1,4,7-Tris(2-cyanoethyl)-4,7-triaza-1-azoniacyclononane perchlorate

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There are three independent molecules in the asymmetric unit of the title compound, $C_{15}H_{25}N_6{}^+ \cdot ClO_4{}^-$. The cations are linked to form an $R_4^4(30)$ ring with two arms and are then linked into columns in the [010] direction by $C(11)$ chains formed *via* C—H$\cdots$N hydrogen bonds.

Comment

The functionalized pendant-arm derivatives of 1,4,7-triazacyclononane have been used as multidentate ligands for enzyme simulations (Wieghardt, 1989), as models of myoglobin (Collman *et al.*, 1997) and as building blocks for the construction of solid-state architectures (Tei *et al.*, 1998, 2002). We chose to investigate macrocyclic frameworks with cyanoethyl groups as the pendant arms, because we believe that nitrile functionalized pendant arms will promote the formation of multinuclear compounds that are similar to the active site in some enzymes. We report here the molecular and supramolecular structure of the title compound, (I). Cyano N atoms act as hydrogen-bond acceptors for aromatic C atoms (Boitsov *et al.*, 2002); however, in the supramolecular structure of (I), the C—H$\cdots$N interactions are between the methyl C—H atoms and the cyano N atoms.
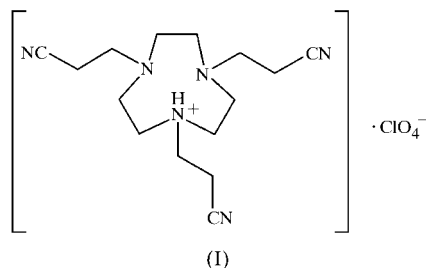
The asymmetric unit of (I) consists of three independent molecules. 1,4,7-Tris(2-cyanoethyl)-1,4,7-triazacyclononane is protonated in a weak acidic solution of Mn^{3+}, and the H atoms are bound to atoms N13, N23 and N33 of the three molecules. The cations and perchlorate anions are shown in Fig. 1.
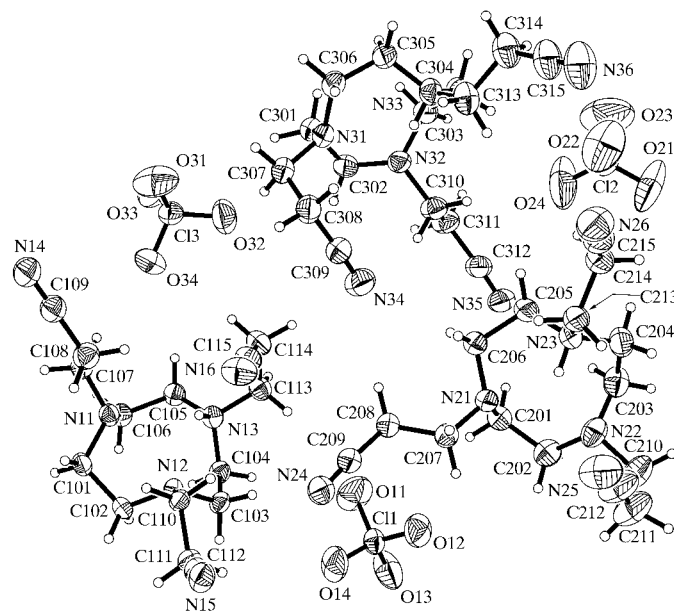

Figure 1
The molecular configuration and atom-numbering scheme for (I), showing displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

The supramolecular structure of the ion is generated by an $R_4^4(30)S(10)$ motif and a $C(11)$ chain (Bernstein *et al.*, 1995). Cyano atom N36 of cation 3 (containing atoms C301 *etc.*) at (x, y, z) acts as an acceptor, *via* atom H213, for atom C207 of cation 2 (containing atoms C201 *etc.*) at ($1 - x$, $\frac{3}{2} + y$, $\frac{1}{2} - z$). Cyano atom N24 of cation 2 at ($1 - x$, $\frac{3}{2} + y$, $\frac{1}{2} - z$) acts as an acceptor, *via* atom H301, for atom C301 of cation 3 at ($-x$, $\frac{3}{2} + y$, $\frac{1}{2} - z$), and cyano atom N36 of cation 3 acts as an acceptor, *via* atom H213, for atom C207 of cation 2 at ($-1 - x$, $-y$, $-z$). Finally, cyano atom N24 of cation 2 at ($-1 + x$, y, z) acts as an acceptor, *via* atom H301, for atom C301 of cation 3 at (x, y, z), thus completing a centrosymmetric $R_4^4(30)$ ring, centred at ($0, \frac{1}{2}, 0$). Cations 1 (containing atoms C101 *etc.*) at ($-1 + x$, $-1 + y$, z) and at ($\frac{1}{2} - x$, $\frac{5}{2} + y$, $\frac{1}{2} - z$) link the rings *via* C303—H305$\cdots$N15 interactions, and a C310—H316$\cdots$N34
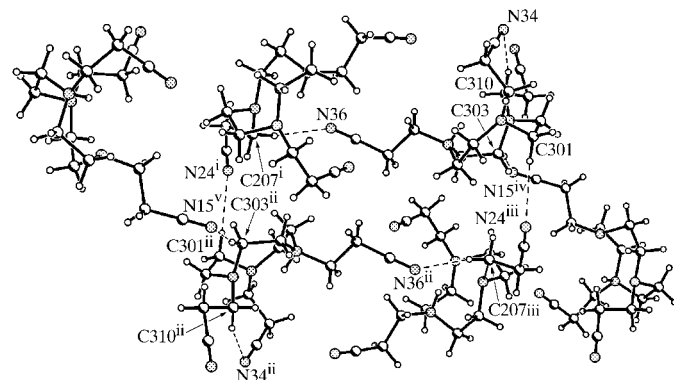

Figure 2
Part of the crystal structure of (I), showing the formation of the $R_4^4(30)$ ring. Perchlorate anions have been omitted for clarity. [Symmetry codes: (i) $1 - x, \frac{3}{2} + y, \frac{1}{2} - z$; (ii) $-x, \frac{2}{3} + y, \frac{1}{2} - z$; (iii) $-1 - x, -y, -z$; (iv) $-1 + x, -1 + y, z$; (v) $\frac{1}{2} - x, \frac{5}{2} + y, \frac{1}{2} - z$.]
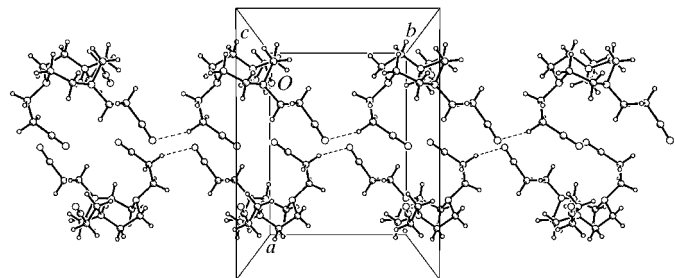
Figure 3
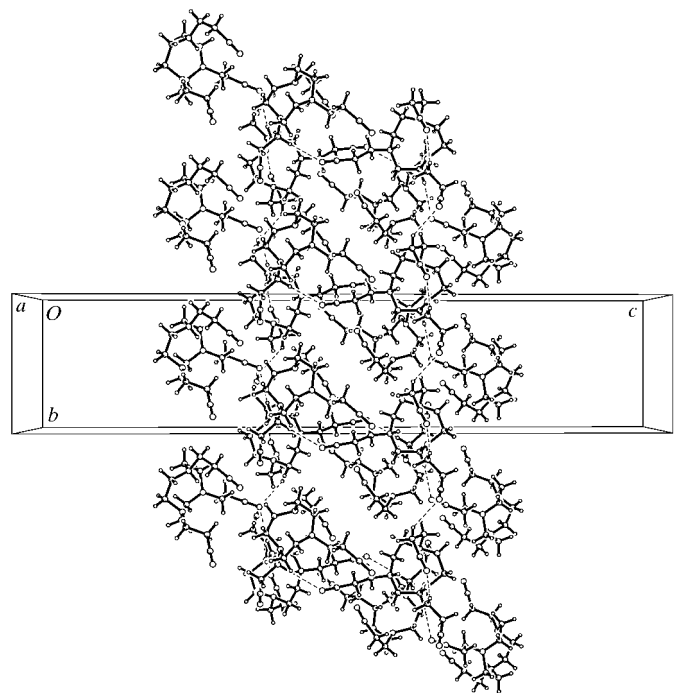Part of the crystal structure of (I), showing the formation of the $C(11)$ chain.

Figure 4
Part of the crystal structure of (I), viewed along the *a* axis, showing the column formed by a combination of $R_4^4(30)$ rings and $C(11)$ chains. Perchlorate anions have been omitted for clarity.

interaction in cation 3 generates an edge-fused $S(10)$ ring (Fig. 2). The propagation of intermolecular C308—H316···N35 interactions between cations 3 produces a $C(11)$ chain running parallel to the [010] direction (Fig. 3). A combination of two $C(11)$ chains and a series of $R_4^4(30)$ rings forms a 'column' running parallel to the [010] direction (Fig. 4). There are also intermolecular C—H···O hydrogen bonds (Table 1).

Experimental

1,4,7-Tris(2-cyanoethyl)-1,4,7-triazacyclononane, (II), was prepared according to the method described by Bushnell *et al.* (1998). Compound (II) (0.1 mmol) was dissolved in methanol (2 ml), and a solution of Mn(DMSO)$_6$(ClO$_4$)$_3$ (0.1 mmol; DMSO is dimethyl sul-foxide) in methanol (5 ml) was added dropwise. The resulting grey solid was removed by filtration and single crystals of (I) were obtained by slow evaporation of the solvent. ^{1}H NMR (CH$_3$CN, p.p.m.): δ 2.75 (*t*, 6H, CH$_2$CN), 2.94 (*m*, 12H, NCH$_2$CH$_2$N), 3.23 (*t*, 6H, NCH$_2$).

Crystal data

C$_{15}$H$_{25}$N$_6$$^+$·ClO$_4$$^-$	Mo $K\alpha$ radiation
$M_r = 388.86$	Cell parameters from 2265
Monoclinic, $P2_1/c$	reflections
$a = 12.973$ (7) Å	$\theta = 2.4$–$17.2°$
$b = 9.708$ (6) Å	$\mu = 0.23$ mm^{-1}
$c = 46.04$ (3) Å	$T = 293$ (2) K
$\beta = 92.544$ (12)°	Block, colourless
$V = 5793$ (6) Å^3	$0.32 \times 0.22 \times 0.15$ mm
$Z = 12$	
$D_x = 1.338$ Mg m^{-3}	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	10 150 independent reflections
	5150 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.032$
Absorption correction: empirical	$\theta_{max} = 25.0°$
(*SADABS*; Bruker, 2000)	$h = -15 \rightarrow 15$
$T_{min} = 0.941$, $T_{max} = 0.966$	$k = 0 \rightarrow 11$
28 731 measured reflections	$l = 0 \rightarrow 54$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$
$wR(F^2) = 0.091$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
10 150 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
703 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N13—H125···N11	0.91	2.30	2.809 (3)	115
N13—H125···N12	0.91	2.23	2.798 (3)	120
N23—H225···N21	0.91	2.05	2.689 (3)	126
N23—H225···N22	0.91	2.22	2.775 (3)	119
N33—H325···N31	0.91	2.28	2.882 (3)	123
N33—H325···N32	0.91	2.17	2.758 (3)	122
C102—H104···O13^{vi}	0.97	2.59	3.557 (4)	171
C104—H108···O13^{vi}	0.97	2.53	3.386 (4)	147
C107—H114···O34	0.97	2.52	3.455 (4)	162
C207—H213···N36^{vii}	0.97	2.56	3.513 (4)	169
C211—H220···O23^{viii}	0.97	2.58	3.030 (5)	108
C301—H301···N24^{ix}	0.97	2.61	3.538 (4)	161
C302—H304···O14^{ix}	0.97	2.56	3.385 (4)	143
C303—H305···N15^{iv}	0.97	2.58	3.540 (4)	169
C308—H316···N35^{x}	0.97	2.62	3.387 (4)	136
C310—H317···O24	0.97	2.50	3.396 (4)	153
C310—H318···N34	0.97	2.54	3.435 (4)	153

Symmetry codes: (iv) $-1 + x, -1 + y, z$; (vi) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $1 - x, 1 - y, -z$; (viii) $1 + x, y, z$; (ix) $x - 1, y, z$; (x) $x, 1 + y, z$.

H atoms were fixed geometrically and refined as riding, with C—H distances of 0.97 Å and N—H distances of 0.91 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1210). Services for accessing these data are described at the back of the journal.

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