Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,4-Bis(carboxymethyl)piperazine-1,4-diium bis(dihydrogen phosphate) dihydrate

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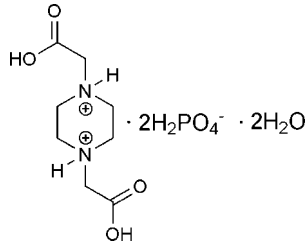
Received 2 September 2010; accepted 10 September 2010

Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.098; data-to-parameter ratio = 13.8.

In the title salt, $C_8H_{16}N_2O_4^{2+}\cdot 2H_2PO_4^-\cdot 2H_2O$, the piperazine ring is located around an inversion center and adopts a chair conformation. The dihydrogen phosphate anions and free water molecules are linked *via* O—H···O hydrogen bonds into two-dimensional hydrogen-bonding layers, which are further connected through O—H···O and N—H···O hydrogen bonds involving the protonated piperazine into a three-dimensional supramolecular network.

Related literature

For related structures, see: Yang *et al.* (2008). For potential applications of optical, electrical, magnetic and microporous materials, see: Evans & Lin (2002); Zhang & Chen (2006).



Experimental

Crystal data

$C_8H_{16}N_2O_4^{2+}\cdot 2H_2PO_4^-\cdot 2H_2O$
M_r = 434.23
Monoclinic, $P2_1/c$
a = 8.716 (3) Å
b = 8.992 (3) Å
c = 12.991 (4) Å
β = 123.310 (17)°
V = 850.9 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 120 K
0.54 × 0.44 × 0.41 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.840, T_{max} = 0.875
3998 measured reflections
1668 independent reflections
1552 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.098
S = 1.09
1668 reflections
121 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O3	0.84	1.69	2.5324 (18)	177
N1—H1···O5^{i}	0.93	1.74	2.658 (2)	170
O4—H4···O1*W*	0.84	1.74	2.5729 (19)	172
O6—H6···O5^{ii}	0.84	1.74	2.5700 (17)	169
O1*W*—H1*WA*···O6^{iii}	0.85	2.08	2.868 (2)	155
O1*W*—H1*WB*···O3^{iv}	0.85	2.02	2.8633 (19)	169

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

The authors thank the Program for Young Excellent Talents in Southeast University for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2598).

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supporting information

Acta Cryst. (2010). E**66**, o2566 [doi:10.1107/S1600536810036342]

1,4-Bis(carboxymethyl)piperazine-1,4-diium bis(dihydrogen phosphate) dihydrate

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S1. Comment

Recent years have witnessed an explosion of great interest in hybrid organic-inorganic framework solids not only for their intriguing architectures and topologies, but also for their potential applications in optical, electrical, magnetic, and microporous materials (Evans *et al.* 2002; Zhang *et al.* 2006). We have synthesized two series of hybrid organic-inorganic frameworks with 1,4-piperazinediacetic acid and lanthanide sulfates (Yang *et al.* 2008). Our aim is to obtain similar hybrid solids by using phosphates instead of sulfates. However, we fail to synthesize the aimed compounds and obtain a three-dimensional supramolecular network, $C_8H_{24}N_2O_{14}P_2$ (**1**.$2H_2PO_4$.$2H_2O$).

The title compound, is a dihydrogen phosphate, in which **1** is a protonated piperazine derivative and the piperazine ring located around inversion center adopts chair conformation (Fig. 1). The asymmetric unit of the title compound, contains half a protonated 1,4-piperazinediacetic acid, a dihydrogen phosphate and a free water molecule. In the carboxylates of protonated 1,4-piperazinediacetic acid, the distance of the C=O bonds is 1.209 (2) Å, which is shorter than those of C—O bond (1.311 (2) Å) and considered to have full double-bond character.

In the compound, the dihydrogen phosphates and free water molecules are linked to each other, *via* O—H···O hydrogen bonds into a two-dimensional hydrogen bonding layers (Table 1, Fig. 2), which are further connected through O—H···O and N—H···O hydrogen bonds involving the protonated 1,4-piperazinediacetic acid into a three-dimensional supramolecular network.

S2. Experimental

A mixture of H_2pda.$2H_2O$ (0.024 g, 0.1 mmol), Nd_2O_3 (0.034 g, 0.1 mmol), H_3PO_4 (0.1 ml), and water (6 ml) were heated ina 15 ml Teflon-lined vessel at 160 ° for 3 days, followed by slow cooling (5 ° h^{-1}) to room temperature. After filtration, colorless block crystals were collected and dried in air (0.025 g, yield *ca* 57% based on H_2pda).

S3. Refinement

All H atoms attached to C, N and O(hydroxyl) atoms were fixed geometrically and treated as riding with C—H = 0.99 Å (methylene), N—H = 0.93 Å and O—H= 0.84 Å with U_{iso}(H) = 1.2U_{eq}(C or N) or U_{iso}(H) = 1.5U_{eq}(O). H atoms of water molecule were located in difference Fourier maps and included in the subsequent refinement using restraints (O-H= 0.85 (1)Å and H···H= 1.40 (2)Å) with U_{iso}(H) = 1.5U_{eq}(O). In the last cycle of refinement, they were treated as riding on their parent O atom.

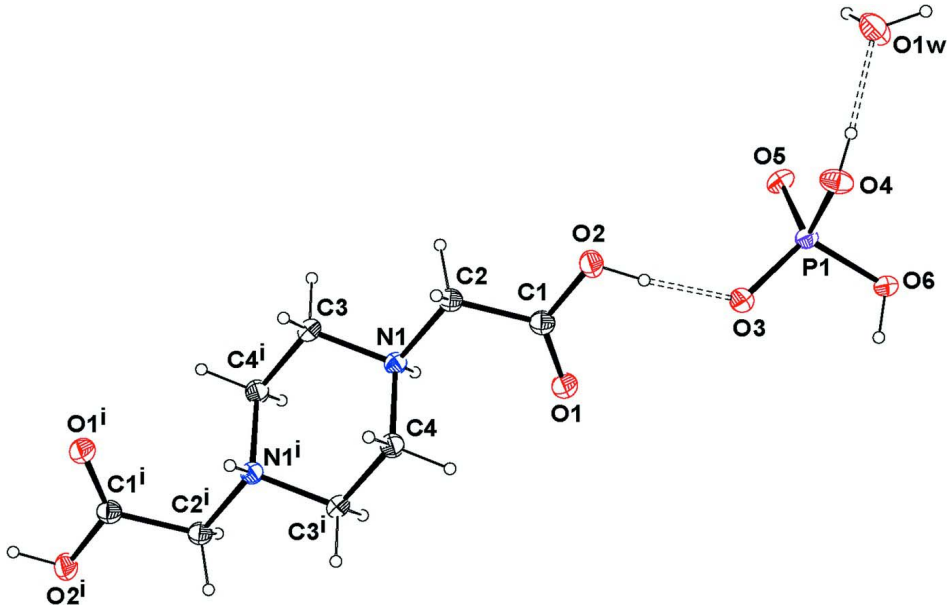

Figure 1

Molecular view of compound (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

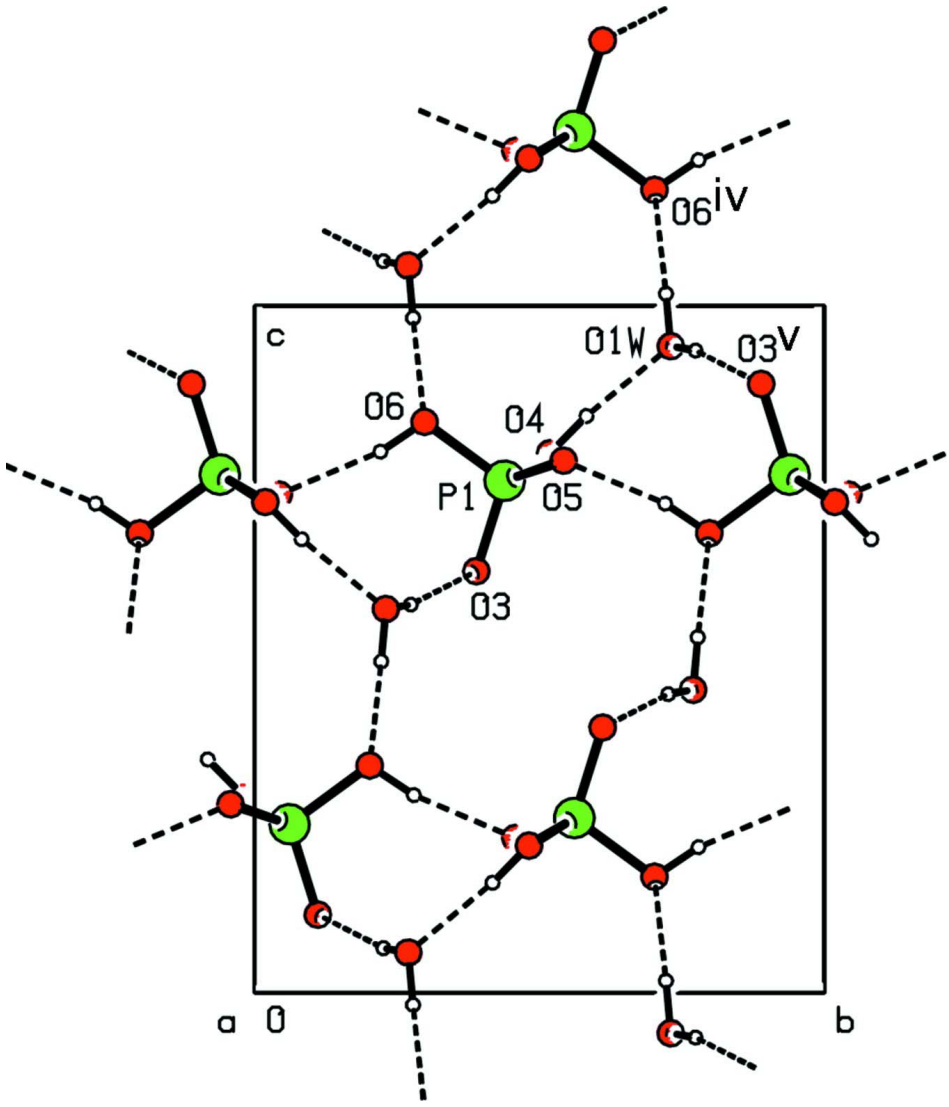

Figure 2

Partial packing view of compound (I), showing the two-dimensional network formed by the hydrogen bonds showed as dashed lines, involving the dihydrogen phosphate and the water molecules. [Symmetry codes:(iv) -*x*+2, -*y*+1,-*z*+2; (v) -*x*+2, *y*+1/2, -*z*+3/2]

1,4-Bis(carboxymethyl)piperazine-1,4-diium bis(dihydrogen phosphate) dihydrate

Crystal data

$C_8H_{16}N_2O_4^{2+}\cdot 2H_2PO_4^-\cdot 2H_2O$
$M_r = 434.23$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.716\ (3)$ Å
$b = 8.992\ (3)$ Å
$c = 12.991\ (4)$ Å
$\beta = 123.310\ (17)°$
$V = 850.9\ (5)$ Å^3
$Z = 2$

$F(000) = 456$
$D_x = 1.695$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 782 reflections
$\theta = 2.4–28.0°$
$\mu = 0.33$ mm^{-1}
$T = 120$ K
Block, colourless
0.54 × 0.44 × 0.41 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scan
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.840, T_{max} = 0.875
3998 measured reflections
1668 independent reflections
1552 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 26.0°, θ_{min} = 2.9°
h = −10→8
k = −11→10
l = −10→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.098
S = 1.09
1668 reflections
121 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 0.4175P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

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.

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
O1	0.69897 (17)	0.37509 (13)	0.33962 (11)	0.0187 (3)
O2	0.64019 (19)	0.56082 (13)	0.42897 (12)	0.0213 (3)
H2	0.6898	0.5039	0.4903	0.032*
N1	0.57511 (19)	0.53648 (15)	0.12844 (13)	0.0131 (3)
H1	0.6924	0.4981	0.1622	0.016*
C1	0.6431 (2)	0.49837 (19)	0.33891 (15)	0.0156 (4)
C2	0.5654 (2)	0.60289 (19)	0.22984 (15)	0.0158 (3)
H2A	0.4360	0.6257	0.1991	0.019*
H2B	0.6353	0.6973	0.2566	0.019*
C3	0.5428 (2)	0.65335 (18)	0.03654 (15)	0.0159 (3)
H3A	0.6332	0.7346	0.0785	0.019*
H3B	0.4184	0.6958	−0.0006	0.019*
C4	0.4392 (2)	0.41261 (19)	0.06352 (16)	0.0163 (4)
H4A	0.3131	0.4513	0.0268	0.020*
H4B	0.4608	0.3343	0.1237	0.020*
P1	0.92100 (6)	0.43880 (4)	0.74544 (4)	0.01286 (17)

O3	0.79926 (16)	0.38920 (13)	0.61380 (11)	0.0174 (3)
O4	0.80098 (16)	0.51844 (14)	0.78556 (12)	0.0200 (3)
H4	0.8650	0.5820	0.8400	0.030*
O5	1.07757 (15)	0.54245 (12)	0.77465 (11)	0.0160 (3)
O6	1.00826 (16)	0.29822 (13)	0.83100 (11)	0.0172 (3)
H6	0.9690	0.2207	0.7879	0.026*
O1W	0.9695 (2)	0.73039 (16)	0.94132 (13)	0.0289 (3)
H1WA	1.0120	0.7221	1.0176	0.043*
H1WB	1.0505	0.7740	0.9349	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0218 (6)	0.0160 (6)	0.0182 (6)	0.0027 (5)	0.0109 (5)	0.0009 (5)
O2	0.0306 (8)	0.0185 (6)	0.0159 (6)	0.0063 (5)	0.0134 (6)	0.0025 (5)
N1	0.0134 (7)	0.0124 (6)	0.0139 (7)	−0.0002 (5)	0.0078 (6)	0.0002 (5)
C1	0.0140 (8)	0.0159 (8)	0.0163 (8)	−0.0012 (6)	0.0080 (7)	−0.0011 (6)
C2	0.0187 (8)	0.0139 (8)	0.0160 (8)	0.0018 (6)	0.0103 (7)	−0.0006 (6)
C3	0.0197 (8)	0.0118 (7)	0.0162 (8)	−0.0006 (6)	0.0098 (7)	0.0013 (6)
C4	0.0170 (8)	0.0159 (8)	0.0150 (8)	−0.0041 (6)	0.0082 (7)	−0.0003 (6)
P1	0.0137 (3)	0.0112 (3)	0.0146 (3)	−0.00065 (14)	0.0084 (2)	−0.00046 (14)
O3	0.0194 (6)	0.0157 (6)	0.0149 (6)	−0.0001 (5)	0.0081 (5)	−0.0004 (5)
O4	0.0180 (6)	0.0201 (6)	0.0253 (7)	−0.0030 (5)	0.0142 (6)	−0.0076 (5)
O5	0.0141 (6)	0.0120 (6)	0.0230 (7)	0.0003 (4)	0.0109 (5)	0.0017 (5)
O6	0.0226 (6)	0.0115 (6)	0.0154 (6)	−0.0025 (5)	0.0092 (5)	−0.0014 (4)
O1W	0.0355 (8)	0.0347 (8)	0.0219 (7)	−0.0153 (6)	0.0192 (6)	−0.0104 (6)

Geometric parameters (Å, º)

O1—C1	1.209 (2)	C3—H3B	0.9900
O2—C1	1.311 (2)	C4—C3^{i}	1.513 (2)
O2—H2	0.8400	C4—H4A	0.9900
N1—C2	1.490 (2)	C4—H4B	0.9900
N1—C3	1.497 (2)	P1—O3	1.5022 (13)
N1—C4	1.503 (2)	P1—O5	1.5186 (12)
N1—H1	0.9300	P1—O4	1.5740 (12)
C1—C2	1.515 (2)	P1—O6	1.5759 (13)
C2—H2A	0.9900	O4—H4	0.8400
C2—H2B	0.9900	O6—H6	0.8400
C3—C4^{i}	1.513 (2)	O1W—H1WA	0.8499
C3—H3A	0.9900	O1W—H1WB	0.8505
C1—O2—H2	109.5	N1—C3—H3B	109.6
C2—N1—C3	110.29 (12)	C4^{i}—C3—H3B	109.6
C2—N1—C4	112.53 (13)	H3A—C3—H3B	108.1
C3—N1—C4	109.14 (13)	N1—C4—C3^{i}	110.54 (13)
C2—N1—H1	108.3	N1—C4—H4A	109.5
C3—N1—H1	108.3	C3^{i}—C4—H4A	109.5

C4—N1—H1	108.3	N1—C4—H4B	109.5
O1—C1—O2	126.25 (16)	C3^{i}—C4—H4B	109.5
O1—C1—C2	123.19 (15)	H4A—C4—H4B	108.1
O2—C1—C2	110.56 (14)	O3—P1—O5	116.28 (7)
N1—C2—C1	111.40 (13)	O3—P1—O4	109.25 (7)
N1—C2—H2A	109.3	O5—P1—O4	107.91 (7)
C1—C2—H2A	109.3	O3—P1—O6	109.29 (7)
N1—C2—H2B	109.3	O5—P1—O6	107.26 (7)
C1—C2—H2B	109.3	O4—P1—O6	106.41 (7)
H2A—C2—H2B	108.0	P1—O4—H4	109.5
N1—C3—C4^{i}	110.32 (14)	P1—O6—H6	109.5
N1—C3—H3A	109.6	H1WA—O1W—H1WB	107.5
C4^{i}—C3—H3A	109.6		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3	0.84	1.69	2.5324 (18)	177
N1—H1···O5^{ii}	0.93	1.74	2.658 (2)	170
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O1*W*—H1*WB*···O3^{v}	0.85	2.02	2.8633 (19)	169

Symmetry codes: (ii) −*x*+2, −*y*+1, −*z*+1; (iii) −*x*+2, *y*−1/2, −*z*+3/2; (iv) −*x*+2, −*y*+1, −*z*+2; (v) −*x*+2, *y*+1/2, −*z*+3/2.