

RefinementRefinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.049$$

$$wR(F^2) = 0.143$$

$$S = 1.071$$

3400 reflections

343 parameters

H atoms: see below

$$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.5731P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.014$$

$$\Delta\rho_{\max} = 0.13 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)Table 1. Selected bond distances (\AA) for compounds (1), (2), (3) and (4)

		(1)	(2) ^a	(3) ^a	(4)
O1	C4	1.357 (2)	1.36 (5)	1.357 (3)	1.350 (4)
O1A	C4A		1.358 (5)	1.359 (3)	
O2	C5	1.260 (2)	1.259 (4)	1.264 (3)	1.275 (4)
O2A	C5A		1.254 (4)	1.260 (3)	
N1	C8	1.451 (2)	1.457 (4)	1.446 (4)	1.480 (5)
N1A	C8A		1.457 (4)	1.451 (3)	
C3	C4	1.365 (3)	1.359 (4)	1.366 (4)	1.375 (5)
C3A	C4A		1.360 (4)	1.365 (4)	
C4	C5	1.435 (3)	1.428 (5)	1.432 (4)	1.410 (5)
C4A	C5A		1.437 (5)	1.431 (4)	

Note: (a) two independent molecules.

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$) for (1), (2) and (3)

Compound	D—H...A	H...A	D...A	D—H...A
(1)	O1—H1...O2 ⁱ	1.72	2.692 (2)	151
(2)	O1—H1...O2A	1.84	2.686 (3)	140
	O1A—H1A...O2	1.88	2.688 (3)	156
(3)	O1—H1A...O2A	1.64	2.635 (3)	162
	O1A—H1AA...O2	1.82	2.654 (3)	142

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

For compound (3), the data collection initially had $\theta_{\max} = 25^\circ$, but it became obvious that no useful diffraction was occurring above $\theta = 22.5^\circ$, so this limit was adopted thereafter. For all three structures, the bridging hydroxyl H atoms were located from difference Fourier syntheses. The positions of the disordered H atoms on C15 for (1) and the H atoms on the disordered methyl C atoms C1B and C1C for (3) were also located from difference Fourier maps. The remaining H atoms were introduced at geometrically calculated positions (C—H = 0.96 \AA). All H atoms were then refined using riding models with a single fixed value for $U_{\text{iso}} = 0.08 \text{ \AA}^2$.

For all compounds, data collection: XSCANS (Fait, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1990a); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: SHELXTL/PC (Sheldrick, 1990b); software used to prepare material for publication: SHELXTL/PC.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1164). Services for accessing these data are described at the back of the journal.

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Inclusion Complex of *rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane with Hydrochloride and Water

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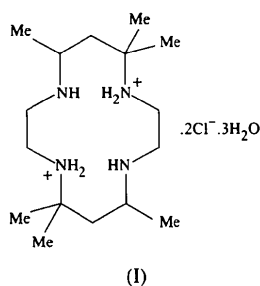
Abstract

In the crystal structure of the title compound, $\text{C}_{16}\text{H}_{38}\text{N}_4^{2+}\cdot 2\text{Cl}^- \cdot 3\text{H}_2\text{O}$, a rather complex hydrogen-bonding network is observed. The macrocycle is stabilized as a dication, 5,5,7,12,12,14-hexamethyl-1,8-diazacyclotetradecane, forming N—H...Cl and N—H...O hydrogen bonds. The water molecules are distinguished by their inequality in structure formation. They are involved in different types of intermolecular hydrogen bonding in the crystal lattice.

Comment

The field of coordination chemistry of polyazamacrocycles has undergone spectacular growth since the early 1960s, following the pioneering contribution of Curtis (1964). The macrocyclic ligand 5,5,7,12,12,14-

hexamethyl-1,4,8,11-tetraazacyclotetradecane (*L*) exists as two isomers, 'teta' (the *meso* form) and 'tetb' (the racemic form), for which crystal structures have been determined as the dihydrate (Gluziński *et al.*, 1980) and the monohydrate (Krajewski *et al.*, 1977), respectively. The metal-free *meso* tetramine crystallizes with an internal centre of symmetry such that all four N atoms are coplanar. Conversely, the racemic isomer as a free molecule crystallizes with twofold rotation symmetry and the four N atoms are not coplanar, deviating by ± 0.66 Å from their mean plane. The coordination behaviour of both of the isomers has been studied extensively, both chemically and crystallographically, with respect to their selective complexation with various metal cations (Lessard *et al.*, 1992; Hu *et al.*, 1996; Muñoz *et al.*, 1995). As ligands, both of these isomers can bind in either a planar or a folded geometry, which results in *trans* or *cis* sixfold-coordinated complexes. What interested us most was their behaviour and conformational changes upon complexation with neutral and charged inorganic entities. In order to investigate the bonding and ligand properties in more detail, we synthesized the title compound, (I), and determined its crystal structure.



The asymmetric unit contains half of a macrocyclic cation, a chloride anion and two water molecules, one occupying a general position, the other on a twofold axis. The additional H atoms (in comparison with the neutral form) were found at the N atoms (N2 and its symmetry equivalent) bonded to the C atoms that bear geminal methyl groups, in the same manner as in *meso*-LH₂²⁺·2SCN⁻ (Drew & Mok, 1987). The N atoms in these positions have stronger basicity than the other pair of N atoms. Two intramolecular hydrogen bonds of the N—H···N type help to stabilize the macrocycle, each forming a six-membered ring in the chair form with an N···N distance of 2.777 (3) Å [*cf.* 2.85 (2) Å in *meso*-LH₂²⁺·2SCN⁻ (Drew & Mok, 1987)]. A comparison of the values of the bond distances and valence angles with those observed in other structures found in the literature that contain teta or tetb moieties shows no significant differences. The macrocycle adopts a conformation with the N atoms non-coplanar [± 0.636 (1) Å] and with four of the six methyl groups on one side, and the other two (C21 and its symmetry equivalent) on the other side

of the mean plane of the N atoms. All C—C bonds are in a *gauche* conformation, while the C—N bonds are in an *anti* conformation, except for two [C4—N2—C5—C1 and its symmetry equivalent are -69.1 (2) and 69.1 (2)^o, respectively].

The organization of the complex can be represented as [LH₂²⁺·2Cl⁻·H₂O]·2H₂O (Fig. 1). This arrangement is stabilized both by electrostatic interactions and by hydrogen bonds. The chloride ion is involved in an N—H···Cl hydrogen bond with a distance of 3.158 (2) Å. The O1W water molecule approaches the opposite side of the macrocycle and is attached *via* both of its lone pairs to two other NH binding sites (at N1 and its symmetry equivalent), being in a 'perching' mode above the tetraaza macrocycle, 3.17 Å from the average plane of the macrocyclic cavity; this is in contrast to HL1-2HBr·H₂O (*L*1 is the acetyl derivative of *meso*-*L*), where a water molecule is attached to the macrocycle through only one hydrogen bond (Xu *et al.*, 1988). In turn, the H atoms of O1W are involved in O—H···Cl hydrogen bonds with the chloride anions that are displaced by one unit-cell translation, thus forming chains along the *b* axis of the crystal (Fig. 2). Thus, O1W realizes all of its opportunities for binding, forming two N—H···O and two O—H···Cl⁻ short contacts. The environment of the other water molecule, O2W, differs from that of O1W. It forms two hydrogen bonds to two centrosymmetrically related chloride ions. The O2W···Cl1 distances are 3.241 (3) and 3.308 (2) Å involving the Cl1⁻ ions in the symmetry-equivalent positions ($-x, -y, -z + 1$) and (x, y, z), respectively. In turn, each chloride anion is also involved in two hydrogen bonds to the two centrosymmetrically related water molecules and, thus, a parallelogram of two chloride ions and two water molecules is formed (Fig. 2). Very similar water-halogen anion parallelograms have been described previously (Nieslanik *et al.*, 1996; Suwińska, 1995). O1W serves as a bridge between such parallelograms, thus uniting

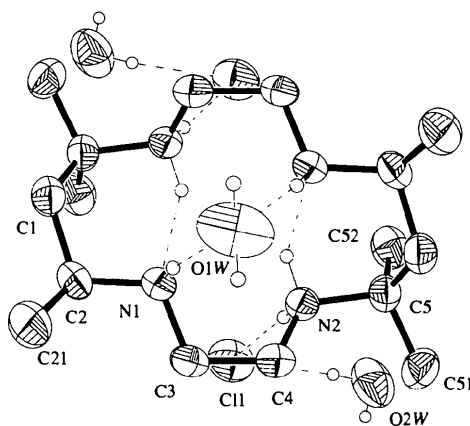


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids. C-bound H atoms have been omitted for clarity.

the aforementioned chains in layers along the [111] direction in the unit cell. Fig. 2 shows a view of one of these layers. There are no intermolecular contacts shorter than the sum of the relevant van der Waals radii between layers. Both independent water molecules appear to be hydrogen bonded to the halogen anion in this structure, as in Ni(*meso-L*)Cl₂·2H₂O (Ito & Toriumi, 1981) and Ni(*meso-L*)F₂·5H₂O (Toriumi & Ito, 1981). Thus, the structure is stabilized by a set of different types of inter- and intramolecular contacts: N—H···Cl, N—H···OW, Cl···OW and N—H···N.

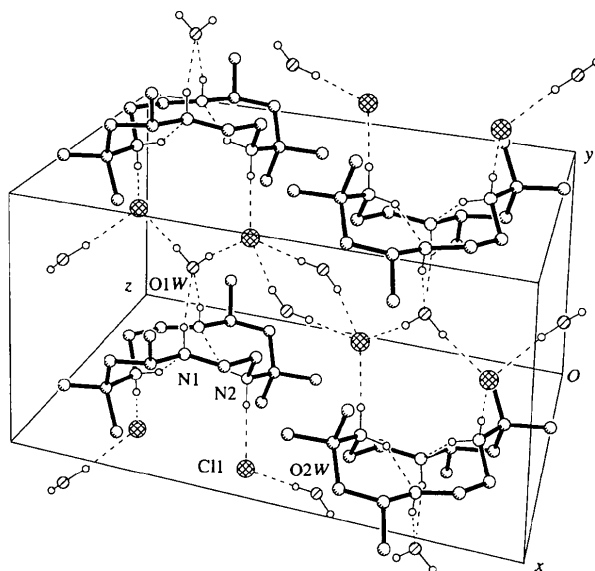


Fig. 2. Unit-cell contents.

Experimental

Complex (I) was easily synthesized by mixing *rac-L* (141 mg, 0.5 mmol) with 7 ml of CCl₄ at room temperature under aerobic conditions. Colourless transparent crystals of the complex were obtained by leaving the solution to evaporate at room temperature for 2–3 d. Elemental analysis found Cl 16.95, N 13.75%; C₁₆H₄₄Cl₂N₄O₃ requires Cl 17.23, N 13.62%.

Crystal data

C₁₆H₃₈N₄²⁺·2Cl⁻·3H₂O

M_r = 411.45

Monoclinic

*C*2/*c*

a = 18.123 (4) Å

b = 7.924 (2) Å

c = 17.732 (4) Å

β = 111.11 (3)°

V = 2375.5 (10) Å³

Z = 4

D_x = 1.150 Mg m⁻³

D_m not measured

Cu Kα radiation

λ = 1.5418 Å

Cell parameters from 30 reflections

θ = 11.55–19.32°

μ = 2.619 mm⁻¹

T = 293 (2) K

Prism

0.50 × 0.30 × 0.25 mm

Colourless

Data collection

Siemens AED four-circle diffractometer

Profile-fitted ω–2θ scans

Absorption correction: none

2352 measured reflections

1305 independent reflections

1279 reflections with

I > 2σ(*I*)

*R*_{int} = 0.055

θ_{max} = 70.05°

h = –16 → 21

k = –9 → 6

l = –21 → 21

3 standard reflections

every 100 reflections

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.037

wR(*F*²) = 0.107

S = 1.023

1280 reflections

115 parameters

H atoms riding

w = 1/[σ²(*F*_o²) + (0.0556*P*)²]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.166 e Å⁻³

Δρ_{min} = –0.132 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0014 (2)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cl1	0.03806 (5)	0.20361 (10)	0.61348 (5)	0.0737 (3)
N1	0.08938 (10)	0.6888 (2)	0.74331 (10)	0.0403 (5)
N2	–0.05345 (10)	0.5283 (2)	0.63500 (10)	0.0407 (5)
C1	0.18294 (14)	0.6648 (3)	0.88516 (14)	0.0483 (6)
C2	0.17432 (13)	0.6832 (3)	0.79597 (15)	0.0499 (6)
C21	0.2208 (2)	0.8354 (5)	0.7848 (2)	0.0800 (10)
C3	0.07616 (14)	0.6617 (3)	0.65736 (13)	0.0491 (6)
C4	–0.01167 (14)	0.6619 (3)	0.60675 (14)	0.0488 (6)
C5	–0.14316 (13)	0.5109 (3)	0.59343 (14)	0.0448 (6)
C51	–0.1639 (2)	0.5001 (4)	0.50194 (14)	0.0619 (8)
C52	–0.1651 (2)	0.3467 (3)	0.6252 (2)	0.0584 (7)
O1W	0	1.0090 (4)	3/4	0.0985 (11)
O2W	–0.12233 (13)	0.0212 (3)	0.4854 (2)	0.0949 (8)

Table 2. Selected geometric parameters (°)

C3—N1—C2	113.1 (2)	N1—C3—C4	110.9 (2)
C4—N2—C5	118.9 (2)	N2—C4—C3	110.6 (2)
C5 ¹ —C1—C2	116.6 (2)	N2—C5—C1 ¹	108.8 (2)
N1—C2—C1	110.3 (2)		
C1—C2—N1—C3	–164.9 (2)	C4—N2—C5—C1 ¹	–69.1 (2)
C2—N1—C3—C4	177.8 (2)	N2—C5—C1 ¹ —C2 ¹	–66.0 (3)
N1—C3—C4—N2	–58.5 (3)	C5—C1 ¹ —C2 ¹ —N1 ¹	57.6 (3)
C3—C4—N2—C5	178.2 (2)		

Symmetry code: (i) –*x*, *y*, $\frac{3}{2}$ – *z*.

Table 3. 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—H1A···O1W	0.90	2.15	3.035 (3)	168
N2—H2A···Cl1	0.90	2.26	3.158 (2)	171
N4—H2B···N1 ¹	0.94	1.96	2.777 (3)	145
O1W—H1W1···Cl1 ⁱⁱ	0.92	2.24	3.149 (2)	171
O2W—H1W2···Cl1 ⁱⁱⁱ	0.93	2.33	3.241 (3)	167
O2W—H2W2···Cl1	0.94	2.37	3.308 (2)	175

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

Application of an empirical absorption correction to the data made no significant difference to the final results, which are based on uncorrected data. Difference Fourier maps showed the sites for the water and N-bound H atoms. All H atoms were refined using a riding model with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: *AED* (Bocelli *et al.*, 1993). Cell refinement: *AED*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1175). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 436–437

2-(N-Acetylamino)pent-4-ynamide

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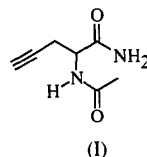
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Abstract

The title compound, C₇H₁₀N₂O₂, displays extensive hydrogen-bonding interactions which give rise to connected 10- and 11-membered rings throughout the lattice.

Comment

Inter- and intramolecular hydrogen-bonding interactions are essential for the biological activity of proteins and oligopeptides. In order to probe the nature of their hydrogen-bonding potential, peptidomimetics have been developed (Gung & Zhu, 1996; Mrksich & Dervan, 1995; Gante, 1994). A systematic study of the hydrogen-bonding characteristics of alkynylamino acid amidates (Crisp *et al.*, 1997) has been undertaken in order to ascertain the structural motifs important in defining



the three-dimensional arrays within oligopeptides. As a part of this study, the title compound, (I), has been investigated crystallographically.

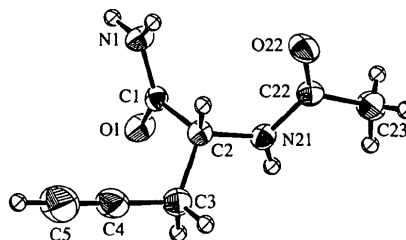


Fig. 1. The title structure drawn with 50% probability ellipsoids.

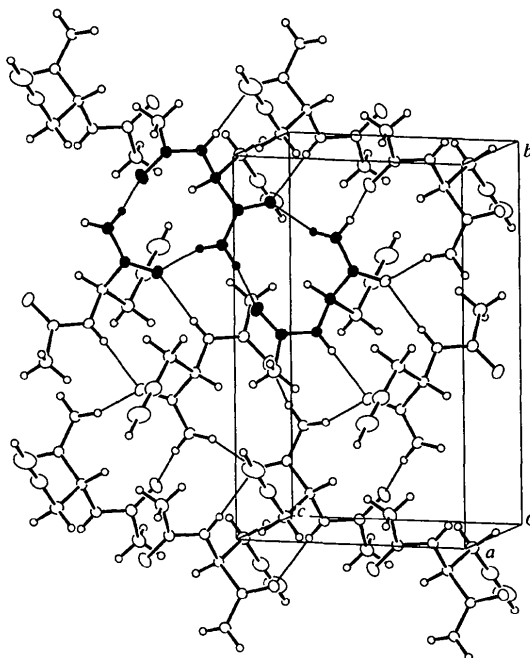


Fig. 2. Unit-cell contents highlighting the different hydrogen-bonding associations.