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# Piperazinium L-Tartrate

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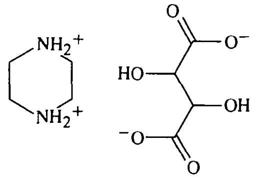
## Abstract

The structure of piperazinium L-tartrate, $C_4H_{12}N_2^{2+}.C_4H_4O_6^{2-}$, exhibits a complex three-dimensional network of hydrogen bonds. The divalent anions create puckered layers *via* two O—H···O hydrogen bonds and neighbouring layers are then crosslinked by four N—H···O interactions through the divalent cations.

## Comment

Recent years have seen considerable interest in the use of hydrogentartrate ions as a means of creating hydrogen-bonded two-dimensional aggregates (Aakeröy & Hitchcock, 1993; Zyss, Pecaut, Levy & Masse, 1993; Watanabe, Noritake, Hirose, Okada & Kurauchi, 1993; Dastidar, Row, Prasad, Subramanian & Bhattacharya, 1993). Such motifs have been employed as structural 'scaffolding' in the crystal engineering of many new materials for nonlinear optics. The cornerstone of the two-dimensional sheet is a head-to-tail (from the carboxylic end to the carboxylate end) O—H···O interaction between adjacent anions. However, if we eliminate the chemical basis of this link (by deprotonating both ends of the acid), the strongest and most important hydrogen-bonding interaction between anions has been removed [observed O···O distances for this interaction are commonly 2.50–2.55 Å (Aakeröy & Hitchcock, 1993)]. Consequently, this should have a considerable effect on the structure of the anionic aggregates in organic tartrate(2−) salts. The anions may still create a layered structure through other O—H···O interactions or, alternatively, the infinite two-dimensional aggregate may be broken up altogether in favour of another motif. In order to examine this scenario, we are currently performing a structural study of pairs of hydrogen-L-tartrate and L-tartrate salts with the same counterion. The crystallographic literature contains only two examples of resolved tartrates(2−) with organic counterions, ethylendiammonium L-tartrate (Fair & Schlemper, 1977; Palmer & Ladd, 1977) and bisguanidinium L-tartrate monohydrate (Krumbe, Haussuhl & Frohlich, 1989). The crystal structure of piperazinium(2+) bis(hydrogen-L-tartrate) has been determined previously (Aakeröy, Hitchcock & Seddon, 1992), and the synthesis and X-ray single crystal structure determination of the corresponding L-tartrate(2−) salt (I) reported herein provides the basis for a valuable structural comparison.



(I)

The divalent cation of the title compound does not show any unusual geometric features (Fig. 1 and Table 1) and displays a chair conformation with expected endocyclic bond lengths and bond angles. The divalent anion exists in the expected *trans* configuration; the torsion angle of the C—C—C—C backbone is 178.42 (11)°. There is some evidence to suggest that glycolic acid moieties normally exhibit a planar conformation in α-hydroxy carboxylic acids (Stouten, Kroon-Batenburg & Kroon, 1989), an arrangement which is often the result of an intramolecular hydrogen-bond interaction. However, in the anion of the title compound, each carboxylate moiety shows considerable deviation from coplanarity with respect to the adjacent hydroxy functional group; O(12′)—C(1′)—C(2′)—O(21′) −8.23 (2)° and O(31′)—C(3′)—C(4′)—O(42′) −14.55(2)°. This variation must be attributed to the specific intermolecular hydrogen-bond interactions between the anion and the strong hydrogen-bond donors of the cation.

Despite the fact that the possibility for a head-to-tail hydrogen bond between adjacent anions has been removed due to the double deprotonation of the acid,

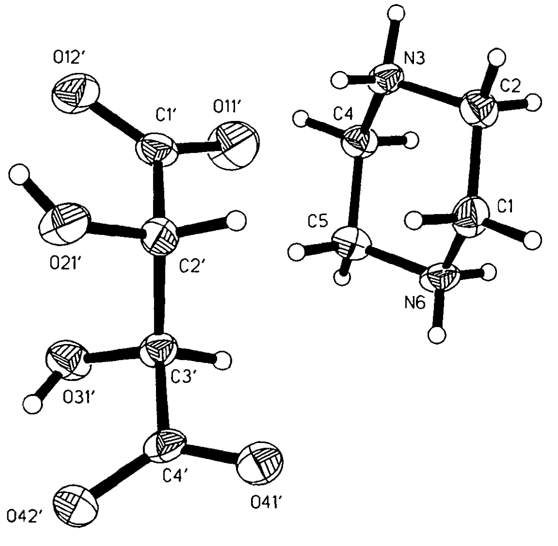


Fig. 1. Geometry, displacement ellipsoids (50% probability) and numbering scheme for the ion pair of the title compound.

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the anions still create an infinite anionic layer, parallel to *ab* (Fig. 2). This motif is created through two O···O interactions between the hydroxy groups (the donors) and the carboxylate moieties (the acceptors) (Table 2); the resulting layers display a puckered geometry.

The divalent cations, each with four strong hydrogen-bond donors involved in hydrogen bonds to four different anions, provide crosslinks between neighbouring puckered anionic layers, through four N···O hydrogen-bond interactions (Fig. 3). This complex three-dimensional hydrogen-bonded network results in a densely packed architecture, $D_x$ = 1.509 g cm$^{-3}$.

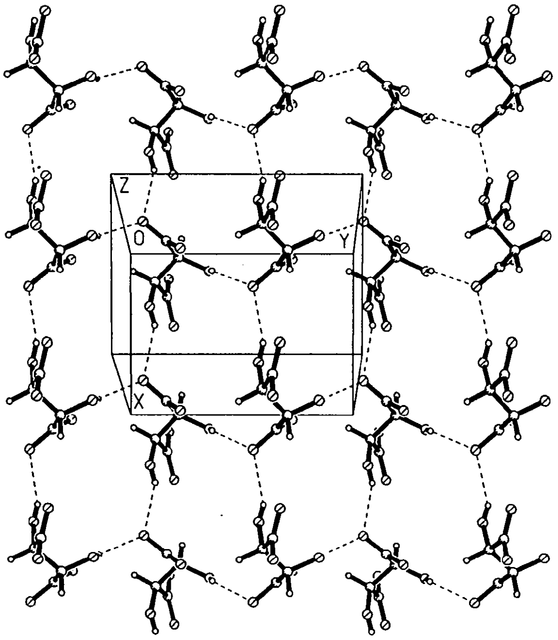

Fig. 2. A view of the infinite anionic layer, parallel with the *ab* plane. Hydrogen bonds are indicated by dashed lines.

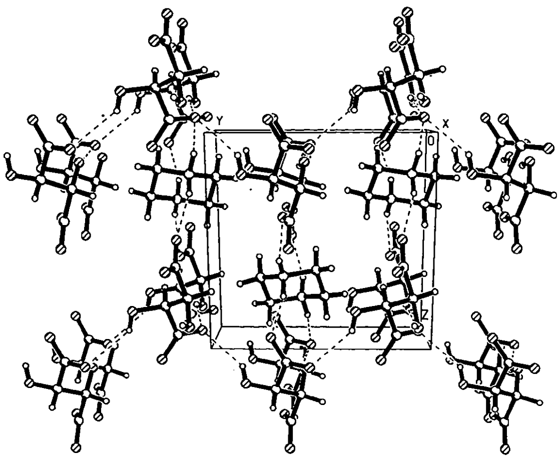

Fig. 3. The piperazinium(2+) crosslink between neighbouring (buckled) anionic layers. The layers are viewed edge on, only three cations are shown for clarity and hydrogen bonds are indicated by dashed lines.

The corresponding piperazinium(2+) bis(hydrogen-L-tartrate) salt (Aakeröy, Hitchcock & Seddon, 1992) also contains two-dimensional layers generated by two O···O hydrogen bonds. In this case, neighbouring anions are linked in the expected head-to-tail fashion. The piperazinium cations form layers, halfway between the anion layers. Each cation is hydrogen bonded to two O atoms in the layer above and by symmetry-related hydrogen bonds to two O atoms in the anion layer below. This compound, with its compact packing of ions throughout the structure, also has a high density, $D_x$ = 1.63 g cm$^{-3}$.

A comparison with the other two resolved organic tartrates(2−), ethylendiammonium L-tartrate and bis-guanidinium L-tartrate monohydrate, shows that in both cases the anions create infinite chains not layers. Consequently, based upon the three extant structures, the tartrate(2−) anions do not seem to be as structurally consistent as the corresponding hydrogentartrate anions (Aakeröy & Hitchcock, 1993). The reason for this is probably that whereas the hydrogentartrate anion contains a powerful hydrogen-bond donor (–COOH) which interacts strongly and preferentially with the (–COO$^-$) acceptor, the only donor on the tartrate anion, (–OH), is not powerful enough to hold the layers together in the presence of cations with differing hydrogen-bond donor abilities.

## Experimental

Piperazinium(2+) L-tartrate(2−) was prepared by mixing equimolar aqueous solutions of piperazine and L-tartaric acid. Transparent colourless crystals were obtained by slow evaporation from water.

*Crystal data*

$C_4H_{12}N_2^{2+}.C_4H_4O_6^{2-}$
$M_r$ = 236.23
Monoclinic
$P2_1$
$a$ = 6.4262 (10) Å
$b$ = 9.1322 (10) Å
$c$ = 9.3627 (10) Å
$\beta$ = 108.850 (10)°
$V$ = 519.98 (11) Å$^3$
$Z$ = 2
$D_x$ = 1.509 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 38 reflections
$\theta$ = 5–12.5°
$\mu$ = 0.13 mm$^{-1}$
$T$ = 293 (2) K
Needle
0.96 × 0.36 × 0.16 mm
Colourless

*Data collection*

Siemens $P4$ diffractometer
$\omega$ scans
Absorption correction: none
1993 measured reflections
1823 independent reflections
1796 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.0124

$\theta_{\rm max}$ = 25°
$h = 0 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 10$
3 standard reflections monitored every 97 reflections
intensity decay: ±1%

*Refinement*

Refinement on $F^2$
$R(F) = 0.0248$
$wR(F^2) = 0.0658$
$S = 1.085$
1823 reflections
146 parameters
$w = 1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$
where $P = [\max F_o^2, 0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.157$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.162$ e Å$^{-3}$
Extinction correction: $F_c^* = F_ck[1 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]$
Extinction coefficient: $\chi = 0.177$ (9)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $U_{\text{eq}}$ |
|---|---|---|---|---|
| C(1) | −0.5779 (3) | 0.4773 (2) | −0.6549 (2) | 0.029 (1) |
| C(2) | −0.5047 (3) | 0.5182 (2) | −0.7866 (2) | 0.029 (1) |
| N(3) | −0.3463 (2) | 0.4081 (1) | −0.8054 (1) | 0.024 (1) |
| C(4) | −0.4425 (3) | 0.2579 (2) | −0.8263 (2) | 0.026 (1) |
| C(5) | −0.5191 (3) | 0.2163 (2) | −0.6958 (2) | 0.029 (1) |
| N(6) | −0.6749 (2) | 0.3277 (2) | −0.6748 (1) | 0.028 (1) |
| C(1′) | 0.1048 (2) | 0.3610 (2) | −0.4015 (2) | 0.027 (1) |
| O(11′) | −0.0590 (2) | 0.3588 (2) | −0.5162 (1) | 0.050 (1) |
| O(12′) | 0.2969 (2) | 0.3290 (2) | −0.3946 (1) | 0.038 (1) |
| C(2′) | 0.0716 (2) | 0.4078 (2) | −0.2529 (2) | 0.024 (1) |
| O(21′) | 0.2753 (2) | 0.4254 (1) | −0.1377 (1) | 0.031 (1) |
| C(3′) | −0.0698 (2) | 0.2957 (2) | −0.2043 (2) | 0.022 (1) |
| O(31′) | 0.0288 (2) | 0.1556 (1) | −0.1869 (1) | 0.030 (1) |
| C(4′) | −0.1082 (2) | 0.3450 (2) | −0.0579 (1) | 0.022 (1) |
| O(41′) | −0.2368 (2) | 0.4501 (1) | −0.0665 (1) | 0.031 (1) |
| O(42′) | −0.0096 (2) | 0.2744 (1) | 0.0589 (1) | 0.031 (1) |

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

| *D*—H···*A* | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|
| N(3)—H···O(41′$^{\text{i}}$) | 1.760 (2) | 2.780 (2) | 170 (4) |
| N(3)—H···O(11′) | 1.936 (2) | 2.777 (2) | 153 (3) |
| N(6)—H···O(12′$^{\text{ii}}$) | 1.907 (2) | 2.688 (2) | 156 (3) |
| N(6)—H···O(42′$^{\text{iii}}$) | 1.859 (2) | 2.759 (2) | 160 (3) |
| O(31′)—H···O(42′$^{\text{iv}}$) | 2.105 (2) | 2.627 (2) | 125 (3) |
| O(21′)—H···O(12′$^{\text{v}}$) | 2.207 (1) | 2.607 (1) | 110 (3) |

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

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# One Bicyclic β-Lactam and Two Bicyclic γ-Lactam Compounds

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## Abstract

The crystal structures of the bicyclic β-lactam, *rac*-(2*R**,4*S**,6*S**)-4-chloro-4-methyl-8-oxo-1-azabicyclo[4.2.0]octane-2-carboxylic acid methyl ester, $C_{10}H_{14}ClNO_3$ (1), and the bicyclic γ-lactams, *rac*-(5*R**,7*S**,9*S**)-7-chloro-7-methyl-3-oxooctahydroindolizine-5-carboxylic acid methyl ester, $C_{11}H_{16}ClNO_3$ (2), and *rac*-(5*R**, 6*S**, 10*R**)-3-oxo-6-vinyloctahydro-1*H*-pyrrolo[1,2-*a*]azepine-5-carboxylic acid methyl ester, $C_{13}H_{19}NO_3$ (3), have been established by X-ray crystallography. In (1) and (2) the α-amino ester function and the Cl atom occupy an axial position in a chair-like piperidine ring. In (3) the methyl ester and the vinyl group are equatorially placed on the chair-like seven-

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