

3,3'-(Piperazine-1,4-diium-1,4-diyl)di-propionate dihydrate

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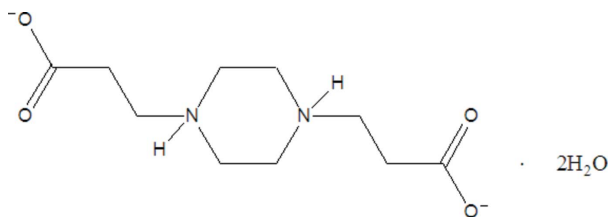
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.040; wR factor = 0.111; data-to-parameter ratio = 13.3.

During the recrystallization of 3-[4-(2-carboxyethyl)piperazin-1-yl]propionic acid, the carboxylic acid H atoms were transferred to the piperazine N atoms, forming the title compound, $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, in which the zwitterion lies about an inversion center. In the crystal, bifurcated $\text{N}-\text{H} \cdots (\text{O},\text{O})$ hydrogen bonds connect the zwitterions into a two-dimensional framework parallel to (102) forming $R_4^4(30)$ rings. $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds involving the solvent water molecules connect the two-dimensional framework into a three-dimensional network. In addition, weak $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds are observed.

Related literature

For general background and applications of carboxylic acids, see: Jin *et al.* (2012); Grossel *et al.* (2006); Rueff *et al.* (2001); Strachan *et al.* (2007); Desiraju (2002). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

$M_r = 266.30$

Monoclinic, $P2_1/c$

$a = 6.8028$ (6) Å

$b = 8.8925$ (7) Å

$c = 10.4301$ (11) Å

$\beta = 101.780$ (1)°

$V = 617.67$ (10) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 0.12$ mm⁻¹

$T = 298$ K

$0.43 \times 0.40 \times 0.32$ mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.951$, $T_{\max} = 0.963$

2951 measured reflections
1087 independent reflections
895 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.111$
 $S = 1.06$
1087 reflections

82 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O3}-\text{H3F} \cdots \text{O2}^{\text{i}}$	0.85	1.93	2.776 (2)	177
$\text{O3}-\text{H3E} \cdots \text{O1}$	0.85	2.11	2.964 (2)	177
$\text{N1}-\text{H1} \cdots \text{O2}^{\text{ii}}$	0.91	2.50	3.0577 (19)	120
$\text{N1}-\text{H1} \cdots \text{O1}^{\text{ii}}$	0.91	1.80	2.7011 (18)	172
$\text{C4}-\text{H4B} \cdots \text{O3}^{\text{iii}}$	0.97	2.58	3.419 (2)	145
$\text{C4}-\text{H4B} \cdots \text{O2}^{\text{ii}}$	0.97	2.53	3.137 (2)	120
$\text{C5}-\text{H5A} \cdots \text{O1}^{\text{iv}}$	0.97	2.51	3.477 (2)	172

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

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5520).

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supporting information

Acta Cryst. (2012). E68, o2827 [https://doi.org/10.1107/S1600536812037312]

3,3'-(Piperazine-1,4-dium-1,4-diyl)dipropionate dihydrate**Shouwen Jin, Yanfei Huang, Hao Fang, Tianyi Wang and Liangliang Ding****S1. Comment**

Carboxylic acids are important compounds, which have been widely used in various fields as coordination chemistry (Rueff *et al.*, 2001), pharmaceutical chemistry (Strachan *et al.*, 2007), and supramolecular chemistry (Desiraju, 2002). Recently the main focus for carboxylic acids has been in crystal engineering *via* hydrogen bonded assembly of organic acids and organic bases (Grossel *et al.*, 2006). As an extension of our study concentrating on hydrogen bonded assembly of organic acids and organic bases (Jin *et al.*, 2012), herein we report the crystal structure of the title compound (I).

During the recrystallization of 3-[4-(2-carboxy-ethyl)-piperazin-1-yl]-propionic acid the carboxylic acid H atoms were transferred to the piperazine N atoms forming (I) (Fig. 1) in which the zwitterion lies across an inversion center. In the crystal, bifurcated N—H \cdots (O,O) hydrogen bonds connect the zwitterions a two-dimensional framework parallel to $(\bar{1}02)$ forming $R^4_4(30)$ rings (Bernstein *et al.*, 1995). Furthermore O—H \cdots O hydrogen bonds involving solvent water molecules connect the two-dimensional framework into a three-dimensional network. In addition, weak C—H \cdots O hydrogen bonds are observed (Fig. 2).

S2. Experimental

3-[4-(2-Carboxy-ethyl)-piperazin-1-yl]-propionic acid (23.0 mg, 0.10 mmol) was dissolved in 6 ml of ethanol, and pyridine (15.8 mg, 0.2 mmol) was added to the ethanol solution. The solution was stirred for 1 h, and then filtered into a test tube. The solution was left standing at room temperature for about one week, colorless block crystals were obtained.

S3. Refinement

All H atoms were visible in difference Fourier maps. They were subsequently included in calculated positions with C—H = 0.97 Å, N—H = 0.91 Å, O—H = 0.85 Å and were constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N,O})$.

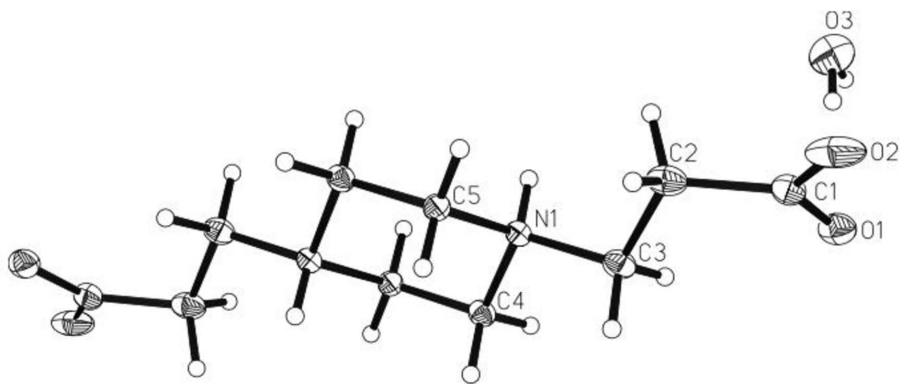


Figure 1

The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level. Unlabeled atoms are related by the symmetry operator $(-x, -y, -z)$. Only the symmetry unique solvent water molecule is shown.

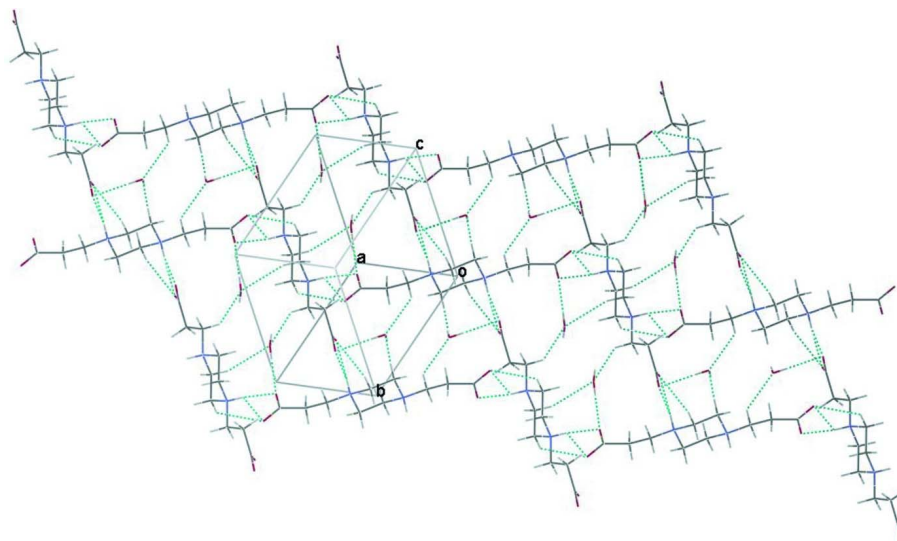


Figure 2

Part of the crystal structure with hydrogen bonds shown as dotted lines.

3,3'-(Piperazine-1,4-dium-1,4-diyl)dipropionate dihydrate

Crystal data

$C_{10}H_{18}N_2O_4 \cdot 2H_2O$

$M_r = 266.30$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 6.8028$ (6) Å

$b = 8.8925$ (7) Å

$c = 10.4301$ (11) Å

$\beta = 101.780$ (1)°

$V = 617.67$ (10) Å³

$Z = 2$

$F(000) = 288$

$D_x = 1.432$ Mg m⁻³

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

Cell parameters from 1525 reflections

$\theta = 3.0$ – 28.2 °

$\mu = 0.12$ mm⁻¹

$T = 298$ K

Block, colorless

$0.43 \times 0.40 \times 0.32$ mm

Data collection

Bruker SMART CCD diffractometer	2951 measured reflections
Radiation source: fine-focus sealed tube	1087 independent reflections
Graphite monochromator	895 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.023$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 3.0^\circ$
$T_{\text{min}} = 0.951$, $T_{\text{max}} = 0.963$	$h = -8 \rightarrow 7$
	$k = -10 \rightarrow 5$
	$l = -12 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H-atom parameters constrained
$wR(F^2) = 0.111$	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.3063P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1087 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
82 parameters	$\Delta\rho_{\text{max}} = 0.21 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.15979 (19)	0.08898 (15)	0.08004 (12)	0.0204 (3)
H1	0.2428	0.0121	0.1137	0.024*
O1	0.56844 (18)	0.37957 (15)	0.31249 (12)	0.0340 (4)
O2	0.7046 (2)	0.4517 (2)	0.14744 (14)	0.0551 (5)
O3	0.8070 (2)	0.10838 (18)	0.40824 (15)	0.0541 (5)
H3E	0.7405	0.1861	0.3781	0.065*
H3F	0.7788	0.0870	0.4818	0.065*
C1	0.5838 (2)	0.3752 (2)	0.19346 (17)	0.0288 (4)
C2	0.4531 (3)	0.2636 (2)	0.10320 (18)	0.0335 (5)
H2A	0.4302	0.3019	0.0143	0.040*
H2B	0.5256	0.1694	0.1049	0.040*
C3	0.2521 (3)	0.23274 (19)	0.13874 (17)	0.0276 (4)
H3A	0.2697	0.2274	0.2333	0.033*
H3B	0.1616	0.3154	0.1084	0.033*
C4	-0.0379 (2)	0.06441 (19)	0.11862 (16)	0.0236 (4)
H4A	-0.1283	0.1462	0.0851	0.028*

H4B	-0.0187	0.0648	0.2134	0.028*
C5	0.1314 (2)	0.08320 (19)	-0.06607 (15)	0.0230 (4)
H5A	0.2604	0.0950	-0.0910	0.028*
H5B	0.0456	0.1656	-0.1042	0.028*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0183 (7)	0.0214 (7)	0.0211 (7)	-0.0005 (5)	0.0031 (5)	-0.0011 (6)
O1	0.0355 (7)	0.0386 (8)	0.0274 (7)	-0.0108 (6)	0.0049 (5)	-0.0046 (6)
O2	0.0584 (9)	0.0713 (11)	0.0388 (8)	-0.0414 (9)	0.0174 (7)	-0.0142 (8)
O3	0.0650 (10)	0.0500 (10)	0.0518 (10)	0.0019 (8)	0.0225 (8)	0.0053 (8)
C1	0.0261 (9)	0.0297 (9)	0.0300 (10)	-0.0040 (7)	0.0044 (7)	-0.0036 (8)
C2	0.0317 (10)	0.0379 (11)	0.0317 (10)	-0.0112 (8)	0.0084 (8)	-0.0090 (8)
C3	0.0249 (9)	0.0256 (9)	0.0317 (9)	-0.0040 (7)	0.0046 (7)	-0.0064 (7)
C4	0.0201 (8)	0.0287 (9)	0.0224 (8)	0.0000 (7)	0.0056 (6)	-0.0013 (7)
C5	0.0214 (8)	0.0279 (9)	0.0202 (8)	-0.0010 (7)	0.0050 (6)	0.0022 (7)

Geometric parameters (Å, °)

N1—C4	1.4966 (19)	C2—H2A	0.9700
N1—C5	1.4975 (19)	C2—H2B	0.9700
N1—C3	1.499 (2)	C3—H3A	0.9700
N1—H1	0.9100	C3—H3B	0.9700
O1—C1	1.267 (2)	C4—C5 ⁱ	1.512 (2)
O2—C1	1.237 (2)	C4—H4A	0.9700
O3—H3E	0.8501	C4—H4B	0.9700
O3—H3F	0.8500	C5—C4 ⁱ	1.512 (2)
C1—C2	1.523 (2)	C5—H5A	0.9700
C2—C3	1.513 (2)	C5—H5B	0.9700
C4—N1—C5	109.42 (12)	N1—C3—H3A	109.2
C4—N1—C3	109.84 (12)	C2—C3—H3A	109.2
C5—N1—C3	113.65 (13)	N1—C3—H3B	109.2
C4—N1—H1	107.9	C2—C3—H3B	109.2
C5—N1—H1	107.9	H3A—C3—H3B	107.9
C3—N1—H1	107.9	N1—C4—C5 ⁱ	111.35 (13)
H3E—O3—H3F	108.3	N1—C4—H4A	109.4
O2—C1—O1	123.88 (16)	C5 ⁱ —C4—H4A	109.4
O2—C1—C2	117.96 (16)	N1—C4—H4B	109.4
O1—C1—C2	118.09 (15)	C5 ⁱ —C4—H4B	109.4
C3—C2—C1	114.16 (15)	H4A—C4—H4B	108.0
C3—C2—H2A	108.7	N1—C5—C4 ⁱ	110.85 (13)
C1—C2—H2A	108.7	N1—C5—H5A	109.5
C3—C2—H2B	108.7	C4 ⁱ —C5—H5A	109.5
C1—C2—H2B	108.7	N1—C5—H5B	109.5
H2A—C2—H2B	107.6	C4 ⁱ —C5—H5B	109.5
N1—C3—C2	112.25 (14)	H5A—C5—H5B	108.1

O2—C1—C2—C3	-151.50 (18)	C5—N1—C4—C5 ⁱ	57.11 (18)
O1—C1—C2—C3	31.5 (2)	C3—N1—C4—C5 ⁱ	-177.48 (13)
C4—N1—C3—C2	179.91 (14)	C4—N1—C5—C4 ⁱ	-56.82 (18)
C5—N1—C3—C2	-57.14 (19)	C3—N1—C5—C4 ⁱ	-179.99 (13)
C1—C2—C3—N1	-160.56 (15)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O3—H3F \cdots O2 ⁱⁱ	0.85	1.93	2.776 (2)	177
O3—H3E \cdots O1	0.85	2.11	2.964 (2)	177
N1—H1 \cdots O2 ⁱⁱⁱ	0.91	2.50	3.0577 (19)	120
N1—H1 \cdots O1 ⁱⁱⁱ	0.91	1.80	2.7011 (18)	172
C4—H4B \cdots O3 ^{iv}	0.97	2.58	3.419 (2)	145
C4—H4B \cdots O2 ⁱⁱⁱ	0.97	2.53	3.137 (2)	120
C5—H5A \cdots O1 ^v	0.97	2.51	3.477 (2)	172

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