

[2,13-Bis(acetamido)-5,16-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane]copper(II) dichloride octahydrate

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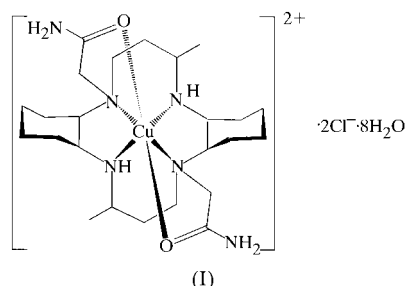
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The title compound, $[\text{Cu}(\text{C}_{24}\text{H}_{46}\text{N}_6\text{O}_2)]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, contains a centrosymmetric cation, with the anions and water molecules on general sites. The coordination geometry around the Cu^{II} ion is an axially elongated octahedron, with $\text{Cu}-\text{N}$ distances of 2.0448 (17) and 2.0847 (17) Å, and a $\text{Cu}-\text{O1}$ distance of 2.3138 (16) Å.

Comment

The transition metal(II) complexes of partially *N*-functionalized 14-membered tetraaza macrocycles have been studied much less extensively than those of the fully *N*-functionalized analogs. This may be due to the fact that the synthesis of partially *N*-substituted macrocycles is complicated and requires several steps (Pallavicini *et al.*, 1987). The crystal structure of the title compound, [2,13-bis(acetamido)-5,16-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane]copper(II) dichloride octahydrate, (I), exhibits a tetragonally elongated octahedral geometry with bonds from the Cu^{II} atom to the secondary and tertiary amines of the macrocycle and to two O atoms of the pendant acetamide groups.



In the complex $[\text{Cu}(\text{C}_{24}\text{H}_{46}\text{N}_6\text{O}_2)]^{2+}$ cation, the two acetamide groups are attached to the less sterically hindered N

atoms of the macrocyclic ligand. The $\text{Cu}-\text{N2}$ (tertiary amine) distance of 2.0847 (17) Å is slightly longer than the $\text{Cu}-\text{N1}$ (secondary amine) distance [2.0448 (17) Å]. The axial $\text{Cu}-\text{O1}$ distance of 2.3138 (16) Å is considerably longer than the equatorial $\text{Cu}-\text{N}$ distances. This long axial $\text{Cu}-\text{O}$ distance may be due to the well established Jahn–Teller effect. The equatorial $\text{Cu}-\text{N}$ and axial $\text{Cu}-\text{O}$ bond lengths are typical of tetraaza macrocyclic copper(II) complexes (Choi *et al.*, 1999). The axial $\text{N2}-\text{Cu}-\text{O1}$ bond angle [99.91 (6)°] of the five-membered chelate ring is expected for the bite angle of this type of macrocyclic ligand. The other angle [$\text{N1}-\text{Cu}-\text{O1}$ 83.64 (6)°] may be due to steric hindrance involving the C13 methyl group. The $\text{O1}=\text{C15}$ bond length [1.234 (3) Å] clearly shows double-bond character. The two pendant acetamide groups in the complex are *trans* with respect to one another,

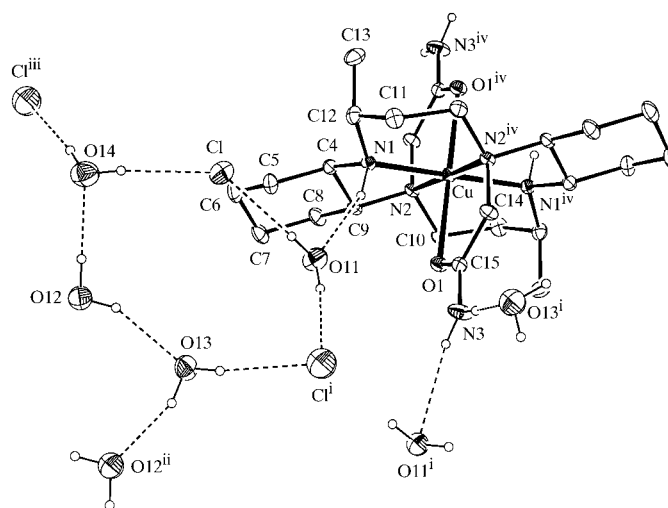


Figure 1

View (Farrugia, 1997) of (I) with 20% probability displacement ellipsoids. The Cu atom occupies an inversion center and only the asymmetric unit is labeled. The symmetry codes are as given in Table 2 with the addition of (iv) $1-x, -y, -z$.

and the configuration of the ligand is *trans*-III in the solid state. Interestingly, the acetamide N3 and secondary amine N1 atoms of the macrocycle form hydrogen bonds with the water molecules. Hydrogen bonds among N1, N3, four water molecules and a chloride ion form a three-dimensional molecular network and are presumably responsible for the stability of this crystal (Table 2).

Experimental

The ligand 2,13-bis(acetamido)-5,16-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane was synthesized according to the method of Maumela *et al.* (1995). A methanol solution (20 ml) of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (185 mg, 0.5 mmol) and the free ligand (225 mg, 0.5 mmol) was heated under reflux for 1 h and then cooled to room temperature. The solution was filtered off and left at room temperature until deep-blue crystals formed. The product was filtered off and recrystallized from a hot water–acetonitrile (1:1, 10 ml) mixture.

Crystal data

[Cu(C₂₄H₄₆N₆O₂)]Cl₂·8H₂O
M_r = 729.24
 Monoclinic, *P*2₁/*c*
a = 11.210 (4) Å
b = 17.709 (3) Å
c = 9.2126 (16) Å
 β = 107.423 (19)°
V = 1745.0 (8) Å³
Z = 2

D_x = 1.388 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 11.4–12.7°
 μ = 0.84 mm⁻¹
T = 293 (2) K
 Block, dark blue
 0.48 × 0.46 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Non-profiled $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.662, *T_{max}* = 0.778
 3262 measured reflections
 3060 independent reflections
 2551 reflections with *I* > 2σ(*I*)

R_{int} = 0.044
 θ_{\max} = 25.0°
h = -13 → 12
k = 0 → 21
l = 0 → 10
 3 standard reflections
 frequency: 300 min
 intensity decay: 3%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.035
wR (*F*²) = 0.092
S = 1.08
 3060 reflections
 222 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.4858P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.46 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu—N1	2.0448 (17)	O1—C15	1.234 (3)
Cu—N2	2.0847 (17)	N3—C15	1.312 (3)
Cu—O1	2.3138 (16)		
N1—Cu—O1	83.64 (6)	N2—Cu—O1	99.91 (6)

The eight H atoms of the water molecules were found from a difference Fourier map, their positions were constrained using *DFIX* and their displacement parameters were refined as a common variable [0.079 (4) Å²]. The positions of all remaining H atoms were calculated geometrically and constrained to ride on their attached atoms (C—H = 0.96–0.98 Å), with isotropic displacement parameters fixed at 1.2 (C or N) or 1.5 (methyl C) times the equivalent isotropic displacement parameters of their parent atoms. The highest peak and deepest hole in the final difference density map were 1.09 Å from Cu and 0.76 Å from Cl, respectively.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O11	0.91	2.35	3.220 (3)	160
N3—H3A...O11 ⁱ	0.86	2.58	3.217 (3)	132
N3—H3B...O13 ⁱ	0.86	2.02	2.878 (3)	177
O11—H111...Cl	0.86 (2)	2.32 (2)	3.184 (3)	174 (3)
O11—H112...Cl ⁱ	0.87 (2)	2.59 (3)	3.447 (3)	167 (3)
O12—H121...O13	0.82 (2)	2.04 (3)	2.812 (4)	156 (4)
O12—H122...O14	0.86 (2)	1.87 (2)	2.734 (4)	177 (4)
O13—H131...Cl ⁱ	0.82 (2)	2.29 (2)	3.090 (2)	167 (3)
O13—H132...O12 ⁱⁱ	0.85 (2)	1.90 (3)	2.706 (4)	158 (3)
O14—H141...Cl ⁱⁱⁱ	0.86 (2)	2.36 (2)	3.216 (3)	172 (3)
O14—H142...Cl	0.84 (2)	2.34 (2)	3.175 (3)	173 (3)

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1322). Services for accessing these data are described at the back of the journal.

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