Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A structural hierarchy in the hydrogen-bonded adduct *N*,*N*′-dimethylpiperazine–tartaric acid–water (1/2/2): an *N*-component *N*-dimensional structure (*N* = 3) with substructures having *N* = 1 and 2

Dorcas M. M. Farrell,[a] George Ferguson,[a]† Alan J. Lough[b] and Christopher Glidewell[a]*

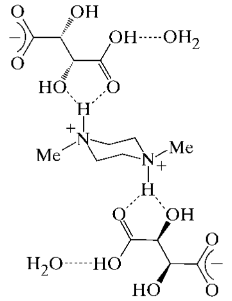
[a]School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and [b]Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 3H6
Correspondence e-mail: cg@st-andrews.ac.uk

Received 15 October 2001
Accepted 16 October 2001
Online 14 December 2001

In the hydrated adduct *N*,*N*′-dimethylpiperazine-1,4-diium bis(3-carboxy-2,3-dihydroxypropanoate) dihydrate, $[\mathrm{MeNH(CH_2CH_2)_2NHMe}]^{2+}\cdot 2(\mathrm{C_4H_5O_6})^{-}\cdot 2\mathrm{H_2O}$ or $\mathrm{C_6H_{16}N_2}^{2+}\cdot 2\mathrm{C_4H_5O_6}^{-}\cdot 2\mathrm{H_2O}$, formed between racemic tartaric acid and *N*,*N*′-dimethylpiperazine (triclinic $P\overline{1}$, $Z' = 0.5$), the cations lie across centres of inversion. The anions alone form chains, and anions and water molecules together form sheets; the sheets are linked by the cations to form a pillared-layer framework. The supramolecular architecture thus takes the form of a family of *N*-dimensional *N*-component structures having *N* = 1, 2 or 3.

Comment

We have recently investigated the salt-like adducts formed by functionalized aromatic carboxylic acids with organic diamines (Burchell, Ferguson *et al.*, 2001; Burchell, Glidewell *et al.*, 2001) and we have now turned our attention to the highly functionalized acyclic acid tartaric acid (2,3-dihydroxy-1,4-butanedioic acid, $\mathrm{C_4H_6O_6}$). Racemic tartaric acid and *N*,*N*′-dimethylpiperazine, $\mathrm{MeN(CH_2CH_2)_2NMe}$, form a hydrated salt, *i.e.* $[\mathrm{MeNH(CH_2CH_2)_2NHMe}]^{2+}\cdot 2(\mathrm{C_4H_5O_6})^{-}\cdot 2\mathrm{H_2O}$, (I) (Fig. 1). This salt crystallizes in space group $P\overline{1}$ with $Z' = 0.5$. The cation adopts a chair conformation, with equatorial *N*-methyl groups, and lies across a centre of inversion, chosen for convenience as that at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. All of the OH units in the anion act as donors in O—H···O hydrogen bonds (Table 1), and the water molecule acts as a double donor and as a single acceptor in O—H···O hydrogen bonds. The overall three-component supramolecular structure is three-dimensional, in the form of a pillared-layer framework, and it is possible to identify a one-dimensional one-component substructure built from anions only, and a two-dimensional two-component substructure built from anions and water molecules. There is thus a family of *N*-dimensional *N*-component structures for *N* = 1, 2 or 3, precisely as observed in the adduct ethane-1,2-diphosphonic acid–4,4′-bipyridyl–water (1/1/2) (Glidewell *et al.*, 2000).



(I)

The carboxyl O3 atom in the anion at (*x*, *y*, *z*) acts as hydrogen-bond donor to the carboxylate O1 atom in the anion at (1 + *x*, *y*, *z*), so generating, by translation, a *C*(7) chain running parallel to the [100] direction. In the same anion at (*x*, *y*, *z*), the hydroxyl O6 atom acts as donor to O1 in the anion at (−*x*, −*y*, 1 − *z*). Propagation of these two hydrogen bonds generates a chain of fused rings (Fig. 2), with $R_2^2(12)$ rings centred at (*n*, 0, $\frac{1}{2}$) (*n* = zero or integer) and $R_4^2(14)$ rings centred at (*n* + $\frac{1}{2}$, 0, $\frac{1}{2}$) (*n* = zero or integer).

The water O7 atom at (*x*, *y*, *z*) acts as hydrogen-bond donor, *via* H71 and H72, respectively, to O5 at (*x*, *y*, *z*) and O2 at (1 + *x*, *y*, *z*), so generating a third type of ring, of $R_3^3(12)$ type (Fig. 2). The hydroxyl O5 atom at (*x*, *y*, *z*) is a component of the chain of fused rings along (*x*, 0, $\frac{1}{2}$); this O5 atom acts as hydrogen-bond donor to the water O7 atom at (1 − *x*, 1 − *y*, 2 − *z*), which is a component of the chain of fused rings along

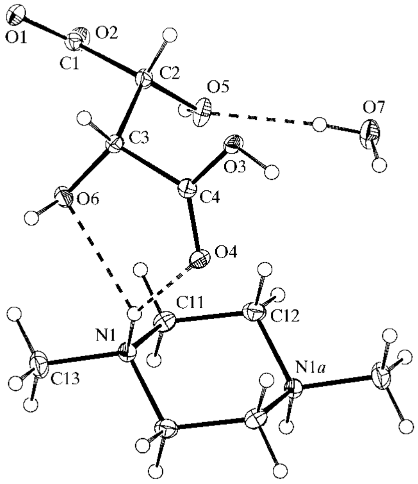


Figure 1
The molecular components of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atom marked '*a*' is at the symmetry position (1 − *x*, 1 − *y*, 1 − *z*).

---

† Permanent address: Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

DOI: 10.1107/S0108270101017449

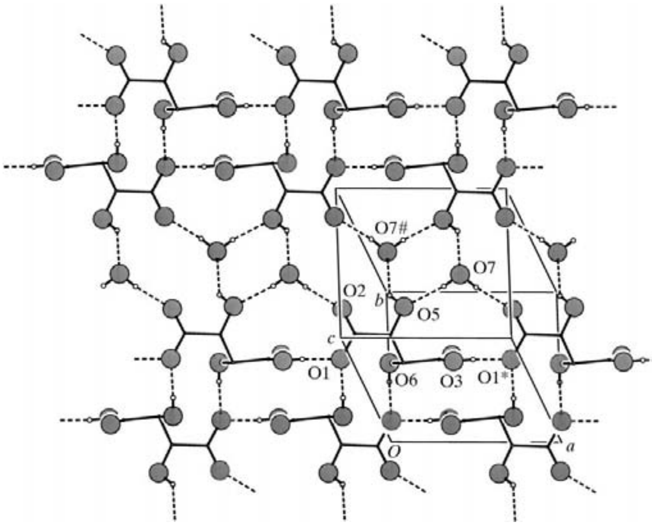


Figure 2
Part of the crystal structure of (I) showing the [100] chains of fused rings, formed by the anions, linked into a $(01\overline{1})$ sheet by the water molecules. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 + x, y, z)$ and $(1 - x, 1 - y, 2 - z)$, respectively.

$(x, 1, \frac{3}{2})$. Thus, this final O—H···O hydrogen bond not only gives rise to a second chain of fused rings along the line $(x, \frac{1}{2}, 1)$ containing two further types of ring, *viz.* $R^4_4(14)$ rings centred at $(n, \frac{1}{2}, 1)$ (n = zero or integer) and $R^4_4(8)$ rings centred at $(n + \frac{1}{2}, \frac{1}{2}, 1)$ (n = zero or integer), but it also serves to link all the [100] chains of fused rings into $(01\overline{1})$ sheets (Fig. 2). Within these sheets, there are no fewer than five different ring motifs, four of which are centrosymmetric; only the $R^3_3(12)$ rings are non-centrosymmetric.

The $(01\overline{1})$ sheets are almost planar and are linked into a continuous framework by the cations. The two N atoms in the cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, and they act as hydrogen-bond donors to O4 atoms at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, respectively, which lie in adjacent sheets. In this manner, each sheet is linked to its two neighbouring sheets by cations arranged as pillars between the anion–water layers (Fig. 3).

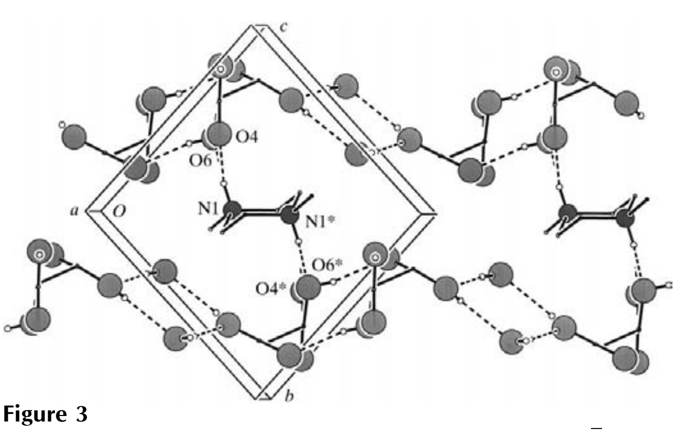


Figure 3
Part of the crystal structure of (I) showing the linking of the $(01\overline{1})$ sheets by the cations. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

Experimental

Equimolar quantities of racemic tartaric acid and *N,N′*-dimethylpiperazine were separately dissolved in methanol. The solutions were mixed and set aside to crystallize, producing analytically pure (I). Analysis: found C 37.4, H 7.0, N 6.2%; $C_{14}H_{30}N_2O_{14}$ requires C 37.3, H 6.7, N 6.2%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_6H_{16}N_2^{2+}\cdot 2C_4H_5O_6^{-}\cdot 2H_2O$
$M_r = 450.40$
Triclinic, $P\overline{1}$
$a = 7.2907\ (3)$ Å
$b = 8.3423\ (4)$ Å
$c = 8.4324\ (4)$ Å
$\alpha = 96.406\ (2)^\circ$
$\beta = 106.359\ (2)^\circ$
$\gamma = 90.430\ (3)^\circ$
$V = 488.63\ (4)$ Å^3

$Z = 1$
$D_x = 1.531$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2102 reflections
$\theta = 2.9$–27.5°
$\mu = 0.14$ mm^{-1}
$T = 150\ (2)$ K
Plate, colourless
$0.35 \times 0.35 \times 0.15$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.953$, $T_{\max} = 0.980$
6667 measured reflections
2237 independent reflections

1691 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$
$\theta_{\max} = 27.5^\circ$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.109$
$S = 1.03$
2237 reflections
149 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.0973P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.035 (9)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4	0.93	1.91	2.761 (2)	151
N1—H1···O6	0.93	2.29	2.947 (2)	127
O3—H3···O1$^{\rm i}$	0.84	1.65	2.483 (2)	172
O5—H5···O2	0.84	2.15	2.643 (2)	117
O5—H5···O7$^{\rm ii}$	0.84	2.17	2.836 (2)	137
O6—H6···O1$^{\rm iii}$	0.84	1.95	2.778 (2)	168
O7—H71···O5	0.86 (2)	1.99 (2)	2.826 (2)	167 (2)
O7—H72···O2$^{\rm i}$	0.89 (3)	1.92 (3)	2.805 (2)	171 (2)

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

Compound (I) crystallized in the triclinic system; space group $P\overline{1}$ was assumed and confirmed by the analysis. The coordinates of the H atoms of the O7 water molecule were determined from a difference map and were then allowed to refine isotropically subject to a *DFIX* restraint. All other H atoms were treated as riding, with distances C—H = 0.98–1.00 Å, N—H = 0.93 Å and O—H = 0.84 Å.

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, 2001); 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: SK1517). Services for accessing these data are described at the back of the journal.

References

Burchell, C. J., Ferguson, G., Lough, A. J., Gregson, R. M. & Glidewell, C. (2001). *Acta Cryst.* B**57**, 329–338.

Burchell, C. J., Glidewell, C., Lough, A. J. & Ferguson, G. (2001). *Acta Cryst.* B**57**, 201–212.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Glidewell, C., Ferguson, G., Gregson, R. M. & Lough, A. J. (2000). *Acta Cryst.* C**56**, 855–858.

Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Spek, A. L. (2001). *PLATON*. August 2001 Version. University of Utrecht, The Netherlands.