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A 13-Membered Cyclic Tetraamine Salt: 12,12-Dimethyl-4,7,10-triaza-1-azoniacyclotridecane Perchlorate Hydrate

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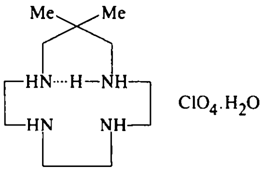
Abstract

The mono-protonated cyclic tetraamine in the title compound, $C_{11}H_{27}N_4^+.ClO_4^-.H_2O$, has the four N atoms in a tetrahedrally twisted [±0.13 (1) Å] square arrangement. The protonated N5 atom forms the only intracyclic hydrogen bond (N5—H···N1); all other NH groups form hydrogen bonds to water or perchlorate O atoms.

Comment

Preparations have been described for compounds of Ni^{II} and Cu^{II} with 13-membered triaminemonoimine tetraaza-macrocyclic ligands, formed by reaction of 3,6-diazaoctane-1,8-diamine (triethylenetetraamine) compounds of the metal ions with aliphatic carbonyl compounds (House & Curtis, 1964). When 2-methylpropanal (isobutyraldehyde) reacts with tris(3,6-diazaoctane-1,8-diamine)dinickel(II) chloride and zinc chloride in methanol, the product is (12,12-dimethyl-1,4,7,10-tetraazacyclotrideca-13-ene)nickel(II) tetrachlorozincate. This compound, rather than the anticipated 3,3-dimethyl-4-(2-methylethyl) compound, is apparently formed by elimination of 2-methylpropene.

The imine group of the ligand is reduced using sodium tetrahydridoborate, to form the cyclic tetraamine macrocyclic compound (12,12-dimethyl-1,4,7,10-tetraazacyclotridecane)nickel(II) tetrachlorozincate, $[Ni(L)][ZnCl_4]$. This and other Ni^{II} compounds of L have been described elsewhere (Curtis & Reader, 1971); $[Ni(L)](ClO_4)_2$ has been structurally characterized (Waters & Whittle, 1972). The ligand is released from the Ni^{II} complex by reaction with 4 mole proportions of sodium cyanide and isolated as the monoperchlorate salt $[H(L)](ClO_4).H_2O$ (Curtis & Reader, 1972). Complexes of L with Co^{III} have been described (Curtis & Reader, 1972). The structure of the salt $[H(L)](ClO_4).H_2O$ is now reported.



$[H(L)](ClO_4).H_2O$

The macrocycle of $[H(L)](ClO_4).H_2O$ is protonated at N5 and has a conformation in which the N atoms are in a tetrahedrally distorted [±0.13 (1) Å] approximate square, the dimensions of which are not too dissimilar from those of the Ni^{II} complex. One intracyclic hydrogen bond (N5—H···N1) is present across the six-membered pseudo-chelate ring, holding the N1 and N5 atoms in *endo* conformations. The other NH groups are all oriented to the same side of the 'plane' and all participate in intermolecular hydrogen bonding with the lone pairs on the N8 and N11 atoms oriented away from the 'centre' in *exo* arrangements. The N1-N5 'chair' and N8-N11 'eclipsed' pseudo-chelate rings are tilted to the same side of the plane, in contrast to the Ni^{II} complex where they are tilted to opposite sides of the plane.

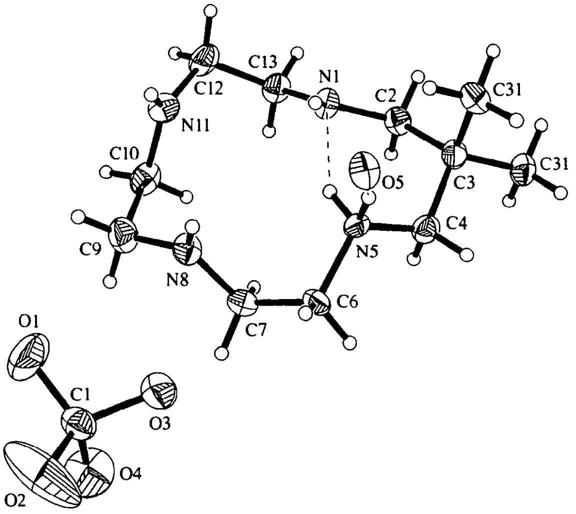


Fig. 1. The salt $[H(L)](ClO_4).H_2O$, showing the intracyclic N5—H···N1 hydrogen bond and the N5—H···O5 hydrogen bond to the water molecule, with displacement ellipsoids for non-H atoms drawn at the 50% probability level.

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Hydrogen bonds involving the water molecule, N5—H···O5, O5—H···N11 and O5—H···O4, form chains parallel to the *b* axis of the unit cell. N1—H···O1 and N8—H···O4 contacts link the macrocyclic cations and perchlorate anions into sheets parallel to the (*xy*0) plane.

The structures of a number of 12-, 14- and 16-membered macrocyclic tetraamines and their salts have been described. Some of these have *endo* conformations, often stabilized by intramolecular hydrogen bonding. In some cases, the geometries of the free and coordinated macrocycles are very similar, while for others, particularly when there are substituents capable of hydrogen bonding, the free macrocycles have a variety of *exo* conformations, quite unlike those of the coordinated macrocycles. The protonated macrocycle $[\mathrm{H}(L)]^+$ is an intermediate case, with the macrocycle conformation similar to that of the $\mathrm{Ni^{II}}$ complex, although the details appear to be determined primarily by the hydrogen-bonding contacts.

Experimental

The title compound was prepared as reported previously (Curtis & Reader, 1972) and recrystallized from water.

Crystal data

$C_{11}H_{27}N_4^+.ClO_4^-.H_2O$
$M_r = 332.83$
Orthorhombic
Pbca
$a = 8.940\,(3)$ Å
$b = 14.259\,(4)$ Å
$c = 25.929\,(7)$ Å
$V = 3305\,(2)$ Å^3
$Z = 8$
$D_x = 1.338$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 4.759–12.014°$
$\mu = 0.257$ mm^{-1}
$T = 158\,(2)$ K
Rectangular block
0.7 × 0.4 × 0.2 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2563 measured reflections
2156 independent reflections
1342 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.0590$

$\theta_{\max} = 22.5°$
$h = -9 \rightarrow 2$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 27$
3 standard reflections every 97 reflections intensity decay: 4.23%

Refinement

Refinement on F^2
$R(F) = 0.0468$
$wR(F^2) = 0.1039$
$S = 1.067$
2156 reflections
196 parameters
H-atom coordinates refined
$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.297$ e Å^{-3}
$\Delta\rho_{\min} = -0.264$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0016 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C13	1.465 (4)	C6—C7	1.514 (5)
N1—C2	1.469 (4)	C7—N8	1.463 (4)
C2—C3	1.547 (5)	N8—C9	1.475 (4)
C3—C4	1.520 (5)	C9—C10	1.504 (5)
C3—C31	1.523 (5)	C10—N11	1.461 (4)
C3—C32	1.527 (5)	N11—C12	1.467 (4)
C4—N5	1.491 (4)	C12—C13	1.520 (5)
N5—C6	1.500 (4)		
C13—N1—C2	110.1 (3)	C4—N5—C6	113.7 (3)
N1—C2—C3	113.5 (3)	N5—C6—C7	110.9 (3)
C4—C3—C31	107.2 (3)	N8—C7—C6	109.0 (3)
C4—C3—C32	111.1 (3)	C7—N8—C9	113.5 (3)
C31—C3—C32	109.4 (3)	N8—C9—C10	109.8 (3)
C4—C3—C2	110.1 (3)	N11—C10—C9	109.4 (3)
C31—C3—C2	107.6 (3)	C10—N11—C12	114.1 (3)
C32—C3—C2	111.3 (3)	N11—C12—C13	116.1 (3)
N5—C4—C3	114.3 (3)	N1—C13—C12	111.0 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1$^{\mathrm{i}}$	1.177 (4)	2.199 (4)	3.131 (4)	133.6 (3)
N5—H5*A*···N1	0.968 (4)	1.942 (4)	2.818 (4)	149.1 (3)
N5—H5*B*···O5$^{\mathrm{ii}}$	1.149 (4)	1.608 (4)	2.726 (4)	162.5 (3)
N8—H8···O4	0.965 (4)	2.319 (4)	3.200 (4)	151.5 (3)
O5—HO5*A*···N11$^{\mathrm{iii}}$	0.920 (3)	1.817 (4)	2.720 (4)	166.3 (3)
O5—HO5*B*···O4$^{\mathrm{iv}}$	0.899 (3)	2.208 (4)	3.007 (4)	147.8 (3)

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

H atoms bonded to N and water O atoms were located and their positions refined with isotropic parameters; the other H atoms are in calculated positions.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XPMA* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

Collection of the diffraction data by Professor W. T. Robinson of the Chemistry Department, University of Canterbury, is gratefully acknowledged.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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