*Acta Cryst.* (1997). C53, 588–590

# *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane Dihydroperchlorate Monohydrate

Huai-Ming Hu,[a] Hong-Sui Sun,[a] Xiao-Ying Huang,[b] Xiao-Hua Chen,[a] Yonyjiang Liu[a] and Xiao-Zeng You[a]

[a]*State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China, and* [b]*State Key Laboratory of Structural Chemistry, Fuzhou 350002, People's Republic of China. E-mail: ccinu@netra.nju.edu.cn*

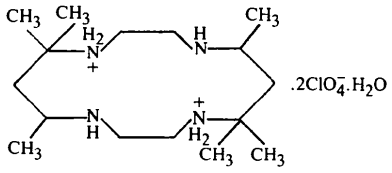
*(Received 17 April 1996; accepted 26 November 1996)*

## Abstract

The crystal structure of the title compound *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-4,11-diium diperchlorate monohydrate, $C_{16}H_{38}N_4^{2+}.2ClO_4^-.H_2O$, has been determined. The cationic ring contains two protonated and two secondary amine N atoms. The protonated N atoms display one long and one short N—C bond, with values of 1.526 (4) and 1.484 (4) Å, respectively. Similarly, the secondary amine N atoms also display one long and one short N—C bond, with values of 1.485 (4) and 1.455 (4) Å, respectively. A rather complicated hydrogen-bonding space system is present in the crystal.

## Comment

The title compound (Curtis, 1964) belongs to the family of 14-membered macrocyclic amines. Their coordination behavior with transition metals has been widely studied both chemically and crystallographically, but the reported crystal structures of macrocyclic amines and their salts are rather few. 7,14-Dimethyl-5,12-diphenyl-1,4,8,11-tetraazacyclotetradecane was studied by Ferguson, Roberts, Lloyd & Hideg (1977), the dihydroperchlorate and tetrahydrochloride salts of 1,4,8,11-tetraazacyclotetradecane by Nave & Truter (1974) and Robinson, Sangokoya, Pennington, Self & Rogers (1989), and the mesomeric dihydrate and the racemic monohydrate of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane by Gluzinski, Krajewski & Urbanczyk-Lipkowska (1980) and Krajewski, Urbanczyk-Lipkowska & Gluzinski (1977). Organoaluminium and gallium inclusion compounds, known as liquid chathrates, have been of interest to us for some time. These inclusion compounds result from the reaction of trialkylaluminium or trialkylgallium with alkali metal or tetraalkylammonium salts in aromatic solvents (Robinson, Zhang & Atwood, 1987). We report here the structure of $[H_2(C_{16}H_{36}N_4)](ClO_4)_2.H_2O$, (I), as part of our long-term research on metal-organic compound precursors for the metal-organic chemical vapour deposition technique (MOCVD) (Sun, Wang, You & Huang, 1995).



(I)

An *ORTEP*II (Johnson, 1976) plot of the cation of (I) with the atomic numbering scheme is shown in Fig. 1. The asymmetric unit of (I) consists of the macrocyclic tetraamine cation, $[H_2(C_{16}H_{36}N_4)]^{2+}$, two perchlorate ions and one water molecule. The cation contains two protonated N atoms (N2 and N4) and two secondary amine N atoms (N1 and N3). The protonated N atoms are in a tetrahedral environment and the other N atoms (N1 and N3) have three bonds arranged pyramidally. A significant bond-length difference may be noticed for various N—C bonds. The N—C bond lengths involving protonated N atoms are longer than those involving non-protonated N atoms with similar substituted groups, *e.g.* N2—C4 [1.484 (5) Å] and N4—C9 [1.483 (4) Å] are longer than N1—C10 [1.452 (4) Å] and N3—C5 [1.457 (4) Å]; similarly for the dihydroperchlorate salt of 1,4,8,11-tetraazacyclotetradecane, protonated N—C [1.497 (5) Å] is longer than non-protonated N—C [1.467 (5) Å] (Nave & Truter, 1974). The N—C bond

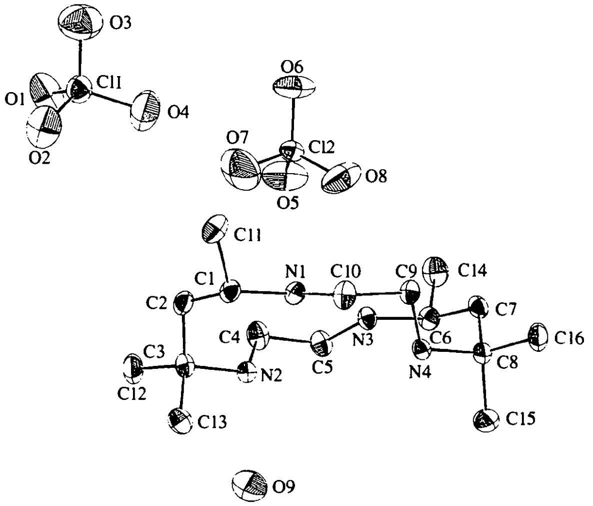


Fig. 1. The structure of the cation of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

lengths involving more substituted groups are longer than those involving less substituted groups for the same kind of N atoms, *e.g.* N2—C3 [1.526 (4) Å] and N4—C8 [1.526 (4) Å] are longer than N2—C4 [1.484 (5) Å] and N4—C9 [1.483 (4) Å], and N1—C1 [1.485 (4) Å] and N3—C6 [1.484 (4) Å] are longer than N1—C10 [1.452 (4) Å] and N3—C5 [1.457 (4) Å].

Intramolecular hydrogen bonds exist in the tetraamine cation [N1···N2 2.822 (4) Å and N2—H4···N1 140.4 (3)°; N3···N4 2.775 (4) Å and N4—H7···N3 141.9 (3)°] and intermolecular hydrogen bonds exist between the tetraamine cation and the $H_2O$ molecule [O9···N2 2.916 (5) Å and O9···H5—N2 144.2 (3)°], between the tetraamine cation and a $ClO_4^-$ anion [O5···N4$^i$ 3.031 (5) Å and O5···H8$^i$—N4$^i$ 160.1 (3)°; symmetry code: (i) $x$, $-1+y$, $z$], and between the $H_2O$ molecule and a $ClO_4^-$ anion [O3···O9$^{ii}$ 2.856 (7) Å and O3···H2$^{ii}$—O9$^{ii}$ 156.6 (3)°; symmetry code: (ii) $1-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$] in the crystal lattice.

## Experimental

The title compound was prepared from the reaction of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (teta) with perchloric acid in aqueous solvent. Teta was prepared according to the procedure of Hay, Lawrance & Curtis (1975). A solution of perchloric acid (4 mmol) was added to a stirred hot solution of teta (570 mg, 2 mmol) in water (50 ml). The resulting solution was allowed to stand at room temperature for a few days during which time crystals suitable for the X-ray structure determination were formed (found: C 38.20, H 7.88, N 10.91%; calculated for $C_{16}H_{40}Cl_2N_4O_9$: C 38.17, H 8.01, N 11.13%).

### *Crystal data*

$C_{16}H_{38}N_4^{2+}.2ClO_4^-.H_2O$
$M_r = 503.42$
Monoclinic
$P2_1/c$
$a = 11.198\,(2)$ Å
$b = 8.836\,(6)$ Å
$c = 25.795\,(7)$ Å
$\beta = 98.34\,(2)°$
$V = 2525\,(3)$ Å$^3$
$Z = 4$
$D_x = 1.32$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 12.61$–$16.00°$
$\mu = 0.303$ mm$^{-1}$
$T = 296$ K
Rectangular
0.90 × 0.45 × 0.28 mm
Colorless

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* $\psi$ scans (Molecular Structure Corporation, 1987)
$T_{\min} = 0.869$, $T_{\max} = 0.919$
4996 measured reflections
4891 independent reflections

3034 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.065$
$\theta_{\max} = 25°$
$h = -13 \rightarrow 0$
$k = 0 \rightarrow 10$
$l = -30 \rightarrow 30$
3 standard reflections every 400 reflections intensity decay: 5.3%

### *Refinement*

Refinement on $F$
$R = 0.061$
$wR = 0.070$
$S = 1.76$
3034 reflections
280 parameters
H atoms not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.07$
$\Delta\rho_{\max} = 0.38$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.31$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| N1—C10 | 1.452 (4) | N4—C8 | 1.526 (4) |
| N1—C1 | 1.485 (4) | C1—C2 | 1.523 (5) |
| N2—C4 | 1.484 (5) | C2—C3 | 1.528 (5) |
| N2—C3 | 1.526 (4) | C4—C5 | 1.510 (5) |
| N3—C5 | 1.457 (4) | C6—C7 | 1.526 (5) |
| N3—C6 | 1.484 (4) | C7—C8 | 1.535 (5) |
| N4—C9 | 1.483 (4) | C9—C10 | 1.527 (6) |
| C10—N1—C1 | 113.7 (2) | N2—C4—C5 | 111.5 (3) |
| C4—N2—C3 | 119.0 (3) | N3—C5—C4 | 112.2 (3) |
| C5—N3—C6 | 113.3 (3) | N3—C6—C7 | 110.3 (3) |
| C9—N4—C8 | 118.2 (2) | C6—C7—C8 | 117.8 (3) |
| N1—C1—C2 | 109.8 (3) | N4—C8—C7 | 108.7 (2) |
| C1—C2—C3 | 118.8 (3) | N4—C9—C10 | 110.6 (2) |
| N2—C3—C2 | 108.9 (2) | N1—C10—C9 | 111.6 (3) |

The title structure was solved by direct methods and refined by full-matrix least squares. All H atoms were located by difference Fourier mapping. All calculations were carried out on a MicroVAX 3100 computer using the *TEXSAN* program (Molecular Structure Corporation, 1987).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

The authors would like to thank the National Nature Science Foundation, the Major Project of State Science and Technology Commission of China, and the Analytic Centre of Nanjing University.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KH1117). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1997). C**53**, 590–592

# α-1*H*-1,2,3,4-Tetrazole

Richard Goddard, Oliver Heinemann and Carl Krüger

*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany. E-mail: goddard@mpi-muelheim.mpg.de*

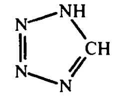
(*Received 24 October 1996; accepted 20 January 1997*)

## Abstract

A polar polymorph of tetrazole is described. α-Tetrazole, $CH_2N_4$, is triclinic (space group $P1$), with one molecule of the 1*H*-tautomeric form of tetrazole in the unit cell. The molecules are connected by N—H···N hydrogen bonds forming chains, which are linked together by C—H···N interactions to give planar sheets separated by 3.35 (1) Å. The structure of α-tetrazole is compared with that of monoclinic β-tetrazole; the difference in the two structures is due to the sheet orientation.

## Comment

McCrone, Grabar & Lieber (1957) reported the crystallographic data of tetrazole crystals derived from crystal morphology measurements and X-ray diffraction data. They concluded that tetrazole crystallizes in a triclinic unit cell of dimensions $a = 5.00$, $b = 5.46$, $c = 3.75$ Å, $\alpha = 130$, $\beta = 111$ and $\gamma = 63°$, but the crystal structure was not determined. We shall call this form α-tetrazole. Later, van der Putten, Heijdenrijk & Schenk (1974) determined the crystal structure of a monoclinic form of tetrazole, which we shall call here β-tetrazole. This structure contains two molecules in a unit cell of dimensions $a = 4.931\,(2)$, $b = 6.451\,(2)$, $c = 5.390\,(1)$ Å, $\beta = 116.69\,(3)°$ and space group $P2_1$ or $P2_1/m$. Unfortunately, the diffraction data were of rather poor quality and the $R$ value was 0.11. As we were interested in obtaining an accurate structure of tetrazole as part of an investigation into the packing and intermolecular hydrogen bonding in N-containing five-membered ring systems, we decided to reinvestigate the crystal structure. Crystals were grown from *n*-pentane by the convection method described by Arend, Huber, Freudenreich & Surbeck (1979), and we were surprised to discover that we had obtained the triclinic form of tetrazole. We report here the crystal structure of α-tetrazole, (I), and compare it with its monoclinic polymorph.



(I)

Bond distances within the ring differ significantly, with the shortest bond between the N2 and N3 atoms [1.295 (3) Å], consistent with the formulation of a formal double bond between these atoms. The neighbouring N3—N4 bond of 1.346 (3) Å is the longest in the ring, suggesting there is considerable localization of charge within the ring. The N1—C5 bond is slightly shorter than the C5—N4 distance, although the formal double bond lies between the latter atoms. The N1—H1 and C5—H5 distances at 0.81 (5) and 0.88 (4) Å, respectively, are artificially short, as expected, but the bond angles around the N1 and C5 atoms are sensible, indicating that the angles associated with the H atoms are reliable.

Except for N4—C5, bond distances within the ring are consistently shorter than those observed at 150 K for 1-methyltetrazole (Palmer & Parsons, 1996) (see Table 3). This is mostly due to libration effects, as shown by **TLS**-corrected values (Schomaker & Trueblood, 1968), though the **TLS** $R$ factors are fairly high at 17% for this structure and 18% for the methyl analogue. Bond angles are similar for the two structures.

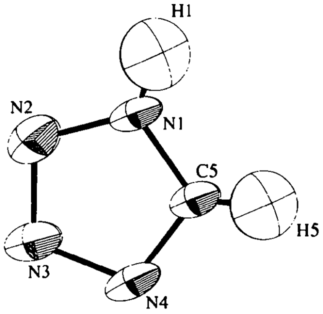


Fig. 1. View of the title molecule showing the atomic labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

*Acta Crystallographica Section C*
ISSN 0108-2701 © 1997