

Piperazine-1,4-dium bis(3-carboxy-2,3-dihydroxypropanoate)

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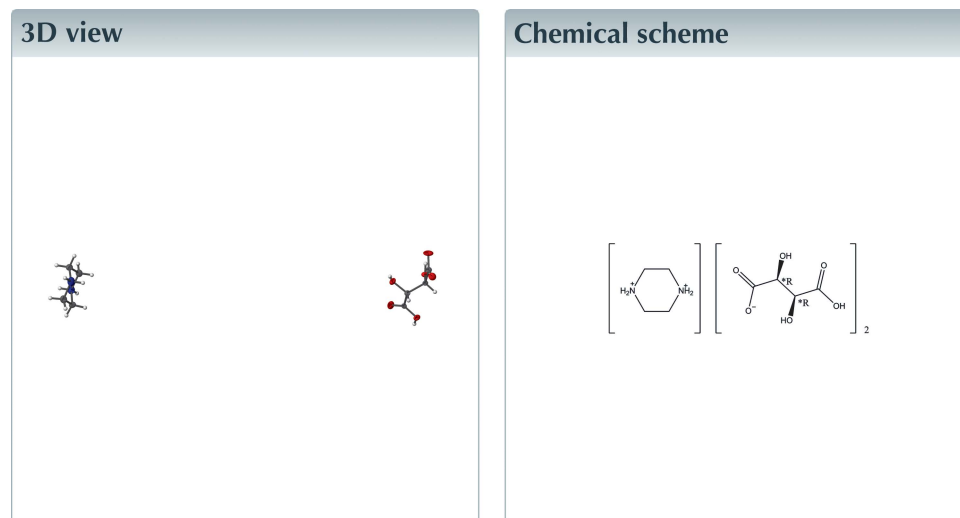
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Keywords: crystal structure; organic salt; hydrogen bonds; three-dimensional network.

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Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title salt, $C_4H_{12}N_2^{2+} \cdot 2C_4H_5O_6^-$, comprises one half of the piperazine-1,4-dium dication lying on a twofold rotation axis and one 3-carboxy-2,3-dihydroxypropanoate anion. In the crystal, the ions are linked into a three-dimensional network by $N-H \cdots O$, $C-H \cdots O$ and $O-H \cdots O$ hydrogen bonds.



Structure description

The asymmetric unit of the title compound comprises one-half of a piperazine-1,4-dium cation, which lies on a twofold rotation axis, and one 3-carboxy-2,3-dihydroxypropanoate anion (Fig. 1). The N–C and C–C bond lengths of this cation are comparable with the values observed in related piperazine-1,4-dium adducts or co-crystals piperazine-1,4-dium bis(2,4,5-tricarboxybenzoate) dihydrate (Narayanam *et al.*, 2013), piperazine-1,4-dium bis(3,5-dicarboxybenzoate) (Dong *et al.*, 2010) and piperazine-1,4-dium 2-(carboxymethyl)-2-hydroxybutanedioate monohydrate (Liu *et al.*, 2010). In addition, the C–C, C–O and C=O bond lengths of the dihydroxypropanoate anion are similar to those in the related compounds 2-amino-4-methylpyridin-1-ium (2*R*,3*R*)-3-carboxy-2,3-dihydroxypropanoate monohydrate (Jovita *et al.*, 2014), (*R*)-doxylaminium (*R,R*)-tartrate (Dayananda *et al.*, 2012) and 2-(1*H*-imidazol-2-yl)-1*H*-imidazol-3-ium 3-carboxy-2,3-dihydroxypropanoate hemihydrate (Gao *et al.*, 2014).

In the crystal, the cations and anions are linked by $N-H \cdots O$, $C-H \cdots O$ and $O-H \cdots O$ hydrogen bonds (Table 1, Fig. 2), forming a three-dimensional network.

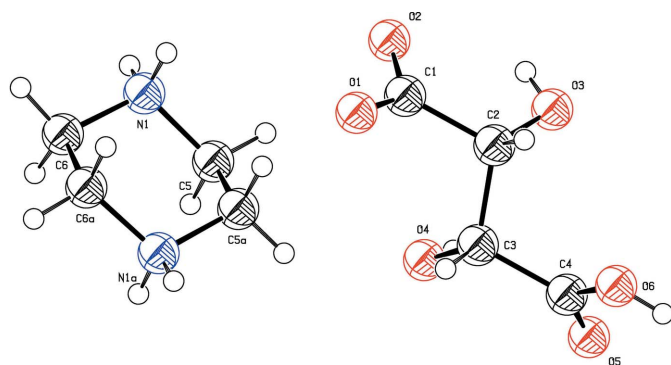


Figure 1
The molecular structure of the title compound, showing the atomic numbering and 30% probability displacement ellipsoids. In the cation, the atoms labelled with the suffix *a* are generated by the twofold axis (symmetry operation $y, x, 2 - z$).

Synthesis and crystallization

At room temperature, a solution of tartaric acid in acetone and propionic acid (as co-solvent), was gradually added with stirring to a solution of piperazine in acetone (in an equimolar ratio). After one day, the supernatant layer was separated and the residue was recrystallized by slow evaporation from a mixture of ethanol–water (1:1).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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References

Bruker (2015). *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dayananda, A. S., Dutkiewicz, G., Yathirajan, H. S. & Kubicki, M. (2012). *Acta Cryst.* **E68**, o1054–o1055.
Dong, G.-Y., Fan, L.-H., Yang, L.-X. & Khan, I. U. (2010). *Acta Cryst.* **E66**, o1097.

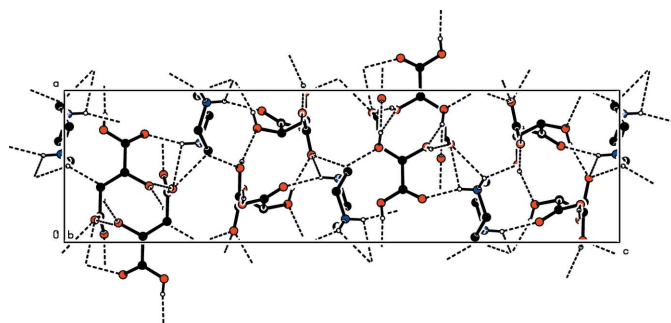


Figure 2
A partial packing diagram of the title compound. The O–H···O, N–H···O and C–H···O hydrogen bonds are shown as dotted lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1 <i>A</i> ···O3 ⁱ	0.89	2.02	2.8118 (10)	147
N1–H1 <i>B</i> ···O5 ⁱⁱ	0.89	1.98	2.8167 (10)	155
O3–H3 <i>A</i> ···O2	0.82	2.17	2.6525 (9)	118
O3–H3 <i>A</i> ···O4 ⁱⁱⁱ	0.82	2.14	2.8581 (9)	146
O4–H4···O1 ⁱⁱⁱ	0.82	1.94	2.7225 (9)	160
O6–H6···O2 ^{iv}	0.82	1.67	2.4810 (9)	172
C2–H2···O1 ^v	0.98	2.60	3.3740 (9)	136
C5–H5 <i>A</i> ···O6 ^{vi}	0.97	2.45	3.1555 (11)	129
C5–H5 <i>B</i> ···O5 ^{vii}	0.97	2.51	3.2553 (11)	133
C5–H5 <i>A</i> ···O6 ^{vi}	0.97	2.45	3.1555 (11)	129

Symmetry codes: (i) $y + 1, x, -z + 1$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{5}{4}$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{4}$; (iv) $x + 1, y, z$; (v) $y, x, -z$; (vi) $x, y, z + 1$; (vii) $y + \frac{1}{2}, -x + \frac{3}{2}, z + \frac{3}{4}$

Table 2
Experimental details.

Crystal data	
Chemical formula	$0.5C_4H_{12}N_2^{2+} \cdot C_4H_5O_6^-$
M_r	193.16
Crystal system, space group	Tetragonal, $P4_12_1$
Temperature (K)	293
<i>a</i> , <i>c</i> (Å)	7.5446 (1), 27.6498 (5)
<i>V</i> (Å ³)	1573.85 (5)
<i>Z</i>	8
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.15
Crystal size (mm)	0.26 × 0.23 × 0.15
Data collection	
Diffractometer	Bruker APEXII CCD detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2015)
T_{min} , T_{max}	0.962, 0.978
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	45806, 7781, 6025
R_{int}	0.029
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	1.058
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.041, 0.117, 1.12
No. of reflections	7781
No. of parameters	120
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.37, –0.22
Absolute structure	Flack <i>x</i> determined using 2104 quotients [$(I^+ - I^-)/(I^+ + I^-)$] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	–0.17 (14)

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Gao, X.-L., Bian, L.-F. & Guo, S.-W. (2014). *Acta Cryst.* **E70**, o1221–o1222.
Jovita, J. V., Sathya, S., Usha, G., Vasanthi, R. & Ramanand, A. (2014). *Acta Cryst.* **E70**, o1036–o1037.
Liu, L.-L. (2010). *Acta Cryst.* **E66**, o2191.
Narayanam, N., Gangu, K. K., Kurra, B. & Mukkamala, S. B. (2013). *Acta Cryst.* **E69**, o574–o575.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2017). 2, x170249 [https://doi.org/10.1107/S2414314617002498]

Piperazine-1,4-dium bis(3-carboxy-2,3-dihydroxypropanoate)

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Crystal data

$0.5\text{C}_4\text{H}_{12}\text{N}_2^{2+}\cdot\text{C}_4\text{H}_5\text{O}_6^-$

$M_r = 193.16$

Tetragonal, $P4_12_12$

$a = 7.5446$ (1) Å

$c = 27.6498$ (5) Å

$V = 1573.85$ (5) Å³

$Z = 8$

$F(000) = 816$

$D_x = 1.630$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 245 reflections

$\theta = 1.6\text{--}31^\circ$

$\mu = 0.15$ mm⁻¹

$T = 293$ K

Prism, colourless

$0.26 \times 0.23 \times 0.15$ mm

Data collection

Bruker APEXII CCD detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and φ scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2015)

$T_{\min} = 0.962$, $T_{\max} = 0.978$

45806 measured reflections

7781 independent reflections

6025 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 48.8^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -14 \rightarrow 14$

$k = -10 \rightarrow 15$

$l = -54 \rightarrow 58$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.117$

$S = 1.12$

7781 reflections

120 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.22$ e Å⁻³

Absolute structure: Flack x determined using

2104 quotients $[(F^-)-(F)]/[(F^+)+(F)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: -0.17 (14)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C3	0.46028 (9)	0.27973 (9)	0.10854 (2)	0.01701 (10)
H3	0.4637	0.4083	0.1035	0.020*
C2	0.36287 (8)	0.19808 (9)	0.06515 (2)	0.01647 (9)
H2	0.4216	0.2397	0.0357	0.020*
C4	0.65177 (9)	0.21412 (10)	0.10980 (2)	0.01791 (10)
O6	0.74013 (8)	0.24921 (10)	0.07049 (2)	0.02337 (11)
H6	0.8415	0.2113	0.0731	0.035*
O3	0.37612 (8)	0.01095 (8)	0.06619 (3)	0.02293 (11)
H3A	0.2772	-0.0321	0.0698	0.034*
O4	0.37208 (9)	0.24868 (9)	0.15256 (2)	0.02348 (11)
H4	0.3843	0.1445	0.1603	0.035*
C1	0.17119 (9)	0.26428 (10)	0.06395 (2)	0.01868 (10)
O1	0.14690 (9)	0.42374 (9)	0.05493 (2)	0.02666 (12)
O2	0.05315 (8)	0.14850 (10)	0.07153 (3)	0.03266 (15)
O5	0.71328 (10)	0.13485 (12)	0.14444 (2)	0.03238 (16)
N1	0.84578 (10)	0.57964 (12)	1.00611 (3)	0.02954 (15)
H1A	0.9225	0.5023	0.9937	0.035*
H1B	0.8509	0.5714	1.0382	0.035*
C5	0.66484 (13)	0.53461 (11)	0.98963 (3)	0.02630 (15)
H5A	0.6346	0.4156	1.0001	0.032*
H5B	0.6598	0.5380	0.9546	0.032*
C6	0.89681 (13)	0.76223 (15)	0.99109 (3)	0.03121 (18)
H6A	0.9043	0.7678	0.9561	0.037*
H6B	1.0126	0.7907	1.0042	0.037*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C3	0.0156 (2)	0.0172 (2)	0.0182 (2)	0.00126 (18)	0.00116 (17)	-0.00002 (18)
C2	0.0125 (2)	0.0185 (2)	0.0184 (2)	0.00121 (17)	0.00160 (17)	-0.00001 (17)
C4	0.0157 (2)	0.0196 (3)	0.0185 (2)	0.00035 (18)	-0.00220 (17)	0.00026 (18)
O6	0.01428 (19)	0.0316 (3)	0.0242 (2)	0.00292 (19)	0.00191 (16)	0.00567 (19)
O3	0.0161 (2)	0.0178 (2)	0.0349 (3)	0.00112 (16)	0.00423 (19)	-0.00378 (19)
O4	0.0273 (3)	0.0229 (2)	0.02022 (19)	0.0026 (2)	0.00757 (18)	-0.00030 (18)
C1	0.0138 (2)	0.0211 (3)	0.0212 (2)	0.00295 (18)	-0.00028 (17)	-0.0001 (2)
O1	0.0257 (3)	0.0220 (3)	0.0323 (3)	0.0067 (2)	-0.0034 (2)	0.0011 (2)
O2	0.0125 (2)	0.0270 (3)	0.0584 (5)	0.00103 (19)	0.0027 (2)	0.0043 (3)
O5	0.0265 (3)	0.0464 (4)	0.0243 (3)	0.0081 (3)	-0.0039 (2)	0.0110 (3)
N1	0.0238 (3)	0.0354 (4)	0.0293 (3)	0.0142 (3)	-0.0004 (2)	0.0020 (3)
C5	0.0335 (4)	0.0183 (3)	0.0270 (3)	0.0018 (3)	-0.0036 (3)	0.0019 (2)
C6	0.0218 (3)	0.0437 (5)	0.0281 (3)	-0.0046 (3)	0.0024 (3)	0.0014 (3)

Geometric parameters (Å, °)

C3—O4	1.4068 (9)	C1—O1	1.2422 (10)
C3—C4	1.5276 (10)	C1—O2	1.2649 (10)
C3—C2	1.5359 (9)	N1—C5	1.4786 (13)
C3—H3	0.9800	N1—C6	1.4894 (15)
C2—O3	1.4157 (9)	N1—H1A	0.8900
C2—C1	1.5304 (9)	N1—H1B	0.8900
C2—H2	0.9800	C5—C5 ⁱ	1.5032 (18)
C4—O5	1.2209 (9)	C5—H5A	0.9700
C4—O6	1.3022 (9)	C5—H5B	0.9700
O6—H6	0.8200	C6—C6 ⁱ	1.518 (2)
O3—H3A	0.8200	C6—H6A	0.9700
O4—H4	0.8200	C6—H6B	0.9700
O4—C3—C4	111.94 (6)	O2—C1—C2	115.87 (7)
O4—C3—C2	112.50 (6)	C5—N1—C6	111.42 (7)
C4—C3—C2	109.90 (5)	C5—N1—H1A	109.3
O4—C3—H3	107.4	C6—N1—H1A	109.3
C4—C3—H3	107.4	C5—N1—H1B	109.3
C2—C3—H3	107.4	C6—N1—H1B	109.3
O3—C2—C1	113.12 (6)	H1A—N1—H1B	108.0
O3—C2—C3	110.51 (6)	N1—C5—C5 ⁱ	109.62 (6)
C1—C2—C3	109.77 (5)	N1—C5—H5A	109.7
O3—C2—H2	107.7	C5 ⁱ —C5—H5A	109.7
C1—C2—H2	107.7	N1—C5—H5B	109.7
C3—C2—H2	107.7	C5 ⁱ —C5—H5B	109.7
O5—C4—O6	124.04 (7)	H5A—C5—H5B	108.2
O5—C4—C3	122.42 (7)	N1—C6—C6 ⁱ	110.81 (6)
O6—C4—C3	113.53 (6)	N1—C6—H6A	109.5
C4—O6—H6	109.5	C6 ⁱ —C6—H6A	109.5
C2—O3—H3A	109.5	N1—C6—H6B	109.5
C3—O4—H4	109.5	C6 ⁱ —C6—H6B	109.5
O1—C1—O2	126.74 (7)	H6A—C6—H6B	108.1
O1—C1—C2	117.37 (7)		

Symmetry code: (i) $y, x, -z+2$.

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A ⁱⁱ ···O3 ⁱⁱ	0.89	2.02	2.8118 (10)	147
N1—H1B ⁱⁱⁱ ···O5 ⁱⁱⁱ	0.89	1.98	2.8167 (10)	155
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Symmetry codes: (ii) $y+1, x, -z+1$; (iii) $-x+3/2, y+1/2, -z+5/4$; (iv) $-x+1/2, y-1/2, -z+1/4$; (v) $x+1, y, z$; (vi) $y, x, -z$; (vii) $x, y, z+1$; (viii) $y+1/2, -x+3/2, z+3/4$.