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trans-Diaqua(*C*-*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)copper(II) dichloride dihydrate

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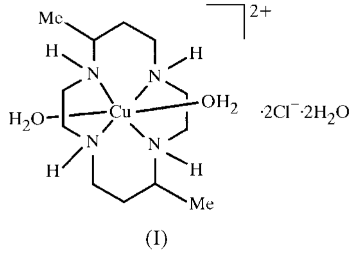
The crystal structure of the title complex, $[Cu(C_{12}H_{28}N_4)(H_2O)_2]Cl_2\cdot 2H_2O$, has been determined. The Cu^{II} atom is octahedrally coordinated by the four N atoms of the tetradentate macrocyclic ligand in equatorial positions and by the O atoms of two water molecules in axial positions. The crystal structure is stabilized by a three-dimensional network of hydrogen bonds.

Comment

The macrocyclic ligand 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane exists as two isomers, *i.e.* *C*-*meso* and *C*-*rac*. The coordination behaviour of transition metal complexes of *C*-*meso*- and *C*-*rac*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane has been widely studied (Chen *et al.*, 1994; Hay *et al.*, 1984; Hay & Govan, 1992; Hay & Piplani, 1977). The crystal structures of complexes of the *C*-*rac* isomer with Cu^{II} and Co^{III} have been reported previously (Panneerselvam *et al.*, 1999; Tahirov *et al.*, 1994). The present paper reports the crystal structure of the copper(II) complex of the *C*-*meso* isomer, (I).



(I)

The Cu^{II} ion is six-coordinated in a distorted octahedral geometry with the four N atoms of the macrocyclic ligand in equatorial positions and two O atoms of two water molecules in axial positions (Fig. 1). This compound is not a symmetric complex, since the two *trans* water molecules and the four N atoms of the tetradentate ligand are coordinated at different distances. In the majority of monomeric *trans*-diaqua-copper(II) complexes, the Cu atom is located at a centre of symmetry or on a twofold axis (Allen & Kennard, 1993). There are only a few examples where the *trans*-diaqua-copper(II) octahedral complex is not centrosymmetric (Kozhemyak *et al.*, 1980; Biagini Cingi *et al.*, 1989; Petrovčič *et al.*, 1999).

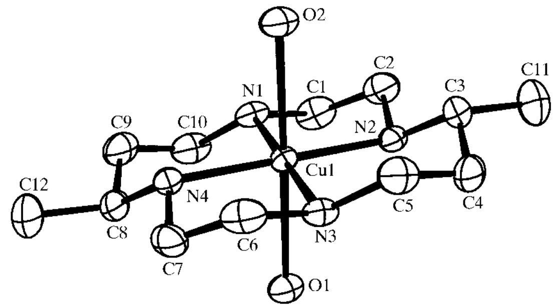


Figure 1
The structure of the title complex showing 30% probability displacement ellipsoids. The chloride anions, the uncoordinated water molecules and the H atoms have been omitted for clarity.

The Cu^{II} ion and the four N-donor atoms are coplanar within 0.004 (1) Å. The Cu—N distances are in the range 1.997 (2)–2.047 (2) Å and the average Cu—N distance, 2.023 (2) Å, is similar to the average Cu—N distance found for Cu^{II} tetraaza macrocyclic complexes [2.03 (3) Å; Lu *et al.*, 1991]. The Cu—O$_{water}$ distances, 2.542 (2) and 2.505 (2) Å, are shorter than those found in *trans*-diaquacopper(II) tetraaza macrocyclic complexes of the type *trans*-[Cu(*C*-*meso*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane)(H$_2$O)$_2$]X_2, *i.e.* 2.624 (3) Å for X = NO$_2$, 2.692 (2) Å for X = Cl, 2.695 (2) Å for X = Br and 2.725 (3) Å for X = I (Lu *et al.*, 1999). The tetradentate ligand adopts a conformation with two six-membered rings in a chair form and two five-membered rings in a *gauche* form. The arrangement of the four chiral nitrogen centers is in the type-III configuration designated by Bosnich *et al.* (1965). The two C-methyl groups occupy equatorial positions. The complex has a 1*SR*,4*RS*,8*RS*,11*SR* configuration for the four chiral N-atom centres and a 5*SR*,12*RS* configuration for the two chiral C-atom centres. The crystal structure is stabilized by hydrogen bonds (Table 2).

Experimental

The ligand *C*-*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane was prepared according to Hay & Piplani (1977). Equimolar quantities of copper(II) sulfate pentahydrate and *C*-*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane were dissolved in water and left to react for *ca* 30 min in a steam bath. The resulting solution was evaporated to dryness by rotatory evaporation. The crystals were obtained from a 2 *M* NaCl aqueous solution on slow evaporation.

Crystal data

$[Cu(C_{12}H_{28}N_4)(H_2O)_2]Cl_2\cdot 2H_2O$
$M_r = 434.89$
Monoclinic, $P2_1/c$
$a = 8.043$ (1) Å
$b = 17.482$ (4) Å
$c = 15.237$ (3) Å
$\beta = 102.30$ (1)°
$V = 2093.4$ (7) Å^3
$Z = 4$
$D_x = 1.380$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.41$–$17.34°$
$\mu = 1.319$ mm^{-1}
$T = 293$ (2) K
Pillar, blue
0.375 × 0.313 × 0.280 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.619$, $T_{max} = 0.691$
7942 measured reflections
3688 independent reflections
2947 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 25°$
$h = 0 \rightarrow 9$
$k = -20 \rightarrow 20$
$l = -18 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.076$
$S = 1.016$
3688 reflections
210 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.3263P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	2.542 (2)	Cu1—N1	2.005 (2)
Cu1—O2	2.505 (2)	Cu1—N2	2.043 (2)
Cu1—N3	1.997 (2)	Cu1—N4	2.047 (2)
O1—Cu1—O2	177.77 (6)	N4—Cu1—O2	88.77 (7)
N1—Cu1—O1	89.51 (7)	N3—Cu1—N1	179.31 (7)
N2—Cu1—O1	90.13 (6)	N3—Cu1—N2	94.36 (8)
N3—Cu1—O1	89.83 (7)	N1—Cu1—N2	85.45 (8)
N4—Cu1—O1	89.56 (6)	N3—Cu1—N4	86.00 (8)
N1—Cu1—O2	92.09 (7)	N1—Cu1—N4	94.18 (8)
N2—Cu1—O2	91.55 (7)	N2—Cu1—N4	179.52 (8)
N3—Cu1—O2	88.58 (7)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *NRCVAX*; software used to prepare material for publication: *SHELXL*97.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···Cl2	0.91	2.52	3.337 (2)	150
N2—H1N2···Cl1^{i}	0.91	2.44	3.343 (2)	175
N3—H1N3···O3	0.91	2.25	3.096 (3)	155
N4—H1N4···Cl1	0.91	2.49	3.341 (2)	167
O1—H1O1···Cl1^{i}	0.88	2.25	3.118 (2)	168
O1—H2O1···Cl2^{i}	0.87	2.32	3.188 (2)	173
O2—H1O2···Cl1	0.91	2.23	3.120 (2)	163
O2—H2O2···O3^{ii}	0.78	2.00	2.746 (3)	161
O3—H1O3···O4^{iii}	0.87	1.87	2.728 (3)	170
O3—H2O3···Cl2^{i}	1.08	2.12	3.131 (2)	154
O4—H1O4···Cl2^{iv}	0.85	2.34	3.175 (2)	167
O4—H2O4···Cl2	0.99	2.18	3.175 (2)	180

Symmetry codes: (i) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (ii) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (iii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $-x, 1-y, 1-z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1090). Services for accessing these data are described at the back of the journal.

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