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The salt-type 1:2 adduct of *meso*-5,5,7,12,12,14-hexa-*C*-methyl-1,4,8,11-tetraazacyclotetradecane (tet-a) and 5-nitroisophthalic acid forms a hydrogen-bonded sheet structure containing two configurational isomers of $[(\text{tet-a})\text{H}_2]^{2+}$

Elizabeth J. MacLean,[a] Simon J. Teat,[a] Dorcas M. M. Farrell,[b] George Ferguson[b] and Christopher Glidewell[b]*

[a]CLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, England, and [b]School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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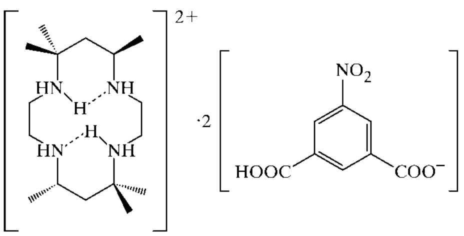
The title compound, *meso*-5,7,7,12,14,14-hexamethyl-4,11-diaza-1,8-diazoniacyclotetradecane bis(3-carboxy-5-nitrobenzoate), $C_{16}H_{38}N_4^{2+}\cdot 2C_8H_4NO_6^-$, is a salt in which the cation is present as two configurational isomers, disordered across a common centre of inversion in $P\overline{1}$, with occupancies of 0.847 (3) and 0.153 (3). The anions are linked into chains by a single O—H···O hydrogen bond [H···O 1.71 Å, O···O 2.5063 (15) Å and O—H···O 156°] and the cations link these anion chains into sheets by means of a range of N—H···O hydrogen bonds [H···O 1.81–2.53 Å, N···O 2.718 (5)–3.3554 (19) Å and N—H···O 146–171°].

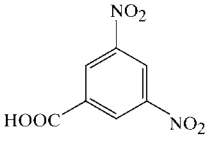
Comment

We report here the structure of the 1:2 salt, (I), formed between the tetraaza macrocycle *meso*-5,5,7,12,12,14-hexa-*C*-methyl-1,4,8,11-tetraazacyclotetradecane (tet-a) and 5-nitroisophthalic acid. We have recently analysed the supramolecular structures of the salt-type adducts formed between tet-a and both monocarboxylic (Gregson *et al.*, 2000) and dicarboxylic acids (Lough *et al.*, 2000; Burchell *et al.*, 2000). With the trigonally trisubstituted benzenecarboxylic acid 3,5-dinitrobenzoic acid, (II), tet-a forms a one-dimensional supramolecular structure, while with 5-hydroxyisophthalic acid, (III), the rather simple hydrogen-bonded array is two-dimensional (Burchell *et al.*, 2000). With the analogous 5-nitroisophthalic acid, whose monoanion, (IV), is isoelectronic with (II), a more complex two-dimensional supramolecular structure is formed in (I).

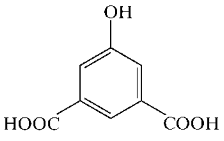
The constitution of (I) is that of a salt, $[(\text{tet-a})\text{H}_2]^{2+}\cdot 2[\text{O}_2\text{NC}_6\text{H}_3(\text{COOH})\text{COO}]^-$ (Fig. 1). The cation lies across a centre of inversion, chosen for the sake of convenience as that at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, while the monoanion lies in a general position. While, in general (Gregson *et al.*, 2000; Lough *et al.*, 2000: Burchell *et al.*, 2000), $[(\text{tet-a})\text{H}_2]^{2+}$ cations adopt the *trans*-III configuration (Barefield *et al.*, 1986), in compound (I), the cation is



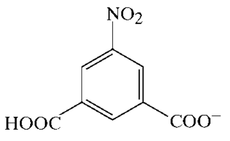
(I)



(II)



(III)



(IV)

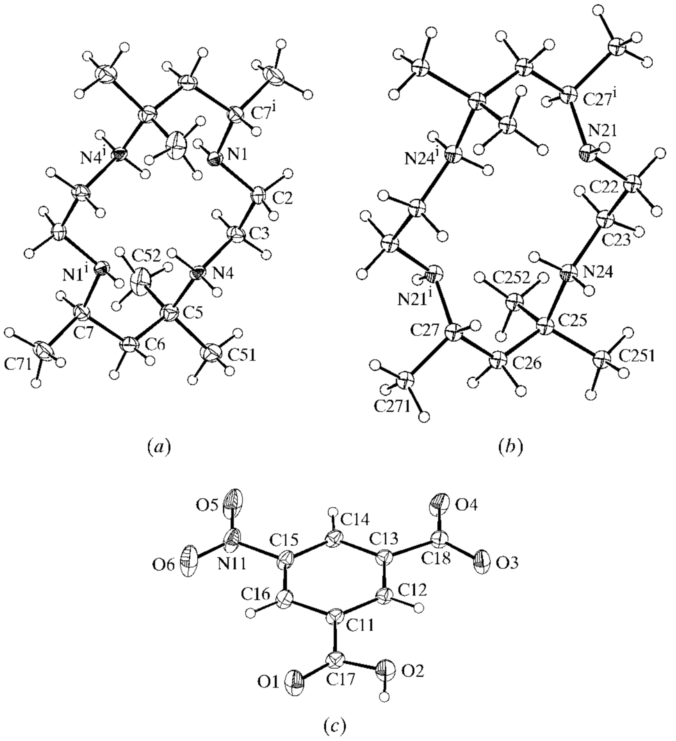


Figure 1
The molecular components of (I), showing the atom-labelling schemes; (*a*) the major isomer of the cation, (*b*) the minor isomer of the cation and (*c*) the anion. Displacement ellipsoids are drawn at the 30% probability level; the minor cation isomer was refined isotropically [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

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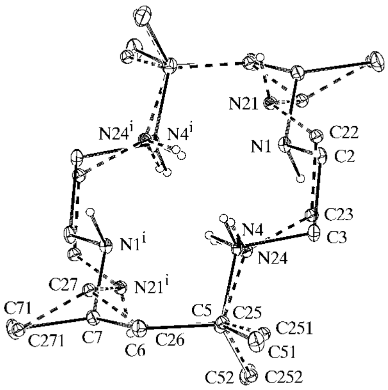

Figure 2
Part of the crystal structure of (I), showing the different configurations of the two isomers of the cation lying across a common centre of inversion. The bonds in the major isomer are shown as full lines and those in the minor isomer as dashed lines. For the sake of clarity, H atoms bonded to C atoms have been omitted. Displacement ellipsoids are drawn at the 10% probability level [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

disordered over two sets of sites, with occupancies 0.847 (3) and 0.153 (3), such that the major form (Fig. 1*a*) is the usual *trans*-III isomer, while the minor form (Fig. 1*b*) is the rather uncommon *trans*-IV isomer. The major differences between these configurational isomers are found in the skeletal torsion angles (Table 1) and in the location of the axial N—H bonds (Figs. 1*a* and 1*b*). In each isomer, there are two axial N—H bonds on each face of the macrocycle, but the two bonds on a common face are separated by a C_3 spacer unit in the *trans*-III isomer and by a C_2 spacer in the *trans*-IV isomer. Both isomers of the cation contain the usual pair of intramolecular N—H$\cdots$N hydrogen bonds (Table 2) and, in the major isomer, the C—N distances clearly reflect the site of protonation at N4. Similarly, in the almost planar anion, the C—O distances clearly reflect the presence of an H atom at O2 only.

The cations and anions in (I) are linked, *via* a number of hydrogen bonds of the O—H$\cdots$O and N—H$\cdots$O types (Table 2), into sheets whose formation is readily analysed by means of the substructure approach (Gregson *et al.*, 2000). The two isomers of the cation display rather different hydrogen-bonding behaviour, despite sharing a common site (Fig. 2), consequent upon the different arrangements of their axial N—H bonds. The anions alone form a simple *C*(8) chain generated by translation along the [100] direction. Carboxyl atom O2 in

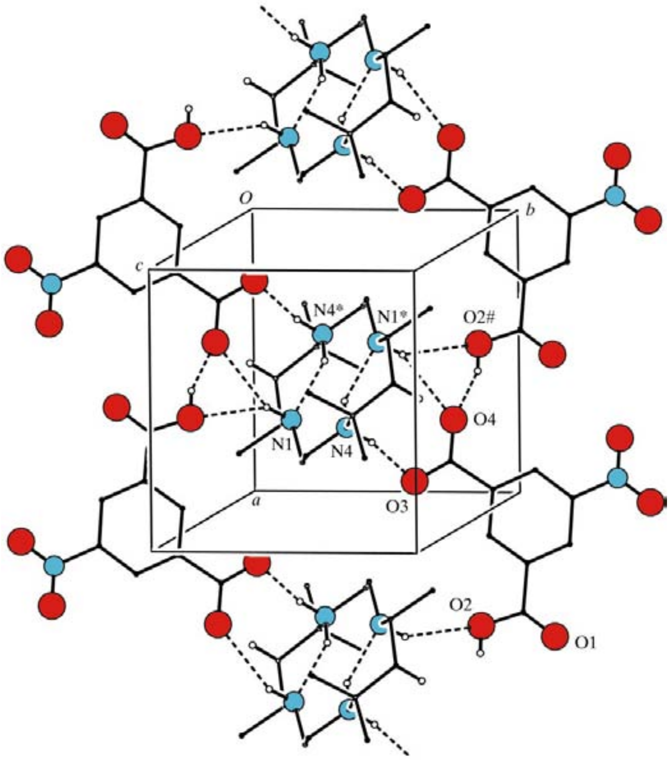

Figure 3
Part of the crystal structure of (I), showing the linking of the anion chains by the major isomer of the cation to form a molecular ladder. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($1 - x, 1 - y, 1 - z$) and ($x - 1, y, z$), respectively.

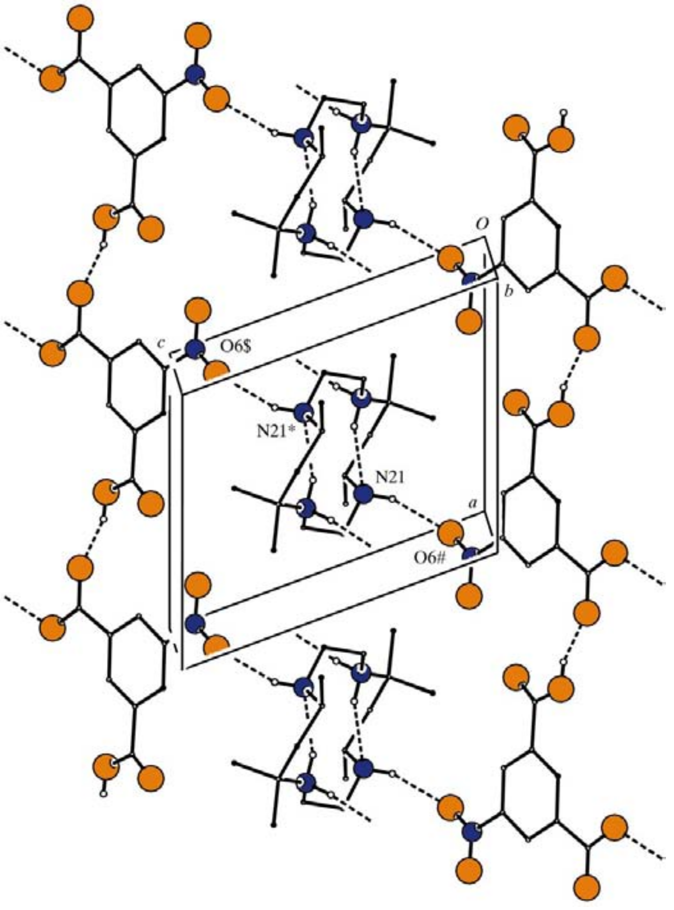

Figure 4
Part of the crystal structure of (I), showing the linking of the molecular ladders by the minor isomer of the cation. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions ($1 - x, 1 - y, 1 - z$), ($2 - x, 2 - y, -z$) and ($x - 1, y - 1, 1 + z$), respectively.

the anion at (x, y, z) acts as a donor to the carboxylate atom O4 in the anion at ($1 + x$, y, z), in a hydrogen bond whose O$\cdots$O distance is very short, but where the H atom is unambiguously located adjacent to one O atom, rather than being centred between the two O sites. Two antiparallel chains, related to one another by centres of inversion, run through each unit cell, and it is the pairwise linking of such chains by the cations which generates the sheet structure.

In the major isomer of the cation centred at ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$), atoms N4 at (x, y, z) and N1 at ($1 - x, 1 - y, 1 - z$) act as hydrogen-bond donors to, respectively, O3 in the anion at (x, y, z) and O2 in the anion at ($x - 1$, y, z), both of which are components of the anion chain lying approximately along the line (x, 1.0, 0.1). The symmetry-related N4 atom at ($1 - x, 1 - y, 1 - z$) and N1 at (x, y, z) in the same cation similarly act as donors to O3 and O2 in the anions at ($1 - x$, $1 - y$, $1 - z$) and ($2 - x$, $1 - y$, $1 - z$), respectively, which are components of the chain lying approximately along the line ($-x$, 0, 0.9). In this way, a chain of edge-fused rings, or a molecular ladder, is formed along the line (x,$\frac{1}{2}$,$\frac{1}{2}$) (Fig. 3).

Adjacent ladders are linked into an (011) sheet by the minor isomer of the cation. In the minor isomer centred at ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$), atoms N24 and N21 at (x, y, z) act as hydrogen-bond donors to, respectively, carboxylate atom O3 in the anion at (x, y, z), part of the (x,$\frac{1}{2}$,$\frac{1}{2}$) ladder, and nitro atom O6 in the anion at ($2 - x$, $2 - y$, $-z$), which is a component of the ladder along (x,$\frac{3}{2}$,$-\frac{1}{2}$) (Fig. 4). The symmetry-related atoms N24 and N21 in the same cation are at ($1 - x$, $1 - y$, $1 - z$), and these act as hydrogen-bond donors to, respectively, O3 in the anion at ($1 - x, 1 - y, 1 - z$), which is another component of the (x,$\frac{1}{2}$,$\frac{1}{2}$) ladder, and atom O6 in the anion at ($x - 1, y - 1, 1 + z$), which lies in the ladder along (x,$-\frac{1}{2}$,$\frac{3}{2}$). Hence, the [100] ladders contain the major isomer of the cation and are linked into an (011) sheet by the minor isomer.

Experimental

Stoichiometric quantities of the two components were individually dissolved in methanol. The solutions were mixed and the mixture set aside to crystallize, yielding microcrystalline (I). Analysis, found: C 54.7, H 6.5, N 11.8%; $C_{32}H_{46}N_6O_{12}$ requires: C 54.4, H 6.6, N 11.9%. Despite many preparations, the crystallites proved to be too small for single-crystal X-ray diffractometry using conventional laboratory sources, but an excellent data set was obtained using synchrotron radiation, collected at the Daresbury synchrotron radiation source, Station 9.8 (Cernik *et al.*, 1997; Clegg *et al.*, 1998).

Crystal data

$C_{16}H_{38}N_4^{2+}\cdot 2C_8H_4NO_6^-$
$M_r = 706.46$
Triclinic, $P\overline{1}$
$a = 8.5183$ (6) Å
$b = 10.2278$ (8) Å
$c = 11.3272$ (9) Å
$\alpha = 66.635$ (1)°
$\beta = 71.387$ (1)°
$\gamma = 82.976$ (1)°
$V = 858.54$ (11) Å^3

$Z = 1$
$D_x = 1.367$ Mg m^{-3}
Synchrotron radiation
Cell parameters from 5312 reflections
$\theta = 2.4$–29.3°
$\mu = 0.11$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.09 × 0.06 × 0.03 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.991$, $T_{max} = 0.997$
8877 measured reflections

4702 independent reflections
4097 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 29.3°$
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 13$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.165$
$S = 1.13$
4702 reflections
262 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 0.2773P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C17	1.1974 (18)	N1—C2	1.475 (2)
O2—C17	1.3147 (18)	C3—N4	1.505 (2)
O3—C18	1.2497 (18)	N4—C5	1.530 (3)
O4—C18	1.2477 (17)	C7—N1^i	1.484 (2)
C7^i—N1—C2—C3	−172.3 (2)	C27^i—N21—C22—C23	−84 (2)
N1—C2—C3—N4	−68.2 (3)	N21—C22—C23—N24	−67 (2)
C2—C3—N4—C5	176.3 (4)	C22—C23—N24—C25	−164 (3)
C3—N4—C5—C6	−175.5 (4)	C23—N24—C25—C26	−168 (4)
N4—C5—C6—C7	66.8 (6)	N24—C25—C26—C27	33 (4)
C5—C6—C7—N1^i	−60.9 (6)	C25—C26—C27—N21^i	37 (3)
C6—C7—N1^i—C2^i	173.2 (3)	C26—C27—N21^i—C22^i	178 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
O2—H2$\cdots$O4^i	0.84	1.71	2.5063 (15)	156
N4—H4$A$$\cdots$N1^{ii}	0.92	2.02	2.764 (4)	137
N1—H1$\cdots$O4^{ii}	0.92	2.48	3.3025 (18)	149
N1—H1$\cdots$O2^{iii}	0.92	2.53	3.3554 (19)	149
N4—H4$B$$\cdots$O3	0.92	1.81	2.718 (5)	169
N24—H24$A$$\cdots$N21^{ii}	0.92	2.25	3.03 (3)	141
N21—H21$\cdots$O6^{iv}	0.92	2.20	3.009 (8)	146
N24—H24$B$$\cdots$O3	0.92	1.91	2.82 (3)	171

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

Compound (I) is triclinic, and space group $P\overline{1}$ was assumed and confirmed by the subsequent analysis. It was apparent from an early stage that the cation was disordered over two sets of sites; with the minor-occupancy atoms refined isotropically, the site-occupancy factors refined to 0.847 (3) and 0.153 (3) for the major and minor sites, respectively. All the H atoms of the anion and the major isomer of the cation were located from difference maps; the locations of the 0.153 (3) occupancy H atoms bonded to N in the minor isomer of the cation were inferred from the non-bonded contact distances involving N21 and N24. All H atoms were treated as riding, with distances O—H 0.84 Å, N—H 0.92 Å, and C—H 0.95 (aromatic), 0.98 (CH_3), 0.99 (CH_2) or 1.00 Å (aliphatic CH). In the final difference map, bonding electron density was clearly apparent in all of the C—C, C—N, C—O and N—O bonds of the anion; the largest densities were in bonds involving C11.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1034). Services for accessing these data are described at the back of the journal.

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