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

Cl—C(4′)	1.741 (3)	N(1)—N(2)	1.315 (2)
N(1)—C(1′)	1.405 (3)	N(2)—C(2)	1.307 (3)
O(1)—C(3)	1.225 (3)	O(2)—C(1)	1.224 (3)
C(1′)—C(2′)	1.389 (3)	C(1′)—C(6′)	1.386 (3)
C(2′)—C(3′)	1.377 (3)	C(3′)—C(4′)	1.375 (4)
C(4′)—C(5′)	1.383 (4)	C(5′)—C(6′)	1.373 (4)
C(2)—C(3)	1.482 (3)	C(2)—C(1)	1.466 (3)
C(3)—C(4)	1.477 (3)	C(4)—C(5)	1.386 (3)
C(4)—C(9)	1.398 (3)	C(5)—C(6)	1.387 (4)
C(6)—C(7)	1.384 (4)	C(7)—C(8)	1.385 (4)
C(8)—C(9)	1.379 (3)	C(9)—C(1)	1.487 (3)
N(2)—N(1)—C(1′)	119.8 (2)	N(1)—N(2)—C(2)	118.8 (2)
N(1)—C(1′)—C(2′)	118.5 (2)	N(1)—C(1′)—C(6′)	122.2 (2)
C(2′)—C(1′)—C(6′)	119.3 (2)	C(1′)—C(2′)—C(3′)	120.5 (2)
C(2′)—C(3′)—C(4′)	119.6 (2)	Cl—C(4′)—C(3′)	119.7 (2)
Cl—C(4′)—C(5′)	120.0 (2)	C(3′)—C(4′)—C(5′)	120.3 (2)
C(4′)—C(5′)—C(6′)	120.2 (3)	C(1′)—C(6′)—C(5′)	120.0 (2)
N(2)—C(2)—C(3)	121.2 (2)	N(2)—C(2)—C(1)	130.3 (2)
C(3)—C(2)—C(1)	108.5 (2)	O(1)—C(3)—C(2)	127.0 (2)
O(1)—C(3)—C(4)	127.1 (2)	C(2)—C(3)—C(4)	105.9 (2)
C(3)—C(4)—C(5)	128.7 (2)	C(3)—C(4)—C(9)	110.1 (2)
C(5)—C(4)—C(9)	121.2 (2)	C(4)—C(5)—C(6)	117.4 (2)
C(5)—C(6)—C(7)	121.4 (2)	C(6)—C(7)—C(8)	121.0 (2)
C(7)—C(8)—C(9)	118.2 (2)	C(4)—C(9)—C(8)	120.7 (2)
C(4)—C(9)—C(1)	109.1 (2)	C(8)—C(9)—C(1)	130.2 (2)
O(2)—C(1)—C(2)	126.5 (2)	O(2)—C(1)—C(9)	127.1 (2)
C(2)—C(1)—C(9)	106.4 (2)		

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HA1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Isomers of 5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradecane

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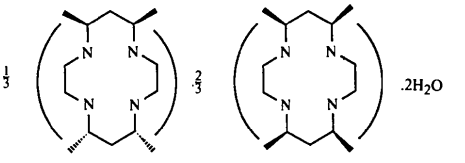
Abstract

The structure of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane dihydrate, $C_{14}H_{32}N_4.2H_2O$, contains molecules of 5*SR*,7*RS*,12*RS*,14*SR*-tetramethyl-1,4,8,11-tetraazacyclotetradecane (which are centrosymmetric) and 5*SR*,7*RS*,12*SR*,14*RS*-tetramethyl-1,4,8,11-tetraazacyclotetradecane, with different macrocycle conformations and different configurations of the four chiral C atoms. The crystal structure is stabilized by hydrogen bonds.

Comment

Polyazamacrocyclic compounds have been studied extensively because they could be potential ligands in transition metal complexes (Lindoy, 1989). Previously, Kolinski & Korybut-Daszkiewicz (1975) described the preparation of the macrocyclic ligand 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The reduction of this ligand can result in five diastereoisomeric tetraamines *A* to *E*. Herein, we report the crystal and molecular structure of the diastereoisomers *A* and *B* of the reduction product, 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane, which crystallized as the dihydrate, (I).



(I)

The structure contains two independent molecules of the diastereoisomers *A* and *B*. The asymmetric unit contains half of molecule *A*, which has a crystallographic inversion center, molecule *B* in a general position and three disordered water molecules. In molecule *A* the four N atoms are exactly coplanar as a result of the sym-

metry of the molecule. The four chiral carbon centers for molecule *A* are 5*SR*,7*RS*,12*RS*,14*SR*. In molecule *B* the four N atoms are coplanar to within ±0.007 (3) Å. The four chiral carbon centers for molecule *B* are 5*SR*,7*RS*,12*SR*,14*RS*. The structures of two nickel(II) complexes of the ligand *A* have been reported (Hay, Jeragh, Ferguson, Kaitner & Ruhe, 1982). The conformation of the free ligand *A* is conserved in both of these complexes and the configurations of the chiral nitrogen centers in these two complexes are 1*RS*,4*RS*,8*SR*,11*SR*. If the conformation of the free ligand *B* is conserved after complexation then the configurations of the chiral nitrogen centers in the bonded ligand *B* should be 1*SR*,4*RS*,8*SR*,11*RS*.

In both ligands *A* and *B* the amine H atoms are disordered. Hydrogen bonds between the N atoms and the water molecules help to stabilize the crystal structure.

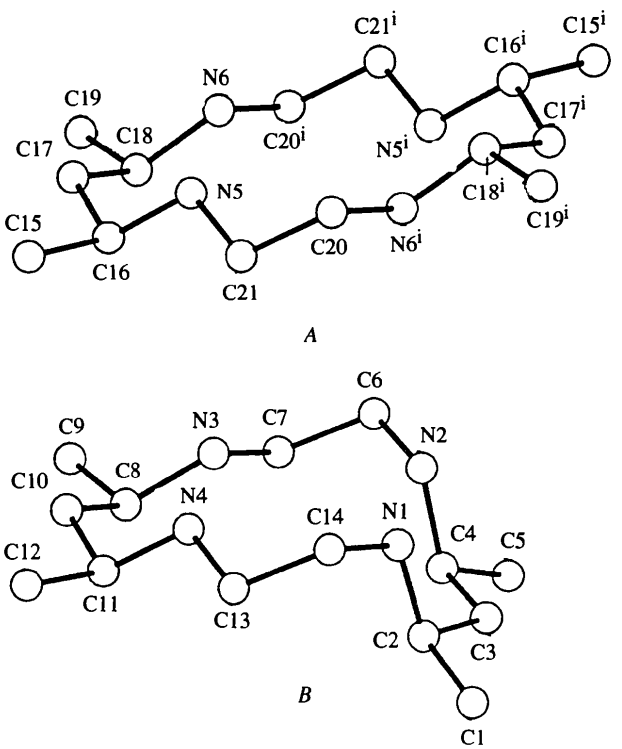


Fig. 1. A perspective view of molecules *A* and *B* showing the atom-numbering scheme. H atoms and water molecules have been omitted. The molecules are oriented separately to show the differences of their conformations more clearly. [Symmetry code: (i) $1-x, 1-y, -z$.]

Experimental

5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate was prepared as a precursor from pent-3-en-2-one and ethylenediamine, as described in the literature (Hay & Jeragh, 1977), as a mixture of C-*meso* and C-*rac* diastereoisomers. 20 g of this precursor were dissolved in methanol–water [1:1 (*v*/*v*), 200 ml] and $NaBH_4$ (12 g, excess) was added in small amounts (*ca* 0.5 g) with stirring over a period of *ca* 1 h. The resulting solution was heated on a water bath for *ca* 1 h until evolution of H_2 ceased. The solvent was removed on a rotary evaporator and sodium hydroxide solution (2 *M*) added. The aqueous solution was then continuously extracted with chloroform. The chloroform extract was dried and dissolved in hot xylene. Colorless transparent crystals were obtained on standing the solution in a refrigerator for several days.

Crystal data

$C_{14}H_{32}N_4.2H_2O$
$M_r = 292.46$
Triclinic
$P\bar{1}$
$a = 8.6917\ (7)$ Å
$b = 11.576\ (1)$ Å
$c = 15.006\ (3)$ Å
$\alpha = 110.10\ (2)°$
$\beta = 103.80\ (1)°$
$\gamma = 91.465\ (9)°$
$V = 1367.3\ (3)$ Å^3
$Z = 3$
$D_x = 1.066$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.42–15.04°$
$\mu = 0.07$ mm^{-1}
$T = 298\ (3)$ K
Cuboid
0.44 × 0.43 × 0.42 mm
Transparent, colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.8178$, $T_{max} = 0.9989$
3860 measured reflections
3572 independent reflections
2688 observed reflections [$I \geq \sigma(I)$]
$R_{int} = 0.008$
$\theta_{max} = 22.5°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = -16 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 14%

Refinement

Refinement on *F*
$R = 0.051$
$wR = 0.068$
$S = 1.21$
2688 reflections
488 parameters
$w = 1/[\sigma^2(F_o) + 0.002F_o^2]$
$(\Delta/\sigma)_{max} = 0.251$
$\Delta\rho_{max} = 0.28\ (4)$ e Å^{-3}
$\Delta\rho_{min} = -0.11\ (4)$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: 1.2 (2) (length in mm)
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)

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

	Occupancy	*x*	*y*	*z*	B_{eq}
O(*W*1)	0.50	0.4984 (10)	0.4259 (9)	0.2579 (7)	7.6 (5)
O(*W*1′)	0.50	0.5805 (9)	0.4121 (9)	0.2732 (7)	6.3 (4)
O(*W*2)	0.55	0.8607 (8)	0.4559 (6)	0.2126 (6)	6.7 (3)
O(*W*2′)	0.30	0.8470 (14)	0.4617 (10)	0.2746 (9)	6.5 (6)
O(*W*2″)	0.15	0.942 (3)	0.462 (3)	0.254 (4)	12.3 (19)
O(*W*3)	0.50	0.3003 (10)	0.5315 (6)	0.2989 (5)	8.7 (4)
O(*W*3′)	0.50	0.1933 (7)	0.5335 (6)	0.2900 (5)	6.9 (3)
N(1)	1.00	0.0222 (3)	0.3246 (2)	0.39019 (16)	4.24 (12)

N(2)	1.00	−0.3051 (3)	0.2442 (2)	0.37760 (16)	4.34 (12)
N(3)	1.00	−0.2010 (3)	0.2166 (2)	0.57267 (16)	4.19 (12)
N(4)	1.00	0.1296 (3)	0.2999 (2)	0.58722 (16)	4.14 (12)
N(5)	1.00	0.6941 (3)	0.39217 (19)	0.00204 (16)	3.85 (12)
N(6)	1.00	0.3792 (2)	0.37867 (19)	0.04593 (16)	3.88 (12)
C(1)	1.00	0.1244 (5)	0.1981 (5)	0.2512 (3)	6.0 (2)
C(2)	1.00	0.0159 (3)	0.2005 (3)	0.3175 (2)	4.37 (15)
C(3)	1.00	−0.1553 (4)	0.1535 (3)	0.2565 (2)	4.56 (16)
C(4)	1.00	−0.2752 (4)	0.1274 (3)	0.3084 (2)	4.25 (15)
C(5)	1.00	−0.4281 (5)	0.0553 (4)	0.2327 (3)	6.3 (2)
C(6)	1.00	−0.4112 (4)	0.2322 (4)	0.4369 (3)	5.17 (19)
C(7)	1.00	−0.3544 (4)	0.1582 (3)	0.5021 (2)	5.09 (18)
C(8)	1.00	−0.1245 (4)	0.1403 (3)	0.6266 (2)	4.47 (16)
C(9)	1.00	−0.2280 (6)	0.1120 (5)	0.6876 (3)	6.7 (3)
C(10)	1.00	0.0388 (4)	0.2031 (3)	0.6907 (2)	4.84 (18)
C(11)	1.00	0.1671 (4)	0.2143 (3)	0.6397 (2)	4.54 (15)
C(12)	1.00	0.3309 (5)	0.2543 (5)	0.7133 (3)	6.9 (2)
C(13)	1.00	0.2375 (4)	0.3057 (4)	0.5275 (2)	4.85 (18)
C(14)	1.00	0.1771 (4)	0.3780 (3)	0.4616 (2)	4.98 (17)
C(15)	1.00	0.8121 (4)	0.1944 (3)	−0.0294 (3)	4.98 (19)
C(16)	1.00	0.6606 (3)	0.2563 (2)	−0.0365 (2)	3.62 (13)
C(18)	1.00	0.3818 (3)	0.2457 (2)	−0.0030 (2)	3.67 (13)
C(17)	1.00	0.5537 (3)	0.2153 (3)	0.0162 (2)	3.77 (14)
C(19)	1.00	0.2791 (4)	0.1679 (4)	0.0291 (3)	5.5 (2)
C(20)	1.00	0.7785 (3)	0.5795 (3)	−0.0241 (3)	4.60 (17)
C(21)	1.00	0.7667 (4)	0.4406 (3)	−0.0583 (3)	4.56 (18)

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

N(1)—C(2)	1.465 (4)	C(3)—C(4)	1.522 (4)
N(1)—C(14)	1.469 (4)	C(4)—C(5)	1.525 (5)
N(2)—C(4)	1.468 (4)	C(6)—C(7)	1.517 (5)
N(2)—C(6)	1.460 (4)	C(8)—C(9)	1.529 (5)
N(3)—C(7)	1.465 (4)	C(8)—C(10)	1.511 (5)
N(3)—C(8)	1.464 (4)	C(10)—C(11)	1.520 (5)
N(4)—C(11)	1.463 (3)	C(11)—C(12)	1.525 (5)
N(4)—C(13)	1.459 (4)	C(13)—C(14)	1.516 (4)
N(5)—C(16)	1.471 (3)	C(15)—C(16)	1.514 (4)
N(5)—C(21)	1.461 (4)	C(16)—C(17)	1.517 (4)
N(6)—C(18)	1.464 (3)	C(17)—C(18)	1.527 (4)
N(6)—C(20^{i})	1.466 (3)	C(18)—C(19)	1.517 (4)
C(1)—C(2)	1.519 (4)	C(20)—N(6^{i})	1.466 (3)
C(2)—C(3)	1.522 (4)	C(20)—C(21)	1.503 (4)
C(2)—N(1)—C(14)	116.4 (2)	C(9)—C(8)—C(10)	111.1 (3)
C(4)—N(2)—C(6)	115.6 (3)	C(8)—C(10)—C(11)	117.7 (3)
C(7)—N(3)—C(8)	114.0 (2)	N(4)—C(11)—C(10)	110.7 (2)
C(11)—N(4)—C(13)	114.2 (2)	N(4)—C(11)—C(12)	111.1 (3)
C(16)—N(5)—C(21)	113.8 (2)	C(10)—C(11)—C(12)	110.8 (3)
C(18)—N(6)—C(20^{i})	114.2 (2)	N(4)—C(13)—C(14)	111.8 (3)
N(1)—C(2)—C(1)	112.1 (3)	N(1)—C(14)—C(13)	114.2 (3)
N(1)—C(2)—C(3)	109.7 (2)	N(5)—C(16)—C(15)	112.0 (2)
C(1)—C(2)—C(3)	110.5 (3)	N(5)—C(16)—C(17)	110.5 (2)
C(2)—C(3)—C(4)	117.7 (2)	C(15)—C(16)—C(17)	110.7 (2)
N(2)—C(4)—C(3)	109.8 (2)	C(16)—C(17)—C(18)	117.2 (2)
N(2)—C(4)—C(5)	112.0 (3)	N(6)—C(18)—C(17)	109.5 (2)
C(3)—C(4)—C(5)	109.8 (3)	N(6)—C(18)—C(19)	112.4 (3)
N(2)—C(6)—C(7)	115.0 (3)	C(17)—C(18)—C(19)	110.6 (2)
N(3)—C(7)—C(6)	110.7 (3)	N(6^{i})—C(20)—C(21)	111.2 (2)
N(3)—C(8)—C(9)	111.4 (3)	N(5)—C(21)—C(20)	112.0 (3)
N(3)—C(8)—C(10)	110.2 (2)		

C(14)—N(1)—C(2)—C(3)	174.1 (3)
C(2)—N(1)—C(14)—C(13)	−62.3 (2)
C(6)—N(2)—C(4)—C(3)	−176.5 (3)
C(4)—N(2)—C(6)—C(7)	60.0 (2)
C(8)—N(3)—C(7)—C(6)	−169.9 (3)
C(7)—N(3)—C(8)—C(10)	175.0 (3)
C(13)—N(4)—C(11)—C(10)	−173.7 (3)
C(11)—N(4)—C(13)—C(14)	170.2 (3)
N(1)—C(2)—C(3)—C(4)	−66.7 (2)
C(2)—C(3)—C(4)—N(2)	68.9 (2)
N(2)—C(6)—C(7)—N(3)	60.8 (2)
N(3)—C(8)—C(10)—C(11)	−68.1 (2)
C(8)—C(10)—C(11)—N(4)	68.1 (2)
N(4)—C(13)—C(14)—N(1)	−61.4 (2)
C(21)—N(5)—C(16)—C(17)	−167.5 (2)
C(16)—N(5)—C(21)—C(20)	172.3 (3)
C(20^{i})—N(6)—C(18)—C(17)	174.0 (2)
C(18)—N(6)—C(20^{i})—C(21^{i})	−167.8 (3)
N(5)—C(16)—C(17)—C(18)	68.7 (2)
C(16)—C(17)—C(18)—N(6)	−72.3 (2)
N(6^{i})—C(20)—C(21)—N(5)	−70.8 (2)

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

H atoms were located using a difference Fourier method. All three water molecules and all H atoms attached to N atoms are disordered. All parameters were refined for ordered H atoms, but only U was refined for disordered H atoms. Program used: *NRCVAX* (Gabe, Le Page, White & Lee, 1987).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, hydrogen-bond geometry, bond distances and angles involving H atoms, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: AS1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Conformational Isomers of 2-Bromo-2,3-dihydro-2,3-(bibenzyl-2,2′-diyl)methano-1,4-naphthoquinone

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Abstract

The crystal structures of the two conformational isomers of the title compound, spiro[5,6-dihydro-11*H*-dibenzo-