

Tris(methylammonium) hydrogenphosphate dihydrogenphosphate

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Received 13 September 2005

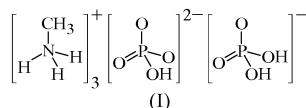
Accepted 14 December 2005

Online 14 January 2006

The title compound, $3\text{CH}_3\text{N}^+\cdot\text{HPO}_4^{2-}\cdot\text{H}_2\text{PO}_4^-$, aggregates with the moieties interconnected by $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, with $\text{O}\cdots\text{O}$ and $\text{N}\cdots\text{O}$ distances in the ranges 2.5366 (16)–2.5785 (14) and 2.7437 (16)–2.9967 (18) Å, respectively. Three $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds are also present, with $\text{C}\cdots\text{O}$ distances in the range 3.2310 (18)–3.3345 (17) Å. All H atoms are ordered. Structures with ordered hydrogenphosphate and dihydrogenphosphate components are rare.

Comment

Interest in the present study was influenced by properties observed in *n*-alkylammonium dihydrogenphosphates, $\text{C}_n\text{H}_{2n+1}\text{NH}_3^+\cdot\text{H}_2\text{PO}_4^-$. In these compounds, ferroelastic phase transitions arise, as discovered by Kroupa & Fuith (1993, 1994). Phase transitions and ferroelastic switching are related to the hydrogen-bond patterns in these derivatives (see, for example, Kasatani *et al.*, 1998; Fábry *et al.*, 2000), and so a goal in this field is to prepare compounds in this class and determine their crystal structures. However, the structure of methylammonium dihydrogenphosphate, (II), the simplest compound in the series, has not been reported to date. Crystals of the title compound, (I), grew accidentally during our attempts to grow crystals of (II). We present here the crystal structure of (I).



The most interesting feature of (I) is the cocrystallization of the dihydrogenphosphate and hydrogenphosphate anions in an ordered arrangement. Although this is not unprecedented, the simultaneous occurrence of both anions in an ordered way is quite rare. Among inorganic structures present in the Inorganic Crystal Structure Database (ICSD, 2004) there are

only two similar structures, namely oxonium phyllo-hexakis[dihydrogenphosphate(V)] bis[hydrogenphosphate(V)]trialuminate tetrahydrate, $(\text{H}_3\text{O})[\text{Al}_3(\text{H}_2\text{PO}_4)_6(\text{HPO}_4)_2](\text{H}_2\text{O})_4$ (Brodalla & Kniep, 1980; $R = 0.051$), and aluminium phyllo-dihydrogenphosphate hydrogenphosphate hydrate, $\text{Al}(\text{H}_2\text{PO}_4)(\text{HPO}_4)(\text{H}_2\text{O})$ (Kniep *et al.*, 1978; $R = 0.033$). In both compounds, the O atoms of the anions are simultaneously coordinated to the Al atoms.

Among the compounds listed in the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002) there are only three structures with the title anions and with R factors ≤ 0.05 , namely tris(hordenine) monohydrogenphosphate dihydrogenphosphate monohydrate (refcode KAWMOK; Mukhopadhyay *et al.*, 1989), hexakis(melaminium) tetrakis(dihydrogenphosphate) monohydrogenphosphate tetrahydrate (refcode XORYAE; Janczak & Perpétuo, 2002) and tris-(2-ammonioethyl)amine dihydrogenphosphate monohydro-

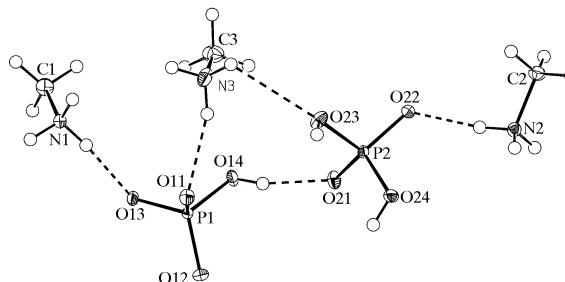


Figure 1

A view of the constituent ions in (I), with anisotropic displacement parameters drawn at the 50% probability level.

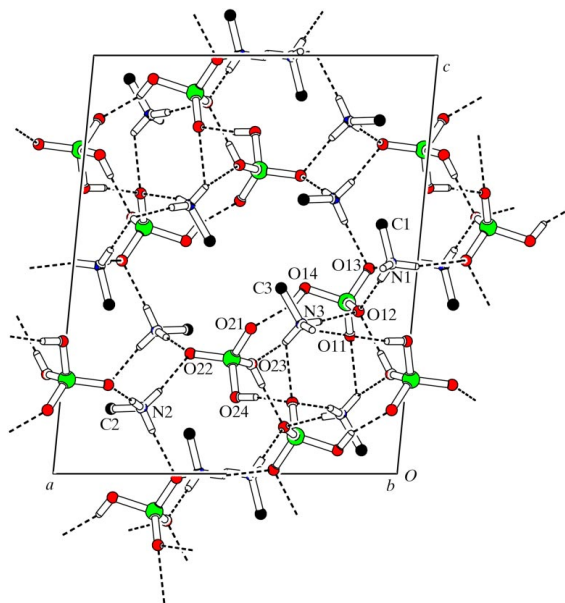


Figure 2

A view of the unit cell of (I) along the *b* axis. Methyl H atoms have been omitted.

genphosphate (refcode WAKBAM; Dakhloui *et al.*, 2004). The P—O bond lengths of these structure determinations correlate well with those in (I).

The moieties in (I) are interconnected by hydrogen bonds and there are several important points regarding the hydrogen-bond pattern. Firstly, the hydrogen-bond donor atoms O14, O23 and O24 do not act as hydrogen-bond acceptors, except for atom O14, which is involved in a weak C—H···O hydrogen bond (Table 2). Secondly, there is a difference between the [HPO₄]²⁻ and [H₂PO₄]⁻ anions in the number of H atoms accepted from the ammonium groups. The O atoms belonging to the [HPO₄]²⁻ anion accept seven H atoms from the ammonium groups, in contrast with the [H₂PO₄]⁻ anion, which accepts only two H atoms of this kind. In addition, the O atoms of the [HPO₄]²⁻ anion accept two other hydroxyl H atoms, so each of these acceptor O atoms of the latter anion is fully saturated by three H atoms. The fact that the [HPO₄]²⁻ anion accepts more H atoms than [H₂PO₄]⁻ can be related to the higher formal negative charge of the former, to the values of the first and second degree dissociation constants pK_a^I and pK_a^{II} (1.3 and 6.70, respectively; Lide, 1997), and to the obvious fact that a hydroxyl group can accept fewer H atoms than an oxo group. Thirdly, O—H···O hydrogen bonds interconnect the [HPO₄]²⁻ and [H₂PO₄]⁻ anions into columns passing through the structure along the *b* axis. The methylammonium groups that interconnect all the molecules into a three-dimensional network are attached to these molecules. Fourthly, the higher displacement parameters of atom N3 in one of the methylammonium groups can be attributed to a weaker hydrogen bond in comparison with atoms N1 and N2 (*cf.* Table 1). Consequently, the same holds for atom C3 in comparison with atoms C1 and C2. The P—O···A angles, where *A* is an acceptor N or O atom, are in the range 108.00 (6)–128.00 (6)°. Finally, three C—H···O hydrogen bonds (Table 2) complete the hydrogen bonding and conform to the criteria given by Desiraju & Steiner (1999).

Experimental

Crystals of (I) were grown from a mixture of methylamine and phosphoric acid in a stoichiometric ratio of 1:1 in an attempt to prepare methylammonium dihydrogenphosphate, (II). An ethanol-water solution (30:70 vol%) of the mixture was placed in a refrigerator at ~280 K and left there for several months. During this period, part of the sample became dry and possibly partially decomposed, as could be judged from a yellowish taint. From this light-yellow bulk grew several centimetre-long colourless needle-like crystals of (I), with cross-sections measuring several millimetres. The beaker also contained the desired crystals of (II), of a size of several tenths of a millimetre. The quality of the crystals of (II) was inferior to the demands of single-crystal diffractometry. The crystals of (I) are clearly less hygroscopic than those of (II). Calorimetric experiments were performed on Perkin-Elmer DSC 7 and Pyris Diamond differential scanning calorimeters using *PYRIS* software (Perkin-Elmer, 2001), with *m* = 5 mg, a temperature interval of 93–398 K and a scanning rate of 10 K min⁻¹. No structural phase transitions were detected, either on heating or on cooling. The symptoms of decomposition commenced at 378 K.

Crystal data

3CH₅N⁺·HPO₄²⁻·H₂PO₄⁻
M_r = 289.2
 Monoclinic, *P*2₁/*n*
a = 12.3571 (6) Å
b = 6.5465 (2) Å
c = 15.1231 (6) Å
 β = 95.556 (4)°
V = 1217.65 (9) Å³
Z = 4

D_x = 1.577 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 20259 reflections
 θ = 3.3–26.4°
 μ = 0.39 mm⁻¹
T = 120 K
 Prism, colourless
 0.41 × 0.27 × 0.11 mm

Data collection

Oxford Diffraction Xcalibur CCD area-detector diffractometer
 Rotation method data acquisition using ω scans
 Absorption correction: analytical [*Crysalis RED* (Oxford Diffraction, 2005); method by Clark & Reid (1995)]
T_{min} = 0.877, *T_{max}* = 0.937

20259 measured reflections
 2498 independent reflections
 2187 reflections with *I* > 3σ(*I*)
R_{int} = 0.026
 θ_{\max} = 26.4°
h = -15 → 15
k = -8 → 8
l = -18 → 18

Refinement

Refinement on *F*²
R(*F*) = 0.026
wR(*F*²) = 0.080
S = 1.89
 2498 reflections
 154 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(I) + 0.0009I^2]$
 (Δ/σ)_{max} = 0.001
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{Å}^{-3}$

Table 1

Selected bond lengths (Å).

P1—O11	1.5274 (11)	P2—O23	1.5831 (11)
P1—O12	1.5412 (11)	P2—O24	1.5836 (11)
P1—O13	1.5369 (11)	N1—C1	1.4859 (19)
P1—O14	1.5758 (11)	N2—C2	1.485 (2)
P2—O21	1.5008 (12)	N3—C3	1.490 (2)
P2—O22	1.5130 (11)		

Table 2

Hydrogen-bonding geometry (Å, °), including weak C—H···O hydrogen bonds (Desiraju & Steiner, 1999).

<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>
O14—HO14···O21	0.820 (8)	1.752 (6)	2.5366 (16)	159.5 (5)
O23—HO23···O12 ⁱ	0.820 (10)	1.771 (9)	2.5785 (14)	167.7 (7)
O24—HO24···O11 ⁱⁱ	0.820 (11)	1.765 (12)	2.5735 (15)	168.3 (12)
N1—H2N1···O13 ⁱⁱⁱ	0.89	1.94	2.7677 (16)	154
N1—H1N1···O13	0.89	1.91	2.7825 (16)	168
N1—H3N1···O12 ^{iv}	0.89	1.94	2.8337 (16)	177
N2—H1N2···O22	0.89	1.91	2.7916 (17)	172
N2—H3N2···O22 ^v	0.89	1.86	2.7437 (16)	173
N2—H2N2···O13 ^{vi}	0.89	1.93	2.8141 (15)	175
N3—H2N3···O11	0.89	2.08	2.9416 (17)	163
N3—H1N3···O12 ^{iv}	0.89	1.92	2.8044 (18)	173
N3—H3N3···O11 ⁱ	0.89	2.31	2.9967 (18)	134
C2—H1C2···O14 ^{vi}	0.96	2.53	3.2310 (19)	130
C2—H2C2···O22 ^{vii}	0.96	2.56	3.3347 (19)	137
C3—H3C3···O21 ^{iv}	0.96	2.58	3.243 (2)	126

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

Although all H atoms could be found in the difference Fourier map and their positions and isotropic displacement parameters refined in the final model, some parameters regarding the H atoms were constrained or restrained as follows. The methylammonium H atoms were constrained and ideal geometry was assumed, with C—H and N—H bond lengths of 0.96 and 0.89 Å, respectively. The O—H

bond lengths were restrained to 0.82 (1) Å and the P—O—H angles were restrained to 109.47 (1)°. For all H atoms, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{parent})$. The structure was examined for rotational disorder in the methyl and ammonium groups and there was no evidence for disorder on analysis of the difference maps and refinement results. A search of the Cambridge Structural Database (Version 5.26; Allen, 2002) revealed that disorder of methylammonium molecules or their groups usually corresponds to structures where no or only weak hydrogen bonds are present, such as between halogen groups. As examples, $(\text{CH}_3\text{NH}_3)[\text{HgCl}_3]$ in the determinations with refcodes QQQBVJ04 and QQQBVJ31 have disordered methyl groups (Korfer & Fuess, 1988).

Data collection: *Crysalis CCD* (Oxford Diffraction, 2005); cell refinement: *Crysalis RED* (Oxford Diffraction, 2005); data reduction: *Crysalis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2000* (Petříček & Dušek, 2000); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *JANA2000*.

Miss Karla Fejfarová is thanked for her help during the measurements. The support of this study by grant Nos. 203/02/0436 and 202/05/0421 of the Grant Agency of the Czech Republic and by grant No. 158/2004/B-CH/PrF is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1289). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Brodalla, D. & Kniep, R. (1980). *Z. Naturforsch. Teil B*, **35**, 403–404.
- Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* **A51**, 887–897.
- Dakhlaoui, A., Smiri, L. S. & Driss, A. (2004). *Acta Cryst.* **E60**, o2241–o2243.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, pp. 58–68. New York: Oxford University Press Inc.
- Fábry, J., Petříček, V., Kroupa, J. & Císařová, I. (2000). *Acta Cryst.* **B56**, 906–914.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- ICSD (2004). Inorganic Crystal Structure Database. Version 1.3.3, Release 2004. FIZ–Karlsruhe. URL: <http://www.Fiz-karlsruhe.de/Fiz/products/icsd/welcome.html>
- Janczak, J. & Perpétuo, G. J. (2002). *Acta Cryst.* **C58**, o455–o459.
- Kasatani, H., Iwata, M., Ishibashi, Y. & Terauchi, H. (1998). *J. Korean Phys. Soc.* **32**, S1807–S1809.
- Kniep, R., Mootz, D. & Wilms, A. (1978). *Z. Naturforsch. Teil B*, **33**, 1047–1048.
- Korfer, M. & Fuess, H. (1988). *Z. Kristallogr.* **183**, 27–41.
- Kroupa, J. & Fuith, A. (1993). *Phys. Rev. B*, **48**, 4119–4121.
- Kroupa, J. & Fuith, A. (1994). *Ferroelectrics*, **159**, 115–119.
- Lide, D. R. (1997). Editor. *CRC Handbook of Chemistry and Physics*, pp. 8–44. Boca Raton: CRC Press.
- Mukhopadhyay, B. P., Dattagupta, J. K. & Simonetta, M. (1989). *Z. Kristallogr.* **187**, 221–229.
- Oxford Diffraction (2005). *CrysAlis RED* (Version 1.171.27p. beta; Release 01-04-2005 CrysAlis171.NET) and *CrysAlis CCD* (Version Sapphire-2). Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Perkin–Elmer (2001). *PYRIS*. Version 4.02. Perkin–Elmer Instruments, 710 Bridgeport Avenue, Shelton, CT 06484-4794, USA.
- Petříček, V. & Dušek, M. (2000). *JANA2000*. Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.