

N4A—C5A	1.326 (4)	C5B—C6B	1.408 (4)
C5A—C51A	1.497 (4)	C6B—C7B	1.358 (4)
C5A—C6A	1.410 (4)	C7B—C71B	1.484 (4)
C6A—C7A	1.356 (4)	C7B—N8B	1.362 (3)
Cl1—Zn—Cl2	117.54 (4)	N1A—N8A—C3aA	110.8 (2)
Cl1—Zn—N3A	110.72 (7)	N1A—N8A—C7A	126.9 (2)
Cl1—Zn—N3B	116.17 (7)	C3aA—N8A—C7A	122.4 (2)
Cl2—Zn—N3A	103.05 (7)	C2B—N1B—N8B	101.5 (2)
Cl2—Zn—N3B	105.41 (7)	N1B—C2B—N3B	116.5 (3)
N3A—Zn—N3B	102.09 (9)	Zn—N3B—C2B	122.9 (2)
C2A—N1A—N8A	102.0 (2)	Zn—N3B—C3aB	130.6 (2)
N1A—C2A—N3A	115.4 (3)	C2B—N3B—C3aB	103.3 (2)
Zn—N3A—C2A	125.4 (2)	N3B—C3aB—N4B	128.4 (2)
Zn—N3A—C3aA	130.2 (2)	N3B—C3aB—N8B	108.3 (2)
C2A—N3A—C3aA	103.9 (2)	N4B—C3aB—N8B	123.4 (2)
N3A—C3aA—N4A	128.6 (2)	C3aB—N4B—C5B	115.2 (2)
N3A—C3aA—N8A	108.0 (2)	N4B—C5B—C51B	116.1 (3)
N4A—C3aA—N8A	123.4 (2)	N4B—C5B—C6B	123.1 (3)
C3aA—N4A—C5A	115.5 (2)	C51B—C5B—C6B	120.8 (3)
N4A—C5A—C51A	116.4 (3)	C5B—C6B—C7B	120.7 (3)
N4A—C5A—C6A	122.8 (3)	C6B—C7B—C71B	127.2 (3)
C51A—Zn—C6A	120.8 (3)	C6B—C7B—N8B	115.1 (2)
C5A—C6A—C7A	121.4 (3)	C71B—C7B—N8B	117.7 (2)
C6A—C7A—C71A	127.2 (3)	N1B—N8B—C3aB	110.5 (2)
C6A—C7A—N8A	114.5 (3)	N1B—N8B—C7B	127.0 (2)
C71A—C7A—N8A	118.3 (3)	C3aB—N8B—C7B	122.5 (2)

Computing was by means of the Enraf-Nonius SDP system (B. A. Frenz & Associates, Inc., 1982) on a DEC MicroVAX II computer at the Centre de Diffractométrie Automatique, Université Lyon I.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71613 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1080]

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(5,5-Dimethyl-4,7-diazadecane-1,10-diamine-N,N',N'',N''')(perchlorato-O)copper(II) Perchlorate

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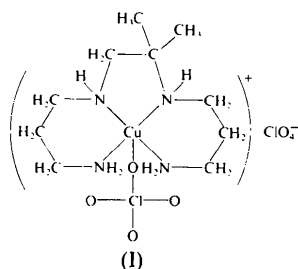
Abstract

The Cu^{II} ion in the title complex, [Cu(ClO₄)₂(C₁₀H₂₆N₄)]ClO₄, is five-coordinate with four N atoms equatorial and one perchlorato O atom axial. The two asymmetric N atoms are of the same *R* or *S* configuration. Each six-membered ring is in a stable chair conformation and the central five-membered ring is in a skew form. Hydrogen bonds help stabilize the crystal structure.

Comment

The thermodynamic and kinetic properties of complexes in which linear tetraamines surround a Cu^{II} ion have been studied extensively. Previously we have reported the crystal structure of [*N,N'*-bis(3-

aminopropyl)-1,2-ethanediamine]perchlorato-copper(II) perchlorate hemihydrate, $[\text{Cu}(\text{ClO}_4)_2(\text{C}_8\text{H}_{22}\text{N}_4)]\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ (Lee, Lee, Hong, Hsieh, Wu & Chung, 1986). In order to study the steric effect of the central five-membered chelating ring on the structure of the Cu^{II} complex, we have prepared and studied the structure of the title complex (I).



The ligand was synthesized by a reported method (Lu, Shan, Chao & Chung, 1987). A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) in methanol was added dropwise to a solution of the ligand (0.01 mol) in ethanol. The solution rapidly became reddish blue and was stirred for 3 h during which a solid formed. The solid was filtered off and dissolved in water. The single crystal used for X-ray diffraction analysis was obtained by slow evaporation of the solvent at room temperature.

The coordination geometry about the Cu^{II} ion is pyramidal with four N atoms in equatorial positions

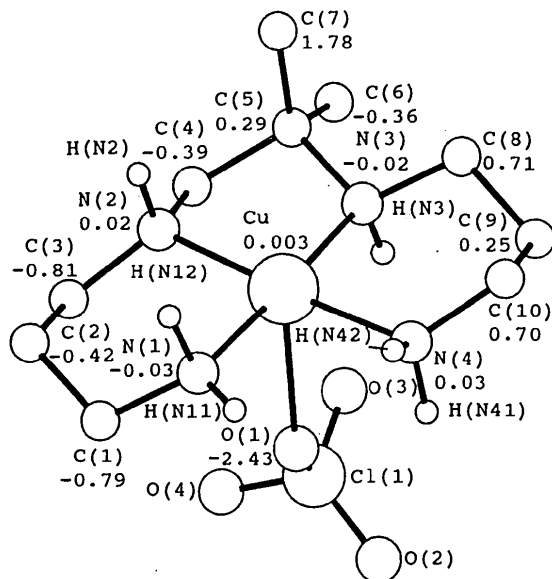


Fig. 1. A perspective view of the title molecule with the atom-numbering scheme, excluding the perchlorate groups and the H atoms attached to C atoms. The displacements from the best plane formed by the four N atoms coordinated to the Cu^{II} ion are also indicated.

and one perchlorate O atom in an axial position. The equatorial N atoms are coplanar to within 0.03 Å. The equatorial Cu—N distances are comparable to the average Cu—N distance of 2.03 (3) Å for Cu^{II} macrocyclic complexes (Lu, Chung & Ashida, 1991); the Cu—O(apical) distance [2.455 (5) Å] falls within the range [2.520 (2)–2.883 (2) Å] reported by Tasker & Sklar (1975). The amine H(N2) and H(N3) atoms are *trans* to the plane formed by the four N atoms. Comparing the structure of the title complex with that of $[\text{Cu}(\text{ClO}_4)_2(\text{C}_8\text{H}_{22}\text{N}_4)]\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ (Lee *et al.*, 1986), we find that they have the same *R* or *S* configuration in the two asymmetric N atoms. In both structures, the central five-membered ring is in a skew conformation and the two terminal six-membered rings are in stable chair forms. The hydrogen bonds between the NH and NH_2 groups and the perchlorate O atoms help stabilize the crystal structure.

Experimental

Crystal data

$[\text{Cu}(\text{ClO}_4)(\text{C}_{10}\text{H}_{26}\text{N}_4)]\text{ClO}_4$

$M_r = 464.79$

Monoclinic

$P2_1/n$

$a = 13.297$ (1) Å

$b = 13.804$ (1) Å

$c = 10.136$ (1) Å

$\beta = 91.05$ (1)°

$V = 1860.2$ (3) Å³

$Z = 4$

$D_x = 1.66$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Cell parameters from 25 reflections

$\theta = 6.21$ – 16.31 °

$\mu = 1.51$ mm⁻¹

$T = 298$ (3) K

Parallelepiped

$0.24 \times 0.22 \times 0.19$ mm

Blue-violet

Data collection

Enraf-Nonius CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction: empirical

$T_{\min} = 0.917$, $T_{\max} = 0.999$

3446 measured reflections

3251 independent reflections

1987 observed reflections

$[I \geq 2.5\sigma(I)]$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 24.9$ °

$h = -15 \rightarrow 15$

$k = 0 \rightarrow 16$

$l = 0 \rightarrow 12$

3 standard reflections

frequency: 60 min

intensity variation: 1%

Refinement

Refinement on F

$R = 0.039$

$wR = 0.039$

$S = 0.54$

1987 reflections

298 parameters

Only H-atom U 's refined

Unit weights applied

$(\Delta/\sigma)_{\max} = 0.668$

$\Delta\rho_{\max} = 0.45$ e Å⁻³

$\Delta\rho_{\min} = -0.36$ e Å⁻³

Extinction correction:

Zachariasen (1967)

Extinction coefficient:

0.60 (3)

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

Occupancy	x	y	z	B _{eq}	
Cu	1.0	0.74126 (4)	0.37845 (6)	0.24688 (7)	2.542 (23)
Cl(1)	1.0	0.64326 (11)	0.62300 (12)	0.26226 (15)	4.10 (6)
Cl(2)	1.0	0.11192 (10)	0.38133 (14)	0.32904 (15)	4.16 (7)
O(1)	1.0	0.7221 (4)	0.5553 (4)	0.2490 (7)	7.7 (3)
O(2)	1.0	0.6726 (6)	0.6980 (5)	0.3424 (9)	12.4 (5)
O(3)	0.8	0.5557 (7)	0.5791 (9)	0.2984 (16)	11.9 (10)
O(3')	0.2	0.599 (3)	0.580 (3)	0.367 (3)	6.0 (16)
O(4)	0.8	0.6130 (10)	0.6513 (11)	0.1383 (10)	15.2 (9)
O(4')	0.2	0.6721 (21)	0.6972 (18)	0.1770 (22)	5.0 (11)
O(5)	1.0	0.0487 (5)	0.4639 (5)	0.3228 (8)	9.7 (4)
O(6)	0.8	0.1514 (11)	0.3626 (9)	0.2073 (10)	11.6 (7)
O(6')	0.2	0.0847 (22)	0.351 (4)	0.218 (4)	11.2 (28)
O(7)	0.8	0.0494 (8)	0.3116 (8)	0.3732 (15)	15.4 (9)
O(7')	0.2	0.142 (3)	0.2874 (19)	0.370 (3)	8.7 (20)
O(8)	0.8	0.1857 (9)	0.3950 (12)	0.4221 (12)	15.0 (9)
O(8')	0.2	0.2003 (16)	0.4346 (23)	0.334 (3)	5.9 (15)
N(1)	1.0	0.8661 (4)	0.4025 (4)	0.1423 (5)	4.2 (3)
N(2)	1.0	0.6578 (3)	0.3516 (3)	0.0825 (4)	2.96 (20)
N(3)	1.0	0.6102 (3)	0.3562 (3)	0.3429 (4)	3.02 (19)
N(4)	1.0	0.8198 (4)	0.4010 (5)	0.4151 (5)	4.5 (3)
C(1)	1.0	0.8589 (5)	0.4519 (6)	0.0124 (7)	4.8 (3)
C(2)	1.0	0.7849 (5)	0.4038 (5)	-0.0788 (6)	4.9 (3)
C(3)	1.0	0.6767 (5)	0.4121 (5)	-0.0363 (6)	4.5 (3)
C(4)	1.0	0.5503 (4)	0.3605 (5)	0.1182 (5)	3.56 (24)
C(5)	1.0	0.5324 (4)	0.3122 (4)	0.2500 (6)	3.52 (25)
C(6)	1.0	0.4264 (5)	0.3398 (6)	0.2959 (8)	5.3 (4)
C(7)	1.0	0.5456 (5)	0.2039 (5)	0.2411 (8)	4.8 (3)
C(8)	1.0	0.6138 (6)	0.3092 (6)	0.4742 (7)	5.1 (3)
C(9)	1.0	0.6847 (5)	0.3631 (6)	0.5685 (6)	5.1 (4)
C(10)	1.0	0.7925 (5)	0.3509 (6)	0.5377 (6)	5.2 (3)

Table 2. Selected geometric parameters (Å, °)

Cu—O(1)	2.455 (5)	N(3)—C(8)	1.480 (8)
Cu—N(1)	2.013 (5)	N(4)—C(10)	1.474 (9)
Cu—N(2)	2.019 (4)	C(1)—C(2)	1.49 (1)
Cu—N(3)	2.035 (4)	C(2)—C(3)	1.51 (1)
Cu—N(4)	2.008 (5)	C(4)—C(5)	1.516 (8)
N(1)—C(1)	1.485 (9)	C(5)—C(6)	1.539 (8)
N(2)—C(3)	1.490 (8)	C(5)—C(7)	1.509 (9)
N(2)—C(4)	1.486 (7)	C(8)—C(9)	1.52 (1)
N(3)—C(5)	1.513 (7)	C(9)—C(10)	1.48 (1)
O(1)—Cu—N(1)	85.9 (2)	Cu—N(3)—C(8)	118.8 (4)
O(1)—Cu—N(2)	97.7 (2)	C(5)—N(3)—C(8)	113.2 (4)
O(1)—Cu—N(3)	93.2 (2)	Cu—N(4)—C(10)	120.7 (4)
O(1)—Cu—N(4)	83.7 (2)	N(1)—C(1)—C(2)	112.0 (6)
N(1)—Cu—N(2)	92.4 (2)	C(1)—C(2)—C(3)	114.2 (6)
N(1)—Cu—N(3)	176.6 (2)	N(2)—C(3)—C(2)	111.3 (5)
N(1)—Cu—N(4)	90.0 (2)	N(2)—C(4)—C(5)	110.2 (4)
N(2)—Cu—N(3)	84.5 (2)	N(3)—C(5)—C(4)	104.8 (4)
N(2)—Cu—N(4)	177.3 (2)	N(3)—C(5)—C(6)	109.4 (5)
N(3)—Cu—N(4)	93.1 (2)	N(3)—C(5)—C(7)	110.9 (5)
Cu—O(1)—Cl(1)	137.4 (3)	C(4)—C(5)—C(6)	108.5 (5)
Cu—N(1)—C(1)	120.2 (4)	C(4)—C(5)—C(7)	111.3 (5)
Cu—N(2)—C(3)	117.8 (4)	C(6)—C(5)—C(7)	111.8 (5)
Cu—N(2)—C(4)	107.5 (3)	N(3)—C(8)—C(9)	111.1 (5)
C(3)—N(2)—C(4)	109.2 (4)	C(8)—C(9)—C(10)	113.7 (6)
Cu—N(3)—C(5)	110.2 (3)	N(4)—C(10)—C(9)	112.3 (5)

The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least-squares techniques; H atoms were located from difference Fourier maps. All computing was performed using the NRCVAX system of programs (Gabe, Le Page, White & Lee, 1987).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and hydrogen-bond lengths have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71619 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1066]

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[(2RS,5SR,8SR,12SR,15SR)-2,5,8,12,15-Pentaazahexadecane-κ⁵N^{2,5,8,12,15}]copper(II) Diperchlorate

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Abstract

The Cu^{II} atom in the title complex, [Cu(C₁₁H₂₉N₅)]-(ClO₄)₂, is five-coordinate and is in a distorted trigonal-bipyramidal conformation. The longer Cu(equatorial)—N bond distances compared to the Cu(axial)—N distances indicate the steric influence of the two N-methyl groups. The ligand is in its stable conformation with the three five-membered chelate rings in stable skew forms and the six-membered ring in a stable chair form.

Comment

The crystal structures of open-chain tetraamine complexes have been studied extensively (Lee *et al.*, 1986;