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Two hydrochlorides of 7-methyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),13,15-triene

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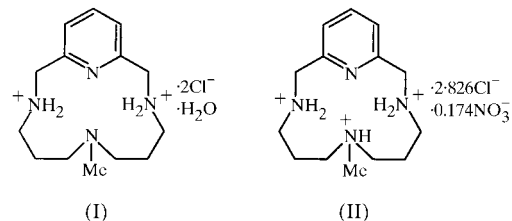
The X-ray structure determinations of the two title compounds, namely 7-methyl-7,17-diaza-3,11-diazoniabicyclo[11.3.1]heptadeca-1(17),13,15-triene dichloride monohydrate, $C_{14}H_{26}N_4^{2+} \cdot 2Cl^- \cdot H_2O$, (I), and 7-methyl-17-aza-3,7,11-triazoniabicyclo[11.3.1]heptadeca-1(17),13,15-triene 2.826-chloride 0.174-nitrate, $C_{14}H_{27}N_4^{3+} \cdot 2.826Cl^- \cdot 0.174NO_3^-$, (II), are reported. Protonation occurs at the secondary amine N atoms in (I) and at all three amine N atoms in (II) to which the Cl^- ions are linked *via* $N-H \cdots Cl$ hydrogen bonds. The macrocyclic hole is quite different in both structures, as is observed by comparing particularly the $N3 \cdots N4$ distances [2.976 (4) and 4.175 (4) Å for (I) and (II), respectively]. In (II), a Cl^- ion alternates with an NO_3^- ion in a disordered structure.

Comment

The synthesis of the macrocyclic ligand by the copper-temple method has been reported previously (Alcock *et al.*, 1984), as well as coordination studies towards several transition metal ions (Alcock, Balakrishnan & Moore, 1985; Alcock, Balakrishnan, Moore & Pike, 1987; Alcock *et al.*, 1988; Balakrishnan *et al.*, 1990). The crystal structures of some related ligands and complexes have also been reported (Alcock, Moore & Omar, 1985, 1987; Blake *et al.*, 1986; Drew *et al.*, 1986; Félix *et al.*, 1996; Foster *et al.*, 1986). Potentiometric studies for the free macrocycle and some divalent complexes were reported by Costa & Delgado (1993).

Bond lengths and angles in (I) and (II) are within expected ranges and confirm the bond orders shown in the scheme. There is evidence of different possible hydrogen bonds mainly involving the Cl^- or NO_3^- ions, and the N atoms of both structures. There is also a possible intermolecular hydrogen-bond interaction between N3 and N4 in (I). Hydrogen-

bonding distances and angles are given in Tables 1 and 2. The pyridine ring is planar (r.m.s. deviations 0.007 Å for both structures). The four N atoms are not coplanar in (I) and (II) (r.m.s. deviations 0.13 Å for both structures), in contrast to their positions in the free macrocycle.



The conformation in the macrocycles is different in the three structures, as is observed by comparing the values of the distances $N2 \cdots N3$ [3.712 (4), 4.288 (4) and 3.238 (2) Å for (I), (II) and the free ligand, respectively] and $N3 \cdots N4$ [2.976, 4.175 (4) and 3.238 (2) Å for (I), (II) and the free ligand, respectively]. In the free ligand, both distances are equal and relatively short. In (I), both distances are clearly different, $N3 \cdots N4$ being shorter than $N2 \cdots N4$. In (II), the distances are again similar, but much longer than in the other two structures.

Experimental

To a stirred solution of 2,6-pyridinecarbaldehyde and copper nitrate (in a mixture of ethanol and water, 1:1 v/v) was added a solution of 1,7-diamino-4-methyl-4-azaheptane in ethanol. The copper(II) diimine complex formed was reduced *in situ* by sodium borohydride and the copper was removed by precipitation of its sulfide with $Na_2S \cdot 9H_2O$. The solution was filtered through a bed of Celite. The filtrate was extracted with dichloromethane, the combined extracts were dried with anhydrous $MgSO_4$, and the dichloromethane removed by evaporation to leave a pale orange gel. Crystals of (I) and (II) were obtained from ethanol solution.

Compound (I)

Crystal data

$C_{14}H_{26}N_4^{2+} \cdot 2Cl^- \cdot H_2O$

$M_r = 339.30$

Monoclinic, Cc

$a = 16.7683$ (3) Å

$b = 9.7089$ (2) Å

$c = 11.116$ (2) Å

$\beta = 90.9963$ (11)°

$V = 1809.4$ (3) Å³

$Z = 4$

$D_x = 1.246$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 6095

reflections

$\theta = 3.0$ – 56.6°

$\mu = 0.364$ mm⁻¹

$T = 293$ (2) K

Needle, colourless

$0.70 \times 0.20 \times 0.15$ mm

Siemens CCD SMART diffractometer

ω scans

Absorption correction: empirical

(SADABS; Sheldrick, 1996)

$T_{min} = 0.785$, $T_{max} = 0.948$

6531 measured reflections

Data collection

2812 independent reflections

2656 reflections with $I > 2\sigma(I)$

$R_{int} = 0.037$

$\theta_{max} = 28.21^\circ$

$h = -16 \rightarrow 22$

$k = -12 \rightarrow 12$

$l = -12 \rightarrow 14$

Intensity decay: -1.55%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.112$
 $S = 1.096$
 2812 reflections
 208 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0749P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983)
 Flack parameter = 0.02 (6)

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N4-H4NA \cdots Cl1$	0.83 (5)	2.77 (5)	3.456 (2)	140 (4)
$N2-H2NB \cdots Cl1$	0.87 (5)	2.48 (5)	3.317 (3)	162 (4)
$N2-H2NB \cdots Cl2$	0.77 (5)	2.31 (5)	3.062 (2)	168 (5)
$N4-H4NA \cdots N3$	0.83 (5)	2.46 (5)	2.973 (3)	121 (4)
$N4-H4NB \cdots Cl1^i$	0.99 (5)	2.19 (5)	3.128 (2)	158 (4)
$O1W-H1W \cdots Cl1$	0.81 (3)	2.57 (5)	3.177 (3)	133 (5)
$O1W-H2W \cdots Cl2^{ii}$	0.82 (3)	2.45 (4)	3.200 (4)	152 (4)

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

Compound (II)

Crystal data

$C_{14}H_{27}N_4^{3+} \cdot 2.826Cl^- \cdot 0.174NO_3^-$
 $M_r = 362.37$
 Monoclinic, $P2_1/n$
 $a = 10.7592$ (3) \AA
 $b = 10.8825$ (3) \AA
 $c = 15.4988$ (3) \AA
 $\beta = 93.9033$ (13°)
 $V = 1810.50$ (8) \AA^3
 $Z = 4$

$D_x = 1.329 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 4178 reflections
 $\theta = 3.0\text{--}56.6^\circ$
 $\mu = 0.484 \text{ mm}^{-1}$
 $T = 293$ (2) K
 Irregular, colourless
 $0.30 \times 0.15 \times 0.10 \text{ mm}$

Data collection

Siemens CCD SMART diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.868, T_{\max} = 0.953$
 9674 measured reflections
 4252 independent reflections

2388 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$
 $\theta_{\text{max}} = 28.29^\circ$
 $h = -11 \rightarrow 13$
 $k = -14 \rightarrow 5$
 $l = -20 \rightarrow 20$
 Intensity decay: -1.97%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.122$
 $S = 0.984$
 4252 reflections
 224 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0457P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.053$
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

Some 576 Friedel pairs were used in the refinement to determine the absolute structure of (I). The relatively high residual electronic density in the environment of Cl3 in (II), as well as the distribution of the peaks in the Fourier map, makes it necessary to adopt a disorder model where a Cl^- ion alternates with a nitrate ion in the structure

(an occupation factor was refined to give values of 0.825 and 0.175). Methyl H atoms were added at calculated positions and refined using a riding model. All other H atoms were located from a difference Fourier map and refined with $U(H)$ equal to 1.2 (or 1.5 for methyl H atoms) times U_{eq} of the parent atom.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N4-H4NB \cdots Cl1^i$	0.92 (3)	2.38 (4)	3.260 (3)	160 (3)
$N2-H2NB \cdots Cl1^i$	0.96 (3)	2.32 (3)	3.237 (3)	159 (3)
$N2-H2NB \cdots Cl2^i$	0.96 (3)	2.11 (3)	3.056 (2)	167 (3)
$N4-H4NA \cdots Cl3^{ii}$	1.03 (3)	2.07 (3)	3.074 (3)	164 (3)
$N4-H4NA \cdots O2^{ii}$	1.03 (3)	1.72 (4)	2.676 (14)	152 (3)
$N4-H4NA \cdots O3^{ii}$	1.03 (3)	1.91 (3)	2.761 (14)	137 (3)
$N3-H3N \cdots Cl2^{iii}$	0.93 (3)	2.20 (3)	3.102 (3)	166 (3)

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

For both compounds, data collection: SMART (Siemens, 1994); cell refinement: SMART; data reduction: SAINT (Siemens, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); software used to prepare material for publication: SHELXL97.

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