Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

meso-5,5,7,12,12,14-Hexamethyl-4,11-diaza-1,8-diazoniacyclotetradecane (*S*)-malate(2–) methanol disolvate: a chain of rings generated by two pairs of N—H···O hydrogen bonds

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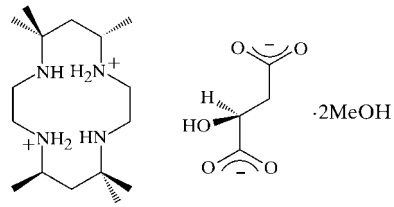
Received 23 April 2003
Accepted 24 April 2003
Online 20 May 2003

The title compound is a methanol-solvated salt, $C_{16}H_{38}N_4^{2+}\cdot C_4H_4O_5^{2-}\cdot 2CH_3OH$, in which the ionic components are linked into chains by two pairs of N—H···O hydrogen bonds [H···O = 1.78–2.21 Å, N···O = 2.702 (14)–3.094 (8) Å and N—H···O = 160–179°]. The methanol molecules are pendent from the chain and are linked to it by O—H···O hydrogen bonds [H···O = 1.86 and 1.89 Å, O···O = 2.691 (9) and 2.708 (16) Å, and O—H···O = 168 and 165°].

Comment

In the salt-type adducts formed between *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($C_{16}H_{36}N_4$, tet-a) and phenols or carboxylic acids, the $(C_{16}H_{36}N_4)H_2^{2+}$ cations generally lie across centres of inversion (Gregson *et al.*, 2000; Lough *et al.*, 2000; Burchell *et al.*, 2000; Bowes, Ferguson, Lough & Glidewell, 2003; Bowes, Ferguson, Lough, Zakaria & Glidewell, 2003). An exception occurs in the salt formed with 5-hydroxyisophthalic acid, in which the cation lies in a general position in space group $P2_12_12_1$ (Burchell *et al.*, 2000). In all of these examples, the cation adopts the *trans*-III configuration (Barefield *et al.*, 1986) and, even in the 5-hydroxyisophthalate salt, the cation is very nearly centrosymmetric.

We have now investigated an example in which a non-centrosymmetric cation environment is specifically imposed by the presence of an enantiopure chiral acid component, chosen in this case to be (*S*)-malic acid [(*S*)-2-hydroxybutane-1,4-dioic acid, $C_4H_6O_5$]. The 1:1 salt formed by tet-a and (*S*)-malic acid crystallizes from methanol solution as the title solvate, (I), in space group *P*1, so that none of the components have any internal crystallographic symmetry. The presence of the chiral anion precludes any further symmetry.



(I)

The fully ordered cation adopts the usual *trans*-III configuration (Fig. 1), with four methyl groups in equatorial sites and two in axial sites, and with paired intra-cation N—H···N hydrogen bonds generating an $R_2^2(10)$ motif (Bernstein *et al.*, 1995). There is almost perfect staggering about all of the C—C and C—N bonds in the cation, and the values of the torsion angles are clearly indicative of the near-centrosymmetric conformation of the cation (Table 1). Four axial N—H bonds are available for intermolecular hydrogen-bond formation, *viz*. two on each face of the disc-like cation.

The anion, by contrast, exhibits orientational disorder, which was modelled using two sets of atomic sites with refined occupancies of 0.702 (8) and 0.298 (8) (Fig. 2). This disorder is such that atoms O22 and O32 are very close to one another, as are atoms O23 and O33. Accordingly, the inter-ion hydrogen bonding is very similar for the two orientations, and hence only the major orientation will be considered further. The anion disorder observed in (I) is similar to that observed for the $C_4H_5O_6^-$ racemic tartrate anions in the salt with the monocation derived from 1,2-bis(4-pyridyl)ethene (Farrell *et*

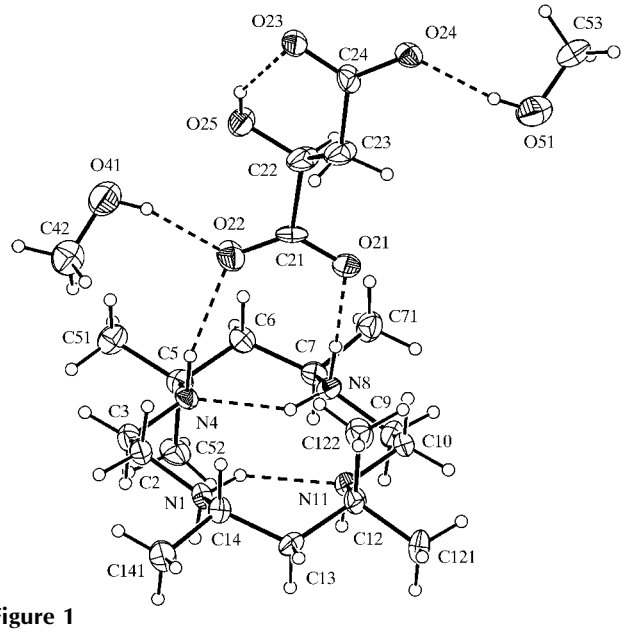


Figure 1
A view of the independent components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and, for the sake of clarity, only the major component of the anion is shown.

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 DOI: 10.1107/S010827010300920X

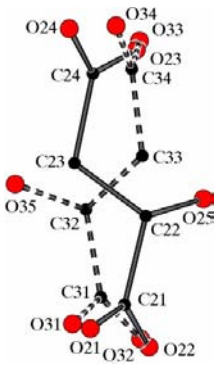

Figure 2
The major (full lines) and minor (broken lines) components of the anion. For the sake of clarity, all H atoms have been omitted.

al., 2002*a*). Within the anion, there is an O—H···O hydrogen bond, forming an $S(6)$ motif, and this bond undoubtedly plays a role in controlling the anion conformation (Fig. 1 and Table 2).

The ionic components within the asymmetric unit are linked by paired N—H···O hydrogen bonds. Atoms N4 and N8 act as hydrogen-bond donors, *via* the axial H4 and H8*A* atoms, respectively, to carboxylate atoms O22 and O21, so generating an $R_2^2(10)$ motif (Fig. 1) of precisely the same type as that observed in the tetrahydrate salt formed between the tet-a cation and the terephthalate anion (Lough *et al.*, 2000). The two independent methanol molecules are linked to the anion *via* O—H···O hydrogen bonds, both having a carboxylate O atom as the acceptor.

Despite the large number of hydrogen bonds within the asymmetric unit, the supramolecular structure depends on just one further pair of N—H···O hydrogen bonds. Atoms N1 and N11 in the cation at (x, y, z) act as hydrogen-bond donors, *via* atoms H1*B* and H11, respectively, to carboxylate atoms O23 and O24 in the anion at $(-1+x, -1+y, z)$, so generating by translation a chain of rings (Fig. 3) running parallel to the [110] direction. The methanol molecules are simply pendent from this chain and play no further role in the supramolecular aggregation. The only significant direction-specific interaction between adjacent chains is provided by a C—H···O hydrogen bond. Atom C2 in the cation at (x, y, z), which is adjacent to the cationic N1 atom, acts as a hydrogen-bond donor, *via* atom H2*B*, to carboxylate atom O21 in the anion at $(-1+x, y, z)$, and propagation of this interaction links the [110] chains generated by the hard (Desiraju & Steiner, 1999) hydrogen bonds into (001) sheets.

As with other amine salts of (*S*)-malic acid (Farrell *et al.*, 2002*b*), the supramolecular structure of (I) closely mimics a centrosymmetric arrangement, even though exact centrosymmetry is ruled out by the chiral anion.

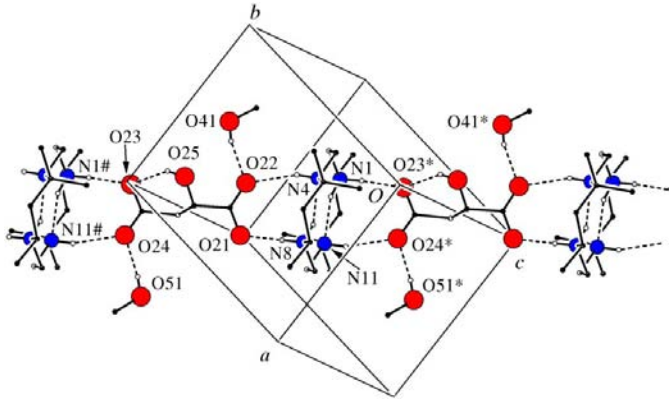

Figure 3
Part of the crystal structure of (I), showing the formation of a chain along [110]. For the sake of clarity, H atoms bonded to C atoms have been omitted, and only the major orientation of the anion is shown. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x-1, y-1, z)$ and $(1+x, 1+y, z)$, respectively.

Experimental

Equimolar quantities of tet-a (Hay *et al.*, 1975) and (*S*)-malic acid (purchased from Aldrich) were separately dissolved in methanol. The solutions were mixed and the mixture was set aside to crystallize, providing analytically pure (I). Analysis found: C 54.7, H 11.0, N 11.7%; $C_{22}H_{50}N_4O_7$ requires: C 54.7, H 10.4, N 11.6%. Crystals of (I) suitable for single-crystal X-ray diffraction were selected directly from the sample as prepared.

Crystal data

$C_{16}H_{38}N_4^{2+}\cdot C_4H_4O_5^{2-}\cdot 2CH_4O$
$M_r = 482.66$
Triclinic, $P\overline{1}$
$a = 8.6559\ (9)$ Å
$b = 9.3275\ (9)$ Å
$c = 10.1044\ (12)$ Å
$\alpha = 113.379\ (5)^\circ$
$\beta = 108.908\ (4)^\circ$
$\gamma = 100.345\ (4)^\circ$
$V = 662.31\ (12)$ Å^3
$Z = 1$
$D_x = 1.210$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8456 reflections
$\theta = 3.5$–27.6°
$\mu = 0.09$ mm^{-1}
$T = 150\ (1)$ K
Plate, colourless
0.30 × 0.28 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*, Otwinowski & Minor, 1997)
$T_{min} = 0.950$, $T_{max} = 0.988$
8456 measured reflections
3022 independent reflections
1802 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 27.6^\circ$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.202$
$S = 1.03$
3022 reflections
333 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1019P)^2 + 0.0709P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.08 (2)

Table 1
Selected torsion angles (°).

N1—C2—C3—N4	−65.0 (9)	N8—C9—C10—N11	65.8 (9)
C2—C3—N4—C5	179.9 (7)	C9—C10—N11—C12	177.4 (7)
C3—N4—C5—C6	179.2 (7)	C10—N11—C12—C13	−178.5 (7)
N4—C5—C6—C7	63.6 (9)	N11—C12—C13—C14	−62.2 (9)
C5—C6—C7—N8	−63.6 (9)	C12—C13—C14—N1	64.9 (9)
C6—C7—N8—C9	168.9 (7)	C13—C14—N1—C2	−169.1 (7)
C7—N8—C9—C10	178.4 (7)	C14—N1—C2—C3	177.7 (7)
O22—C21—C22—C23	119.7 (14)	O25—C22—C23—C24	−47.8 (15)
C21—C22—C23—C24	−176.7 (10)	C22—C23—C24—O23	55.5 (16)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N11	0.92	2.05	2.799 (8)	138
N8—H8B···N4	0.92	2.00	2.758 (8)	138
O25—H25···O23	0.84	1.98	2.721 (12)	146
N4—H4···O22	0.92	2.17	3.046 (15)	160
N8—H8A···O21	0.92	1.78	2.702 (14)	179
O41—H41···O22	0.84	1.89	2.708 (16)	165
O51—H51···O24	0.84	1.86	2.691 (9)	168
N1—H1B···O23^{i}	0.92	1.85	2.760 (11)	172
N11—H11···O24^{i}	0.92	2.21	3.094 (8)	161
C2—H2B···O21^{ii}	0.99	2.45	3.39 (2)	159

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

Crystals of (I) are triclinic; space group $P\overline{1}$ was chosen as the acid component was enantiopure (*S*)-malic acid. The anion is disordered over a major and a minor orientation, with refined occupancies of 0.702 (8) and 0.298 (8). Standard DFIX (*SHELXL*97; Sheldrick, 1997) restraints were used for the dimensions of the disordered anion. The atoms of the minor anion were refined with a common U_{iso} value, and all other non-H atoms were refined anisotropically. H atoms were visible in difference maps and were subsequently treated as riding atoms, with C—H distances of 0.98 (CH_3), 0.99 (CH_2) and 1.00 Å (CH), N—H distances of 0.92 Å, and O—H distances of 0.84 Å. The cation was positioned so as to lie with its centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the anion was then centred approximately at $(1, 1, \frac{1}{2})$. In the absence of any significant anomalous scattering, the Flack parameter (Flack, 1983) was indeterminate (Flack & Bernardinelli, 2000). Hence, the Friedel equivalents were merged prior to the final refinements, and the absolute structure was set by reference to the known chirality of the enantiopure acid employed.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC, Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1635). Services for accessing these data are described at the back of the journal.

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