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Aqua(1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane-N,N',N'',N''')copper(II) Diperchlorate

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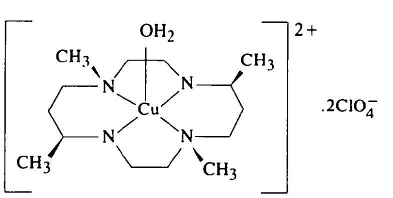
Abstract

The Cu^{II} ion in the title compound, $[Cu(C_{14}H_{32}N_4)(H_2O)](ClO_4)_2$, is five-coordinate in a distorted square-pyramidal geometry, with the four N atoms of the macrocyclic ligand equatorial and the O atom of the aqua group axial. The tetradentate ligand adopts its most stable conformation with the two six-membered rings in chair conformations and the two five-membered rings in *gauche* conformations. The complex has a 1*SR*,4*SR*,8*SR*,11*SR* configuration for the four chiral N-atom centers and a 5*RS*,12*RS* configuration for the two chiral C-atom centers.

Comment

The macrocyclic ligand 1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane exists as two isomers, namely, *C-meso-* and *C-rac*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Miyamura *et al.*, 1987). The crystal structure of the nickel(II) complex of the *C-meso* isomer has been reported previously (Miyamura *et al.*, 1987). This paper reports the crystal structure of the copper(II) complex of *C-rac*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane, (I).



(I)

The Cu^{II} ion is five-coordinate in a distorted square-pyramidal geometry, with the four N atoms of the macrocyclic ligand equatorial and the O atom of the aqua group axial. The four N atoms are coplanar within ±0.18 Å. The Cu—N distances span a very narrow range [2.030 (3)–2.039 (3) Å] and are similar to the average Cu—N distance of 2.03 (3) Å found for Cu^{II} macrocyclic tetraamine complexes (Lu, Chung & Ashida, 1991). The Cu—O_{water} distance is in good agreement with the usual Cu—O_{axial} distances found in Cu^{II} macrocyclic complexes. The two *N*-methyl groups, the two amine H atoms and the coordinated water molecule are on the same side of the equatorial N_4 plane. The tetradentate ligand adopts its most stable conformation with the two six-membered rings in chair conformations and the two five-membered rings in *gauche* conformations. The two C-methyl groups occupy equatorial positions. The complex has a 1*SR*,4*SR*,8*SR*,11*SR* configuration for the four chiral N-atom centers and a 5*RS*,12*RS* configuration for the two chiral C-atom centers. Hydrogen bonds between perchlorate and the water molecule or NH group stabilize the crystal structure.

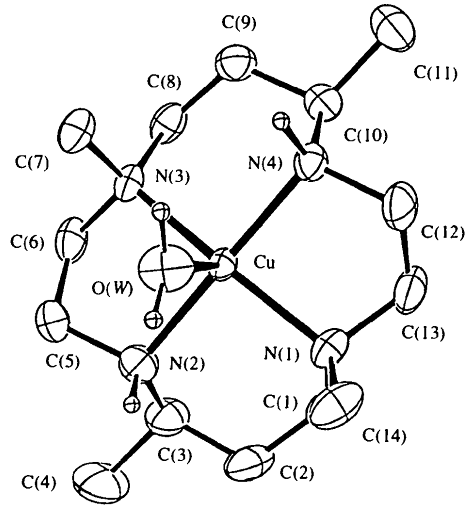


Fig. 1. A perspective view (*SHELXTL-Plus*; Sheldrick, 1986) of the complex cation with the atom-numbering scheme, excluding the perchlorate ions and H atoms attached to C atoms. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

C-rac-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane dihydroperchlorate was prepared according to the method of Miyamura *et al.* (1987). Copper(II) perchlorate hexahydrate

(0.6 g) [or copper(II) acetate (0.5 g)] and *C-rac*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane dihydroperchlorate (1 g) were dissolved in aqueous methanol (*v*/*v* 1/1, 200 ml) and stirred for 4 h at 298 K. Sodium perchlorate (2 g) was added and the resulting solution was placed in a refrigerator for several days whereupon blue crystals were formed.

Crystal data

$[Cu(C_{14}H_{32}N_4)(H_2O)]$-
$(ClO_4)_2$
$M_r = 536.89$
Monoclinic
$P2_1/c$
$a = 7.795$ (4) Å
$b = 15.347$ (2) Å
$c = 19.245$ (2) Å
$\beta = 99.53$ (4)°
$V = 2271$ (1) Å^3
$Z = 4$
$D_x = 1.571$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.64$–16.12°
$\mu = 1.24$ mm^{-1}
$T = 298$ (3) K
Parallelepiped
0.45 × 0.40 × 0.38 mm
Blue

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.57$, $T_{\max} = 0.62$
4305 measured reflections
3993 independent reflections

3111 observed reflections $[I \geq 2.5(I)]$
$R_{\rm int} = 0.015$
$\theta_{\max} = 25°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity decay: ±0.5%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.062$
$S = 1.35$
3111 reflections
368 parameters
H atoms: see below
$w = 1/[\sigma(F_o)^2 + 0.0016|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.303$
$\Delta\rho_{\max} = 0.53$ (7) e Å^{-3}
$\Delta\rho_{\min} = -0.30$ (7) e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cu	0.40813 (5)	0.69984 (2)	0.16085 (2)	3.03 (1)
Cl(1)	0.24906 (12)	0.44310 (5)	0.30516 (5)	4.59 ((4)
Cl(2)	0.02866 (14)	0.36891 (6)	0.06892 (5)	4.90 (4)
O(*W*)	0.1940 (4)	0.5909 (2)	0.1360 (2)	5.8 (1)
O(1)	0.2457 (4)	0.3514 (2)	0.2994 (2)	6.8 (2)
O(2)†	0.1100 (5)	0.4800 (3)	0.2543 (2)	7.0 (2)
O(2′)‡	0.1007 (19)	0.4797 (11)	0.3023 (17)	13 (2)
O(3)†	0.2192 (7)	0.4631 (3)	0.3732 (2)	8.9 (3)
O(3′)‡	0.365 (3)	0.4839 (12)	0.3652 (9)	8.3 (10)
O(4)†	0.4043 (5)	0.4738 (3)	0.2910 (3)	9.6 (3)
O(4′)‡	0.338 (2)	0.4785 (8)	0.2446 (8)	5.7 (7)
O(5)†	−0.0065 (6)	0.3530 (3)	−0.0055 (2)	7.3 (2)
O(5′)‡	−0.008 (4)	0.4294 (18)	0.0188 (15)	17 (2)
O(6)†	−0.0821 (6)	0.4311 (4)	0.0885 (3)	10.7 (3)
O(6′)‡	−0.084 (5)	0.3665 (18)	0.1110 (17)	17 (2)
O(7)†	0.2054 (6)	0.3976 (3)	0.0880 (3)	8.28 (4)
O(7′)‡	0.173 (3)	0.3587 (13)	0.1049 (12)	12.3 (13)
O(8)†	0.0104 (10)	0.2910 (4)	0.1020 (3)	12.4 (4)
O(8′)‡	0.007 (4)	0.3000 (12)	0.0284 (14)	12.8 (14)
N(1)	0.3101 (3)	0.7566 (2)	0.2417 (1)	3.6 (1)
N(2)	0.5671 (4)	0.6194 (2)	0.2263 (2)	3.9 (1)
N(3)	0.5530 (4)	0.6696 (2)	0.0855 (2)	4.4 (1)
N(4)	0.2503 (5)	0.7792 (2)	0.0942 (2)	5.0 (1)
C(1)	0.4516 (5)	0.7822 (3)	0.3005 (2)	4.7 (2)
C(2)	0.5591 (6)	0.7067 (3)	0.3332 (2)	5.0 (2)
C(3)	0.6773 (5)	0.6625 (2)	0.2880 (2)	4.3 (2)
C(4)	0.7958 (6)	0.5977 (3)	0.3339 (3)	6.5 (2)
C(5)	0.6669 (6)	0.5697 (3)	0.1794 (2)	5.8 (2)
C(6)	0.7133 (6)	0.6309 (3)	0.1248 (3)	5.9 (2)
C(7)	0.4694 (7)	0.6089 (3)	0.0315 (2)	6.6 (2)
C(8)	0.6023 (6)	0.7511 (3)	0.0496 (2)	5.5 (2)
C(9)	0.4494 (8)	0.8027 (3)	0.0110 (2)	6.6 (3)
C(10)	0.3368 (6)	0.8460 (3)	0.0580 (2)	6.0 (2)
C(11)	0.2041 (9)	0.9049 (4)	0.0113 (3)	9.5 (3)
C(12)	0.1257 (6)	0.8165 (3)	0.1380 (2)	5.8 (2)
C(13)	0.2247 (5)	0.8376 (3)	0.2115 (2)	5.4 (2)
C(14)	0.1824 (5)	0.7007 (2)	0.2701 (2)	4.9 (2)

† Site occupancy = 0.8. ‡ Site occupancy = 0.2.

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

Cu—O(*W*)	2.355 (3)	N(3)—C(8)	1.508 (5)
Cu—N(1)	2.039 (3)	N(4)—C(10)	1.465 (6)
Cu—N(2)	2.031 (3)	N(4)—C(12)	1.502 (5)
Cu—N(3)	2.034 (3)	C(1)—C(2)	1.506 (6)
Cu—N(4)	2.030 (3)	C(2)—C(3)	1.526 (6)
N(1)—C(1)	1.496 (5)	C(3)—C(4)	1.534 (6)
N(1)—C(13)	1.483 (5)	C(5)—C(6)	1.498 (6)
N(1)—C(14)	1.484 (4)	C(8)—C(9)	1.518 (7)
N(2)—C(3)	1.500 (5)	C(9)—C(10)	1.514 (7)
N(2)—C(5)	1.495 (5)	C(10)—C(11)	1.544 (7)
N(3)—C(6)	1.474 (6)	C(12)—C(13)	1.529 (7)
N(3)—C(7)	1.466 (5)		

O(*W*)—Cu—N(1)	96.6 (1)	Cu—N(3)—C(8)	110.5 (2)
O(*W*)—Cu—N(2)	91.9 (1)	C(6)—N(3)—C(7)	110.3 (3)
O(*W*)—Cu—N(3)	98.8 (1)	C(6)—N(3)—C(8)	108.1 (3)
O(*W*)—Cu—N(4)	87.9 (1)	C(7)—N(3)—C(8)	108.6 (3)
N(1)—Cu—N(2)	93.1 (1)	Cu—N(4)—C(10)	116.2 (3)
N(1)—Cu—N(3)	164.6 (1)	Cu—N(4)—C(12)	104.7 (2)
N(1)—Cu—N(4)	87.8 (1)	C(10)—N(4)—C(12)	113.0 (3)
N(2)—Cu—N(3)	87.1 (1)	N(1)—C(1)—C(2)	113.8 (3)
N(2)—Cu—N(4)	179.1 (1)	C(1)—C(2)—C(3)	116.8 (3)
N(3)—Cu—N(4)	92.1 (1)	N(2)—C(3)—C(2)	109.0 (3)
Cu—N(1)—C(1)	111.5 (2)	N(2)—C(3)—C(4)	112.4 (3)
Cu—N(1)—C(13)	105.0 (2)	C(2)—C(3)—C(4)	108.8 (3)
Cu—N(1)—C(14)	113.1 (2)	N(2)—C(5)—C(6)	108.3 (3)
C(1)—N(1)—C(13)	107.7 (3)	N(3)—C(6)—C(5)	109.3 (3)
C(1)—N(1)—C(14)	109.2 (3)	N(3)—C(8)—C(9)	114.7 (4)
C(13)—N(1)—C(14)	110.1 (3)	C(8)—C(9)—C(10)	115.0 (3)
Cu—N(2)—C(3)	115.7 (2)	N(4)—C(10)—C(9)	109.5 (4)
Cu—N(2)—C(5)	105.1 (2)	N(4)—C(10)—C(11)	111.7 (4)
C(3)—N(2)—C(5)	114.6 (3)	C(9)—C(10)—C(11)	108.0 (4)
Cu—N(3)—C(6)	104.5 (2)	N(4)—C(12)—C(13)	109.0 (3)
Cu—N(3)—C(7)	114.6 (3)	N(1)—C(13)—C(12)	108.1 (3)

The structure was solved by direct and Fourier methods, and refined using full-matrix least-squares techniques. H atoms were found by difference Fourier methods, placed in theoretical positions and their B values refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Program(s) used to solve structure: *NRCVAX* (Gabe, Le Page, White & Lee, 1987). Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1986).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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catena-Poly[[(diethylenetriamine-*N*,*N*′,*N*″)-copper(II)]-*μ*-succinato-*O*,*O*′:*O*″]

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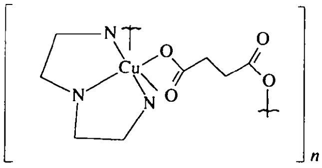
Abstract

The title compound, *catena*-poly[{[*N*-(2-aminoethyl)-1,2-ethanediamine-*N*,*N*′,*N*″]copper(II)}-*μ*-succinato-*O*,*O*′:*O*″], $[Cu(C_4H_4O_4)(C_4H_{13}N_3)]_n$, has a polymeric structure in which the central Cu atom is coordinated by three N atoms from the diethylenetriamine molecule, two O atoms from the succinate ion and one O atom from the succinate ion of the adjacent complex unit. The coordination polyhedron around the Cu atom can be regarded as a severely distorted octahedron.

Comment

Complexes of the tridentate ligand diethylenetriamine (dien) with copper and carboxylic acids exhibit many types of bridging. Most of the complexes are polymeric, such as the formato (Davey & Stephens, 1971), acetato (Towle, Hoffmann, Hatfield, Singh & Chaudhuri, 1988), phthalato (Shakhatreh *et al.*, 1991) and terephthalato (Bakalbassis *et al.*, 1991) complexes. The title compound, (I), which contains a bridging succinate ion, belongs to this family of complexes.



(I)

The structure of the title complex is shown in Fig. 1, which also indicates the atom numbering in the asymmetric unit. The complex possesses a crystallographic mirror plain passing through Cu and N2, and the O and C atoms of the succinate ion. The structure is composed of polymeric chains of complexes running parallel to the *b* axis (Fig. 2). Each unit in the chain is related to the next by a glide operation along the *b* axis. The equatorial plane is composed of the three N atoms of the diethylenetriamine ligand and the O1 atom of the succinate ion. The two apical positions are occupied by the O2 atom of the same succinate ion and the O3[i] atom of the succinate ion from the next molecule along the chain [symmetry code: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$]. Because of the unequal Cu—O2 and Cu—O3[i] bond lengths [2.663 (2) and 2.393 (2) Å, respectively], and the unequal O1—Cu—O2 and N2—Cu—O2 angles [54.20 (8) and 114.57 (8)°, respectively], the local geometry around the Cu atom is severely distorted. The coordination about the Cu atom can be regarded as distorted octahedral, with a *mer* configuration for the N and O atoms. The largest deviation of atoms N1, N2, N1[ii] and O1 from their mean basal

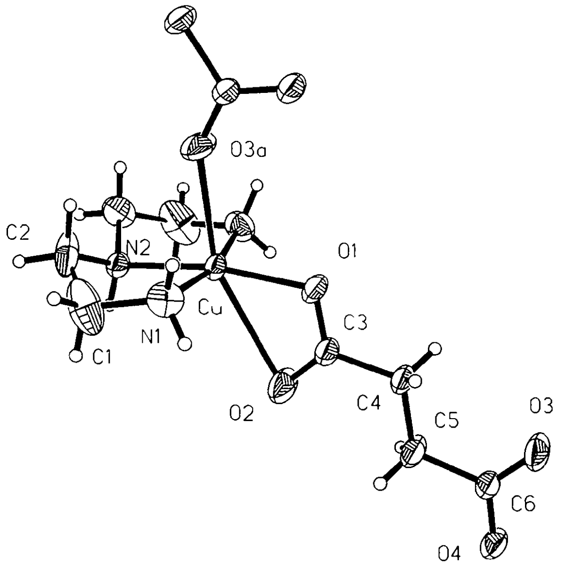


Fig. 1. The structure of compound (I) showing 50% probability displacement ellipsoids.

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