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Piperazine-1,4-diium Dihydrogendiphosphate

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Abstract

$(C_4H_{12}N_2)H_2P_2O_7$ is a typical layer organization built by organic and inorganic groups centred by planes parallel to (1 0 0). Unit formula consists of one acidic anion and two half organic cations crystallografically independent. $H_2P_2O_7$ have no internal symmetry whereas the piperazinium cations are centrosymmetric. Inorganic layers are built by strong hydrogen bonds. The cohesion of the structure results from a network of a weak hydrogen bonds.

Comment

The diphosphate class has been well investigated when compared with the other classes of condensed phosphates. Acidic anions of formula $HP_2O_7^{3-}$, $H_2P_2O_7^{2-}$ and $H_3P_2O_7^{-}$, usually observed in the diphosphate chemistry, where frequently associated to mineral cations. So that several anhydrous inorganic diphosphates have been described. Nevertheless a few sructure of organic diphosphates were crystallographically established. Among them the greater part of compounds are anhydrous and found to include the $H_2P_2O_7^{2-}$ anion. Their atomic arrangements are always organized in infinite networks which can adopt two geometries; (i) ribbons such as observed in $(NH_3C_2H_4OH)H_2P_2O_7$ (Averbuch-Pouchot and Durif, 1992) and in $(NH_3C_2H_4HH_3)H_2P_2O_7$ (Averbuch-Pouchot and Durif, 1993), (ii) layers as encountered in $(C_3H_{12}NO)_2H_2P_2O_7$ (Gharbi and Jouini, 1996). The title compound is an additional example for such compounds. It has a typical layer organization. Two types of layers are present in this structure; the first one, centred by planes at x=1/4 and 3/4, consists of the $H_2P_2O_7$ phosphoric groups; the second one, at x=0 and 1/2, parallel to the first, contains organic cations. Each $H_2P_2O_7$ is linked to four neighbour groups, by two donors and two acceptors strong hydrogen bonds since the corresponding O—O distances [2.457 (2) and 2.611 (2) Å] are as short as in the PO_4 tetrahedron. In a such formed polyanion of formula $[H_2P_2O_7]_n^{2n-}$, the diphosphoric group has no internal symmetry and so is built by two independent PO_4 tetrahedra. As observed in all structures involving $H_2P_2O_7^{2-}$ anion, the P—O bonds, shorter than the P—OH ones, are in accordance with data relative to oxoanions (Ferrris and Ivaldi, 1984). Organic layer, constituted by two crystallographically independent piperazinium dications, is anchored onto both adjacent inorganic ones by N—H···O bonds. Organic dications are located respectively arround the inversion centres at (0 0 1/2) and (1/2 0 1/2). The two interactions O—H···O and N—H···O are responsible for the structure cohesion. The main geometric features of the organic and inorganic entities are reported in table 1. They are in accordance with what is previously observed for the substitued piperazinium cations in bis [1-(2-ammoniumethyl)piperazinium] cyclohexaphosphate hexahydrate (Charfi and Jouini, 1996) and in [1-(2-ammoniumethyl)piperazinium] cyclotetraphosphate trihydrate (Thabet and Jouini, 1997).

Computing details

Data collection: Kappa CCD Nonius; cell refinement: Kappa CCD Nonius; data reduction: *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93*

(Sheldrick, 1993); molecular graphics: *MOLVIEW*; software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993).

Piperazinium dihydrogendiphosphate

Crystal data

$C_4H_{12}N_2^{2+}\cdot H_2P_2O_7^{2-}$	V = 1012.7 (4) Å^3
M_r = 264.11	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$
a = 11.749 (2) Å	μ = 0.45 mm^{-1}
b = 6.849 (2) Å	T = 293 (2) K
c = 12.592 (2) Å	0.35 × 0.15 × 0.12 mm
β = 91.80 (3)°	

Data collection

Kappa CCD Nonius diffractometer	2005 independent reflections
Absorption correction: none	1765 reflections with $I > 2\sigma(I)$
2005 measured reflections	R_{int} = 0.0

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032	193 parameters
$wR(F^2)$ = 0.090	All H-atom parameters refined
S = 1.07	$\Delta\rho_{max}$ = 0.25 e Å^{-3}
2005 reflections	$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Selected geometric parameters (Å, °)

P1—OE11	1.4132 (14)	P2—OE22	1.621 (2)
P1—OE13	1.537 (2)	P1—P2	2.932 (1)
P1—OE12	1.539 (2)	N1—C2	1.495 (3)
P1—OL12	1.6387 (14)	N1—C1	1.526 (3)
P2—OE21	1.4068 (14)	N2—C4	1.478 (3)
P2—OE23	1.544 (2)	N2—C3	1.526 (3)
P2—OL12	1.5680 (14)	C1—C2^{i}	1.482 (3)
OE11—P1—OE13	110.45 (10)	OE21—P2—OE22	110.44 (9)
OE11—P1—OE12	110.43 (10)	OE23—P2—OE22	112.77 (9)
OE13—P1—OE12	117.64 (12)	OL12—P2—OE22	105.41 (8)
OE11—P1—OL12	107.93 (8)	P2—OL12—P1	132.24 (9)
OE13—P1—OL12	98.48 (10)	C2—N1—C1	112.9 (2)
OE12—P1—OL12	111.02 (9)	C4—N2—C3	105.9 (2)
OE21—P2—OE23	115.67 (9)	C2^{i}—C1—N1	106.8 (2)
OE21—P2—OL12	106.11 (8)	C1^{i}—C2—N1	115.3 (2)

OE23—P2—OL12	105.55 (9)

Symmetry codes: (i) −*x*+1, −*y*−1, −*z*+2.

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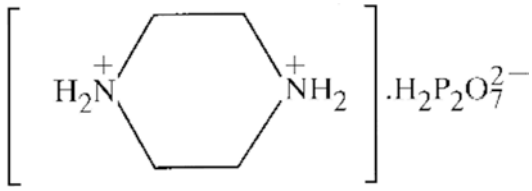
CIF access

Scheme 1



supplementary materials

Piperazinium dihydrogendiphosphate

Crystal data

$C_4H_{12}N_2^{2+}\cdot H_2P_2O_7^{2-}$	F_{000} = 552
	D_x = 1.732 Mg m^{-3}
M_r = 264.11	D_m = 1.71 Mg m^{-3}
	D_m measured by pycnometry (toluene as pycnometric liquid)
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
	λ = 0.71069 Å
a = 11.749 (2) Å	Cell parameters from 25 reflections
b = 6.849 (2) Å	θ = 3–25º
c = 12.592 (2) Å	μ = 0.45 mm^{-1}
β = 91.80 (3)º	T = 293 (2) K
V = 1012.7 (4) Å^3	Elongated prism, colourless
Z = 4	0.35 × 0.15 × 0.12 mm

Data collection

Kappa CCD Nonius diffractometer	1765 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.0
Monochromator: graphite	θ_{max} = 25º
T = 293(2) K	θ_{min} = 3º
φ scans	h = −14→14
Absorption correction: none	k = −8→0
2005 measured reflections	l = 0→14
2005 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.032	All H-atom parameters refined
$wR(F^2)$ = 0.090	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.6486P]$ where $P = (F_o^2 + 2F_c^2)/3$?
S = 1.07	$\Delta\rho_{max}$ = 0.25 e Å^{-3}
2005 reflections	$\Delta\rho_{min}$ = −0.31 e Å^{-3}
193 parameters	Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.012 (4)

Special details

Experimental. A dilute solution of diphosphoric acid is neutralized by the stoichiometric amount of the piperazin solution. The obtained solution, slowly evaporated at room temperature, gives thin single crystals unstable under normal condition of temperature and humidity. Indeed, the hydrate phase is converted to the studied anhydrous one over some mounths.

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 on F^2 for ALL reflections except for 0 with very negative F^2 or flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses 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 observed criterion of $F^2 > 2\mathrm{sigma}(F^2)$ is used only for calculating *R* - factor obs *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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.28701 (4)	0.11903 (7)	0.86547 (4)	0.0230 (2)
P2	0.21989 (4)	0.47375 (7)	0.74909 (4)	0.0230 (2)
OE11	0.39636 (11)	0.0411 (2)	0.88861 (13)	0.0359 (4)
OE21	0.10981 (11)	0.3931 (2)	0.74137 (12)	0.0319 (3)
OE22	0.26092 (13)	0.5417 (2)	0.63308 (13)	0.0348 (4)
OE23	0.23814 (13)	0.6331 (2)	0.83463 (12)	0.0361 (4)
OL12	0.30149 (11)	0.3022 (2)	0.78325 (12)	0.0318 (4)
OE12	0.23101 (15)	0.1859 (3)	0.96815 (13)	0.0493 (5)
OE13	0.2185 (2)	−0.0184 (3)	0.7912 (2)	0.0582 (6)
N1	0.46950 (15)	−0.2988 (3)	0.9883 (2)	0.0336 (4)
N2	0.02650 (14)	0.0835 (3)	0.60963 (15)	0.0301 (4)
C1	0.5219 (2)	−0.4035 (3)	0.8947 (2)	0.0338 (5)
C2	0.4084 (2)	−0.4341 (3)	1.0603 (2)	0.0369 (5)
C3	−0.0243 (2)	0.2022 (3)	0.5172 (2)	0.0335 (5)
C4	0.0916 (2)	−0.0761 (3)	0.5611 (2)	0.0339 (5)
HO22	0.250 (3)	0.459 (5)	0.574 (3)	0.077 (11)*
HO13	0.230 (3)	−0.137 (6)	0.812 (3)	0.069 (10)*
H1N1	0.424 (3)	−0.200 (4)	0.953 (2)	0.056 (8)*
H2N1	0.516 (3)	−0.232 (5)	1.033 (2)	0.064 (9)*
H1N2	−0.018 (2)	0.035 (4)	0.653 (2)	0.036 (6)*
H2N2	0.067 (3)	0.169 (4)	0.660 (2)	0.057 (8)*
H1C1	0.565 (2)	−0.311 (4)	0.854 (2)	0.045 (7)*
H2C1	0.470 (2)	−0.452 (4)	0.844 (2)	0.046 (7)*
H1C2	0.350 (2)	−0.485 (4)	1.001 (2)	0.047 (7)*
H2C2	0.380 (2)	−0.362 (4)	1.123 (2)	0.051 (8)*
H1C3	0.029 (2)	0.263 (4)	0.4808 (18)	0.031 (6)*
H2C3	−0.062 (2)	0.296 (4)	0.552 (2)	0.043 (7)*
H1C4	0.118 (2)	−0.155 (4)	0.625 (2)	0.041 (6)*

H2C4	0.148 (2)	−0.015 (4)	0.517 (2)	0.046 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0181 (3)	0.0197 (3)	0.0309 (3)	0.0010 (2)	−0.0023 (2)	0.0011 (2)
P2	0.0217 (3)	0.0174 (3)	0.0298 (3)	0.0008 (2)	−0.0003 (2)	−0.0001 (2)
OE11	0.0192 (7)	0.0291 (8)	0.0590 (10)	0.0058 (5)	−0.0033 (6)	0.0075 (7)
OE21	0.0168 (6)	0.0337 (8)	0.0453 (9)	0.0008 (5)	−0.0010 (5)	−0.0059 (6)
OE22	0.0405 (8)	0.0295 (8)	0.0347 (9)	−0.0052 (6)	0.0037 (6)	0.0034 (7)
OE23	0.0459 (9)	0.0226 (7)	0.0397 (9)	−0.0027 (6)	−0.0020 (6)	−0.0050 (6)
OL12	0.0182 (6)	0.0242 (7)	0.0533 (9)	0.0046 (5)	0.0060 (6)	0.0113 (6)
OE12	0.0473 (10)	0.0621 (12)	0.0393 (9)	0.0256 (8)	0.0122 (7)	0.0114 (8)
OE13	0.0557 (11)	0.0220 (8)	0.094 (2)	−0.0036 (7)	−0.0460 (10)	0.0001 (9)
N1	0.0240 (8)	0.0214 (9)	0.0551 (12)	0.0044 (6)	−0.0058 (7)	0.0034 (8)
N2	0.0197 (8)	0.0387 (10)	0.0321 (10)	−0.0093 (7)	0.0019 (7)	−0.0060 (8)
C1	0.0258 (10)	0.0356 (12)	0.0401 (12)	−0.0019 (8)	0.0020 (8)	0.0075 (9)
C2	0.0227 (10)	0.0371 (12)	0.0514 (14)	0.0048 (8)	0.0074 (9)	−0.0004 (10)
C3	0.0244 (10)	0.0289 (11)	0.0473 (13)	−0.0016 (8)	0.0041 (9)	−0.0021 (9)
C4	0.0199 (9)	0.0401 (12)	0.0413 (13)	0.0007 (8)	−0.0038 (8)	0.0026 (10)

Geometric parameters (Å, °)

P1—OE11	1.4132 (14)	N2—C3	1.526 (3)
P1—OE13	1.537 (2)	N2—H1N2	0.84 (3)
P1—OE12	1.539 (2)	N2—H2N2	0.97 (3)
P1—OL12	1.6387 (14)	C1—C2^{i}	1.482 (3)
P2—OE21	1.4068 (14)	C1—H1C1	0.97 (3)
P2—OE23	1.544 (2)	C1—H2C1	0.93 (3)
P2—OL12	1.5680 (14)	C2—C1^{i}	1.482 (3)
P2—OE22	1.621 (2)	C2—H1C2	1.05 (3)
P1—P2	2.932 (1)	C2—H2C2	1.00 (3)
OE22—HO22	0.94 (4)	C3—C4^{ii}	1.515 (3)
OE13—HO13	0.87 (4)	C3—H1C3	0.89 (2)
N1—C2	1.495 (3)	C3—H2C3	0.90 (3)
N1—C1	1.526 (3)	C4—C3^{ii}	1.515 (3)
N1—H1N1	0.96 (3)	C4—H1C4	1.01 (3)
N1—H2N1	0.90 (3)	C4—H2C4	0.97 (3)
N2—C4	1.478 (3)		
OE11—P1—OE13	110.45 (10)	H1N2—N2—H2N2	97.1 (23)
OE11—P1—OE12	110.43 (10)	C2^{i}—C1—N1	106.8 (2)
OE13—P1—OE12	117.64 (12)	C2^{i}—C1—H1C1	113.9 (15)
OE11—P1—OL12	107.93 (8)	N1—C1—H1C1	109.4 (15)
OE13—P1—OL12	98.48 (10)	C2^{i}—C1—H2C1	109.6 (17)
OE12—P1—OL12	111.02 (9)	N1—C1—H2C1	115.1 (16)
OE21—P2—OE23	115.67 (9)	H1C1—C1—H2C1	102.3 (21)
OE21—P2—OL12	106.11 (8)	C1^{i}—C2—N1	115.3 (2)

OE23—P2—OL12	105.55 (9)	C1^{i}—C2—H1C2	111.2 (14)
OE21—P2—OE22	110.44 (9)	N1—C2—H1C2	95.1 (14)
OE23—P2—OE22	112.77 (9)	C1^{i}—C2—H2C2	105.2 (15)
OL12—P2—OE22	105.41 (8)	N1—C2—H2C2	110.5 (16)
P2—OE22—HO22	120.3 (21)	H1C2—C2—H2C2	119.9 (20)
P2—OL12—P1	132.24 (9)	C4^{ii}—C3—N2	112.1 (2)
P1—OE13—HO13	108.4 (21)	C4^{ii}—C3—H1C3	107.0 (15)
C2—N1—C1	112.9 (2)	N2—C3—H1C3	112.2 (15)
C2—N1—H1N1	116.3 (17)	C4^{ii}—C3—H2C3	117.6 (16)
C1—N1—H1N1	102.2 (16)	N2—C3—H2C3	101.3 (16)
C2—N1—H2N1	103.2 (20)	H1C3—C3—H2C3	106.5 (22)
C1—N1—H2N1	118.2 (20)	N2—C4—C3^{ii}	115.1 (2)
H1N1—N1—H2N1	104.4 (26)	N2—C4—H1C4	102.4 (14)
C4—N2—C3	105.9 (2)	C3^{ii}—C4—H1C4	110.6 (14)
C4—N2—H1N2	108.6 (17)	N2—C4—H2C4	106.7 (15)
C3—N2—H1N2	117.8 (17)	C3^{ii}—C4—H2C4	102.8 (15)
C4—N2—H2N2	117.8 (17)	H1C4—C4—H2C4	119.7 (20)
C3—N2—H2N2	110.1 (17)		

Symmetry codes: (i) −*x*+1, −*y*−1, −*z*+2; (ii) −*x*, −*y*, −*z*+1.