Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

$(NH_4)_7(HPO_4)_2(PO_4)$, heptaammonium bis(hydrogenphosphate) phosphate

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Received 6 April 2005
Accepted 18 April 2005
Online 23 April 2005

The asymmetric unit of the compound $(NH_4)_7(HPO_4)_2(PO_4)$ consists of two hydrogen phosphate anions, one phosphate anion and seven ammonium cations, all of them located in general positions. The two $[PO_3(OH)]^{2-}$ anions are linked to the PO_4^{3-} anion *via* an O—H···O hydrogen bond to form a three-anion unit, which is surrounded by the ammonium cations. The anions and cations are further connected *via* N—H···O hydrogen bonding.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.002 Å
R factor = 0.031
wR factor = 0.084
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The crystal chemistry of ammonium phosphate and hydrogen phosphates has been the subject of intense work for several decades. Mootz & Wunderlich (1970) reported the crystal structure of $(NH_4)_3PO_4\cdot3H_2O$. $(NH_4)_2HPO_4$ has been investigated on the basis of a single-crystal structure determination by Khan *et al.* (1972). However, a mixed compound containing both hydrogen phosphate and phosphate anions has so far not been investigated by single-crystal X-ray diffraction. In our own work, we have now synthesized and structurally characterized the title compound, $(NH_4)_7(HPO_4)_2(PO_4)$. All H atoms were located in a difference map and therefore the actual hydrogen-bonding pattern was determined. Additionally, we can distinguish between the PO_4^{3-} and HPO_4^{2-} anions by comparing the bond lengths and angles in the anions with the values found in the literature (Mootz & Wunderlich, 1970; Khan *et al.*, 1972).

The structure of $(NH_4)_7(HPO_4)_2(PO_4)$ consists of HPO_4^{2-}, PO_4^{3-} and NH_4^+ tetrahedra, which are connected by O—H···O and N—H···O interactions (Fig. 1). The interatomic distances

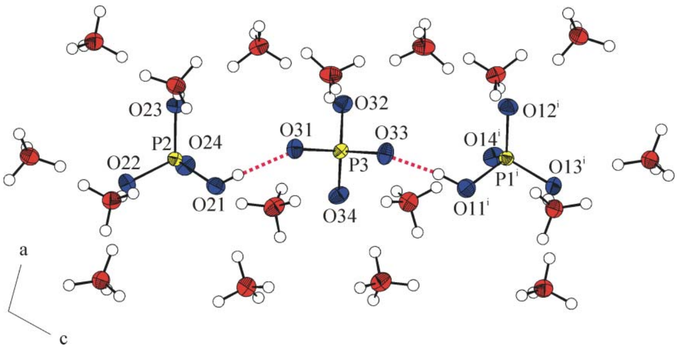

Figure 1
The crystal structure of the title compound, with the atom-labelling scheme, showing a view of a group of three anions, which is surrounded by ammonium cations. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary size and O—H···O hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x + 1, \frac{1}{2} + y, -z + 2$.]

and angles have normal values. One of the four P—O bonds within the PO_4 tetrahedron of both crystallographically independent HPO_4^{2-} anions is longer than the remaining three, which is typical for a $[PO_3(OH)]^{2-}$ group. Also typical for such groups are the O—P—O angles (Table 1). The average value of the angles containing the P—O(H) bonds is 107.4°, smaller than the ideal tetrahedral angle, whereas the angles not involving the P—O(H) group are larger (average 111.4°). Within the PO_4^{3-} anion, all bond lengths and angles are comparable (Table 1). This also holds for the values of the O—P—O angles (Table 1).

In the crystal structure of the title compound, the PO_4^{3-} anions are connected to the two crystallographically independent hydrogen phosphate anions *via* O—H···O hydrogen bonds, to form linear groups of three anions (Fig. 1). Two different PO_4^{3-} O atoms act as acceptors and are involved in this interaction. The three-anion groups are isolated from each other by a cage of ammonium cations (Figs. 1 and 2).

Each H atom of the NH_4^+ ion interacts with the phosphate and hydrogen phosphate O atoms *via* N—H···O hydrogen bonds. From this arrangement a complex three-dimensional network is formed. Relevant interatomic distances and angles are listed in Table 2.

Experimental

$(NH_4)_7(HPO_4)_2(PO_4)$ was prepared under solvothermal conditions. Equimolar quantities of $(NH_4)_2HPO_4$ and $Hg(NO_3)_2$ were placed in a Teflon container with a capacity of 10 ml. The container was half-filled with 25% aqueous ammonia solution and sealed in a steel autoclave. After heating to 453 K over a period of 10 h, maintaining that temperature for 6 d and then cooling to room temperature over 3 d, the resulting material was transferred to a beaker. A suitable colourless single crystal (0.5 × 0.25 × 0.25 mm) was carefully selected out of the mother liquor under a microscope and mounted with some mother liquor in a glass capillary for subsequent structure analysis. The crystals decompose rapidly in contact with air, with release of ammonia. Recrystallization from water led to crystals of the composition $(NH_4)_2HPO_4$ (Khan *et al.*, 1972).

Crystal data

$(NH_4)_7(HPO_4)_2(PO_4)$
$M_r = 413.22$
Monoclinic, $P2_1$
$a = 10.4667$ (17) Å
$b = 6.2976$ (7) Å
$c = 14.072$ (2) Å
$\beta = 103.738$ (19)°
$V = 901.0$ (2) Å^3
$Z = 2$
$D_x = 1.523$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1206 reflections
$\theta = 1.9$–28.2°
$\mu = 0.39$ mm^{-1}
$T = 293$ (2) K
Column, colourless
0.5 × 0.25 × 0.25 mm

Data collection

Stoe IPDS I diffractometer
φ scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 2001), after optimizing the crystal shape using *X-SHAPE* (Stoe & Cie, 1999).
$T_{min} = 0.902$, $T_{max} = 0.962$
8608 measured reflections
4004 independent reflections
3538 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 28.1°$
$h = -13 \rightarrow 13$
$k = -7 \rightarrow 7$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.084$
$S = 1.06$
4004 reflections
320 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.081 (5)
Absolute structure: Flack (1983), 1786 Friedel pairs
Flack parameter: −0.02 (8)

Table 1
Selected geometric parameters (Å, °).

P1—O14	1.5210 (20)	P2—O21	1.5740 (20)
P1—O12	1.5233 (18)	P3—O34	1.5312 (18)
P1—O13	1.5237 (17)	P3—O32	1.5352 (18)
P1—O11	1.5730 (20)	P3—O33	1.5356 (19)
P2—O24	1.5230 (20)	P3—O31	1.5548 (19)
P2—O23	1.5266 (17)	O11—H111	0.87 (4)
P2—O22	1.5292 (18)	O21—H211	0.72 (6)
O14—P1—O12	110.20 (12)	O24—P2—O21	108.55 (12)
O14—P1—O13	111.85 (11)	O23—P2—O21	108.38 (11)
O12—P1—O13	112.33 (11)	O22—P2—O21	105.51 (11)
O14—P1—O11	108.96 (12)	O34—P3—O32	110.16 (11)
O12—P1—O11	109.20 (12)	O34—P3—O33	110.71 (11)
O13—P1—O11	104.07 (11)	O32—P3—O33	109.56 (11)
O24—P2—O23	111.42 (11)	O34—P3—O31	110.92 (11)
O24—P2—O22	111.24 (11)	O32—P3—O31	108.16 (11)
O23—P2—O22	111.48 (10)	O33—P3—O31	107.24 (11)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O11—H111···O33^{i}	0.87 (4)	1.69 (5)	2.535 (3)	164 (5)
O21—H211···O31	0.72 (6)	1.79 (6)	2.510 (3)	177 (8)
N1—H11···O21^{i}	0.88 (2)	2.04 (2)	2.899 (3)	165 (4)
N1—H12···O33	0.90 (2)	1.93 (2)	2.802 (3)	163 (3)
N1—H13···O34^{ii}	0.86 (2)	1.97 (2)	2.828 (3)	174 (3)
N1—H14···O14^{i}	0.88 (2)	1.92 (2)	2.789 (3)	170 (4)
N2—H21···O34^{iii}	0.88 (2)	2.01 (2)	2.847 (3)	159 (3)
N2—H22···O24	0.89 (2)	2.05 (3)	2.833 (3)	146 (4)
N2—H23···O31^{iv}	0.88 (2)	2.03 (2)	2.907 (3)	176 (3)
N2—H24···O34	0.89 (2)	1.88 (2)	2.768 (3)	174 (4)
N3—H31···O23^{v}	0.89 (2)	1.93 (2)	2.814 (3)	176 (4)
N3—H32···O14	0.89 (2)	1.93 (2)	2.776 (3)	158 (3)
N3—H33···O32^{v}	0.86 (2)	1.95 (2)	2.801 (3)	173 (4)
N3—H34···O12^{iv}	0.87 (2)	1.94 (2)	2.797 (4)	170 (3)
N4—H41···O13^{iv}	0.85 (2)	1.99 (2)	2.840 (3)	172 (3)
N4—H42···O22^{iv}	0.89 (2)	1.95 (2)	2.818 (4)	166 (3)
N4—H43···O23^{vi}	0.88 (2)	2.01 (2)	2.872 (3)	167 (3)
N4—H44···O24	0.86 (2)	1.94 (2)	2.791 (3)	167 (4)
N5—H51···O22	0.89 (2)	1.93 (2)	2.794 (3)	165 (3)
N5—H52···O13^{iv}	0.88 (2)	2.03 (2)	2.879 (4)	163 (3)
N5—H53···O13^{vii}	0.90 (2)	1.88 (2)	2.764 (3)	169 (3)
N5—H54···O14	0.86 (2)	1.93 (2)	2.796 (3)	178 (4)
N6—H61···O12^{vii}	0.87 (2)	1.94 (2)	2.807 (3)	173 (3)
N6—H62···O22	0.88 (2)	1.92 (2)	2.797 (3)	174 (4)
N6—H63···O23^{vi}	0.87 (2)	1.96 (2)	2.821 (4)	169 (3)
N6—H64···O24^{viii}	0.87 (2)	1.93 (2)	2.761 (3)	160 (4)
N7—H71···O32^{ix}	0.88 (2)	1.91 (2)	2.776 (3)	166 (3)
N7—H72···O32	0.89 (2)	1.89 (2)	2.765 (3)	166 (3)
N7—H73···O31^{iv}	0.86 (2)	2.17 (2)	2.977 (3)	156 (3)
N7—H73···O33^{iv}	0.86 (2)	2.55 (3)	3.266 (3)	141 (3)
N7—H74···O12^{x}	0.89 (2)	1.97 (2)	2.850 (3)	169 (5)

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

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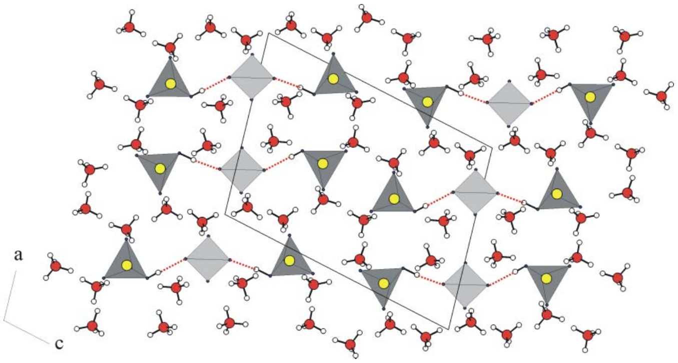

Figure 2
The crystal structure of $(NH_4)_7(HPO_4)_2(PO_4)$, viewed along the crystallographic b axis. O—H···O hydrogen bonds are shown as dashed lines.

All H atoms were located in a difference Fourier map and refined freely with isotropic displacement parameters.

Data collection: *IPDS* (Stoe & Cie, 1996); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *CIF-Editor* (Wieczorrek, 2004).

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