* = 1/1).

Crystal data

$[Cu(C_{14}H_{32}N_4)(ClO_4)_2]$
M_r = 518.9
Monoclinic
$P2_1/c$
a = 8.678 (3) Å
b = 16.152 (2) Å
c = 8.421 (1) Å
β = 112.75 (1)°
V = 1088.4 (5) Å^3
Z = 2
D_x = 1.583 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 7.65–17.27°
μ = 1.296 mm^{-1}
T = 300 K
Bulk
0.5 × 0.5 × 0.5 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North, Phillips & Matthews, 1968)
T_{min} = 0.786, T_{max} = 0.999
5197 measured reflections
2492 independent reflections
2074 observed reflections [$F > 4\sigma(F)$]
R_{int} = 0.0199
θ_{max} = 27.5°
$h = 0 \rightarrow 11$
$k = -20 \rightarrow 20$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 100 reflections
intensity decay: 0.07%

Refinement

Refinement on F
R = 0.0492
wR = 0.0510
S = 1.01
2074 reflections
133 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.017
$\Delta\rho_{max}$ = 0.76 e Å^{-3}
$\Delta\rho_{min}$ = −0.5 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1991)

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

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cu(1)	1/2	1/2	0	0.032 (1)
Cl(1)	0.2686 (2)	0.4615 (1)	0.2687 (2)	0.069 (1)
N(1)	0.3414 (4)	0.4321 (2)	−0.1975 (4)	0.040 (1)
N(2)	0.6776 (4)	0.4103 (2)	0.0786 (4)	0.041 (1)
O(1)	0.3929 (5)	0.4378 (2)	0.2149 (5)	0.082 (2)
O(2)	0.2487 (9)	0.5484 (3)	0.2494 (9)	0.152 (4)
O(3)	0.2706 (10)	0.4355 (4)	0.4154 (7)	0.164 (4)
O(4)	0.1158 (6)	0.4237 (4)	0.1394 (9)	0.140 (3)
C(1)	0.3287 (6)	0.3419 (3)	−0.1653 (6)	0.054 (2)
C(2)	0.4983 (7)	0.3029 (3)	−0.1128 (6)	0.060 (2)
C(3)	0.6236 (6)	0.3226 (2)	0.0660 (6)	0.052 (2)
C(4)	0.1777 (5)	0.4748 (3)	−0.2565 (5)	0.054 (2)
C(5)	0.2019 (8)	0.3000 (4)	−0.3258 (8)	0.092 (3)
C(6)	0.7742 (8)	0.2634 (3)	0.1149 (9)	0.089 (3)
C(7)	0.7903 (5)	0.4337 (3)	0.2536 (5)	0.055 (2)

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

Cu(1)—N(1)	2.023 (3)	N(2)—C(3)	1.482 (5)
Cu(1)—N(2)	2.030 (3)	N(2)—C(7)	1.469 (5)
Cl(1)—O(1)	1.376 (5)	C(1)—C(2)	1.501 (7)
Cl(1)—O(2)	1.416 (5)	C(1)—C(5)	1.531 (7)
Cl(1)—O(3)	1.298 (7)	C(2)—C(3)	1.511 (6)
Cl(1)—O(4)	1.484 (5)	C(3)—C(6)	1.542 (8)
N(1)—C(1)	1.495 (5)	C(4)—C(7^i)	1.502 (7)
N(1)—C(4)	1.481 (5)	Cu(1)—O(1)	2.539 (2)
N(1)—Cu(1)—N(2)	94.0 (1)	C(3)—N(2)—C(7)	112.8 (3)
N(2)—Cu(1)—N(1^i)	86.0 (1)	N(1)—C(1)—C(2)	109.2 (4)
O(1)—Cl(1)—O(2)	108.3 (4)	N(1)—C(1)—C(5)	110.4 (4)
O(1)—Cl(1)—O(3)	120.0 (4)	C(2)—C(1)—C(5)	111.3 (4)
O(2)—Cl(1)—O(3)	112.7 (5)	C(1)—C(2)—C(3)	116.8 (4)
O(1)—Cl(1)—O(4)	103.6 (3)	N(2)—C(3)—C(2)	111.0 (3)
O(2)—Cl(1)—O(4)	106.8 (3)	N(2)—C(3)—C(6)	111.3 (4)
O(3)—Cl(1)—O(4)	104.2 (4)	C(2)—C(3)—C(6)	110.1 (4)
Cu(1)—N(1)—C(1)	117.0 (2)	N(1)—C(4)—C(7^i)	107.8 (3)
Cu(1)—N(1)—C(4)	106.4 (2)	N(2)—C(7)—C(4^i)	108.4 (3)
C(1)—N(1)—C(4)	112.7 (3)	Cu(1)—O(1)—Cl(1)	132.4 (2)
Cu(1)—N(2)—C(3)	118.6 (3)	N(1)—Cu(1)—O(1)	92.9 (1)
Cu(1)—N(2)—C(7)	105.7 (3)	N(2)—Cu(1)—O(1)	85.8 (1)

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *ORTEP*II (Johnson, 1976); *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Boeyen, J. C. A. & Dobson, S. M. (1987). *Stereochemical and Stereophysical Behaviour of Macrocycles*, Vol. 2, pp. 48–70. New York: Elsevier.

Bosnich, B., Poon, C. K. & Tobe, M. L. (1965). *Inorg. Chem.* **4**, 1102–1108.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kolinski, R. A. & Korybut-Daszkiewicz, B. (1975). *Inorg. Chim. Acta*, **14**, 237–245.

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

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

Tasker, P. A. & Sklar, L. (1975). *J. Cryst. Mol. Struct.* **5**, 329–344.