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3,5,7-Triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane perchlorate

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(Cl–O) = 0.003 Å
R factor = 0.076
wR factor = 0.202
Data-to-parameter ratio = 12.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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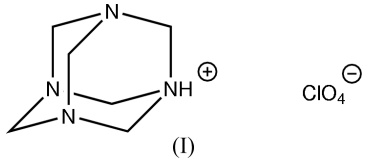
The title compound, $C_6H_{13}N_4^+\cdot ClO_4^-$, crystallizes in the space group $P2_1/n$. The structure can be solved in the orthorhombic space group *Pnma*, but analysis of the refinement parameters showed that the choice of the $P2_1/n$ space group is the correct one. All interatomic distances can be considered as normal. Molecules are assembled by intermolecular N—H···O hydrogen bonds into a zigzag chain structure along the *b* axis. In the structure, weak intermolecular C—H···N hydrogen bonds create a two-dimensional net structure in the (011) plane.

Comment

The title compound, (I), crystallizes in space group $P2_1/n$, with $Z = 4$ (Fig. 1*a*). Among other non-crystallographic symmetry elements, both molecules have internal reflection planes. Taking into account that the β unit-cell angle is close to 90°, the structure can be solved in the orthorhombic space group *Pnma* (Fig. 1*b*), but analysis of the refinement parameters (*e.g.* for space group *Pnma*, $S = 2.31$, $R[F^2 > 2\sigma(F_o^2)] = 0.206$ and $wR(F_o^2) = 0.568$; see supplementary material) showed that the choice of the $P2_1/n$ space group is the correct one. In addition, because the molecule reflection plane is slightly inclined to the *Pnma* space group reflection plane, some of the atoms exhibit large displacement ellipsoids (Fig. 1*b*).



(I)

A perspective view of (I) together with the atom-numbering scheme is shown in Fig. 1. All interatomic distances can be considered as normal. Molecules of the title compound are assembled by intermolecular N—H···O hydrogen bonds into a zigzag chain structure along the *b* axis (Fig. 2 and Table 2). Additional intermolecular C—H···N interactions are found in the structure (Fig. 2 and Table 2), which, according to Desiraju & Steiner (1999), can be classified as weak hydrogen bonds. In this way, a two-dimensional net structure is created in the (011) plane.

Experimental

The aim of this work was to prepare $Ln(ClO_4)_3\cdot 2[N_4(CH_2)_6]\cdot nH_2O$ salts by reaction of hydrated lanthanum chlorate(VII) with hexamethylenetetramine (HMTA) in water, using a 1:2 molar ratio. The solutions were stirred at room temperature and left to crystallize at

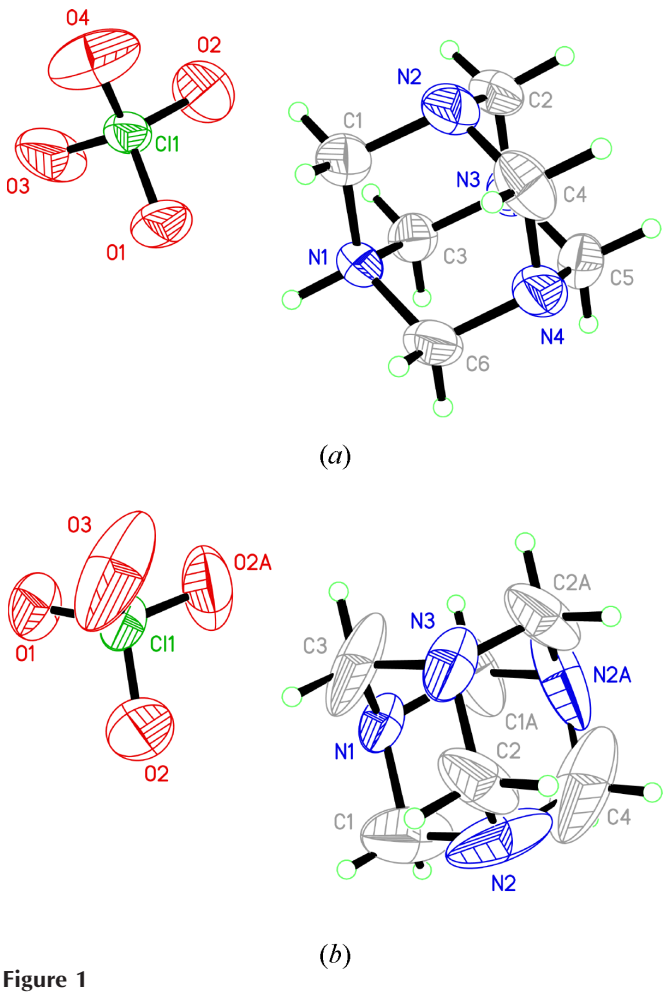


Figure 1
The molecular structure of (I) refined in (*a*) the space group $P2_1/n$ and (*b*) *Pnma*. Displacement ellipsoids are drawn at the 50% probability level.

278 K. After a few days, crystals were formed from the solutions. However, crystallographic investigation of the products from solutions containing La, Nd and Dy salts showed that they were hexamethylenetetramin-1-ium perchlorate. In order to obtain good quality single crystals of this salt, the preparation process was modified. The weighed sample of hexamethylenetetramine was dissolved in water, cooled and then mixed with diluted perchloric acid in a 1:1 molar ratio. The mixture was placed in a refrigerator and left to crystallize. No crystals grew in the solution. Qualitative analysis of the samples showed the presence of NH_4^+ ions. It can be supposed that HMTA was hydrolysed to ammonia and formaldehyde in acid solution (Smolin & Rapoport, 1959); thus, preparation *via* perchlorate salts seems to be a reasonable synthesis pathway.

Crystal data

$C_6H_{13}N_4^+\cdot ClO_4^-$
M_r = 240.65
Monoclinic, $P2_1/n$
a = 9.2662 (19) Å
b = 9.6794 (16) Å
c = 10.854 (2) Å
β = 90.061 (17)°
V = 973.5 (3) Å^3
Z = 4
D_x = 1.642 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3276 reflections
θ = 2–25°
μ = 0.40 mm^{-1}
T = 291 (2) K
Ellipsoid, colourless
0.50 × 0.47 × 0.43 mm

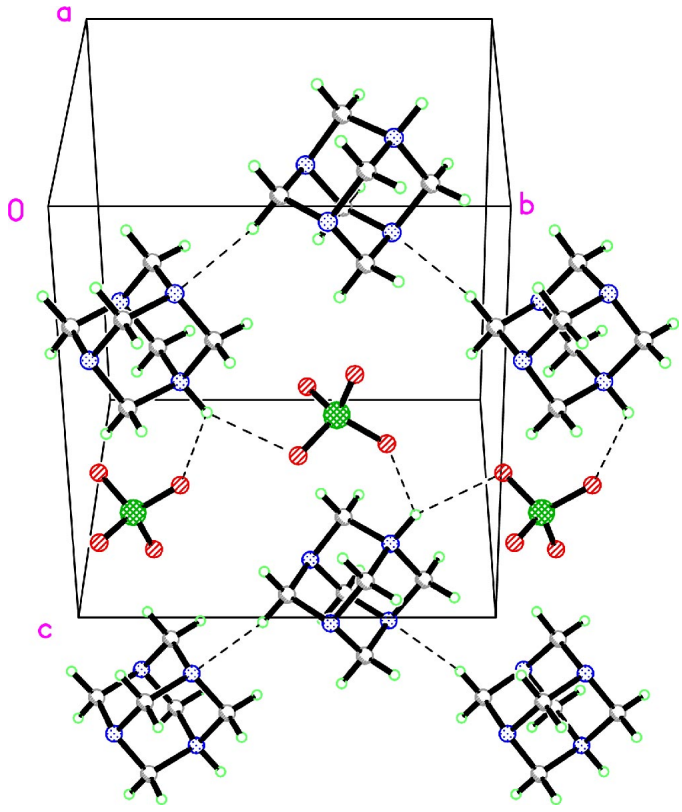


Figure 2
Part of the molecular packing of the title compound, showing the intermolecular hydrogen bonds creating a net structure in the (011) plane. Hydrogen bonds are indicated by dashed lines.

Data collection

Kuma KM-4 CCD diffractometer
ω scans
Absorption correction: numerical (*X-RED*32; Stoe & Cie, 1999)
T_{min} = 0.821, T_{max} = 0.850
12 433 measured reflections
1736 independent reflections
1599 reflections with $I > 2\sigma(I)$
R_{int} = 0.179
θ_{max} = 25.1°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.202
S = 1.11
1736 reflections
136 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1322P)^2 + 0.3022P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.68 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—O4	1.407 (3)	Cl1—O2	1.411 (3)
Cl1—O3	1.408 (3)	Cl1—O1	1.434 (2)
O4—Cl1—O3	109.9 (2)	O4—Cl1—O1	110.62 (18)
O4—Cl1—O2	108.2 (2)	O3—Cl1—O1	108.95 (18)
O3—Cl1—O2	108.4 (2)	O2—Cl1—O1	110.68 (18)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O2^{i}	0.97	2.37	3.189 (4)	142
N1—H1N···O1	0.97	2.30	2.944 (4)	123
C2—H2B···N4^{ii}	0.97	2.58	3.531 (4)	166

Symmetry codes: (i) $\frac{1}{2}-x,\frac{1}{2}+y,\frac{3}{2}-z$; (ii) $\frac{1}{2}-x,y-\frac{1}{2},\frac{5}{2}-z$.

Data collection: *CrysAlis CCD* (UNIL IC & Kuma, 2000); cell refinement: *CrysAlis RED* (UNIL IC & Kuma, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC Software* (Sheldrick, 1990*b*) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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