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L-Histidinol Phosphate Tetrahydrate: Redetermination at 110 and 240 K

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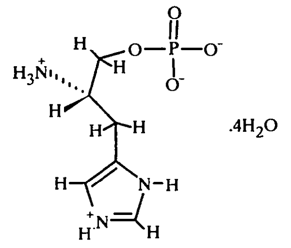
Abstract

In the crystal of L-histidinol phosphate tetrahydrate, $C_6H_{12}N_3O_4P.4H_2O$, at 110 and 240 K, the L-histidinol phosphate residue exists as a zwitterion in which the phosphate group is doubly ionized with the amino and imidazole moieties each accepting a proton from the acid group.

Comment

During the analysis of the geometrical parameters of L-histidinol phosphate tetrahydrate, (I), at ambient temperature (Suga & Okabe, 1997), it was found that the P—O(H) distance does not differ from other P—O(terminal) distances. Since this was rather unexpected (Lis, 1987, and references therein), it was decided to reinvestigate this structure.



(I)

The present studies show that in the crystal of L-histidinol phosphate tetrahydrate at 110 and 240 K, L-histidinol phosphate exists as a zwitterion (Fig. 1) in which the phosphate group is doubly ionized with the amino and imidazole moieties each accepting a proton from the acid group.

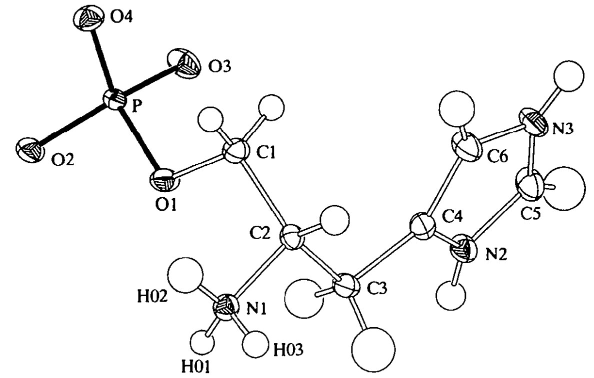


Fig. 1. The structure and numbering scheme of the L-histidinol phosphate residue at 110 K. Displacement ellipsoids are shown at the 50% probability level.

The new atomic coordinates for the heavy atoms do not differ significantly from those of the previous refinement (Suga & Okabe, 1997), although the new s.u.'s are lower. The principal interatomic distances and angles at 110 K do not differ significantly either from those at 240 K or from those of Suga & Okabe (1997). The P—O(terminal) bond lengths may be accepted as normal P—O(terminal) bond lengths in the doubly ionized monoesterified phosphate group (Starynowicz *et al.*, 1986).

The determination of all H-atom positions showed that the hydrogen-bonding pattern postulated by Suga & Okabe (1997) is correct. The crystal structure is stabilized by a three-dimensional network utilizing all O- and N-bonded H atoms. Furthermore, two short C—H···O contacts may be distinguished (Tables 2 and 3).

Experimental

Colourless crystals of the title compound were provided by Suga & Okabe (1997).

(I) at 110 K

Crystal data

$C_6H_{12}N_3O_4P.4H_2O$
$M_r = 293.22$
Monoclinic
$P2_1$
$a = 9.337\,(8)$ Å
$b = 7.597\,(4)$ Å
$c = 9.321\,(6)$ Å
$\beta = 104.46\,(7)°$
$V = 640.2\,(8)$ Å^3
$Z = 2$
$D_x = 1.521$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 44 reflections
$\theta = 8–17°$
$\mu = 0.253$ mm^{-1}
$T = 110\,(1)$ K
Plate
0.40 × 0.30 × 0.18 mm
Colourless

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Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3873 measured reflections
2007 independent reflections
1773 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.028$
$\theta_{\rm max} = 30°$
$h = -13 \rightarrow 11$
$k = 0 \rightarrow 10$
$l = -13 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.027$
$wR(F^2) = 0.065$
$S = 1.131$
2007 reflections
242 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.012P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.081$
$\Delta\rho_{\rm max} = 0.51$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.06 (8)

Table 1. *Selected geometric parameters (Å, °) at 110 K*

P—O1	1.607 (2)	N2—C4	1.375 (2)
P—O2	1.504 (2)	N3—C5	1.318 (2)
P—O3	1.512 (2)	N3—C6	1.380 (2)
P—O4	1.520 (2)	C1—C2	1.513 (3)
O1—C1	1.430 (2)	C2—C3	1.520 (2)
N1—C2	1.485 (2)	C3—C4	1.484 (3)
N2—C5	1.330 (3)	C4—C6	1.358 (2)
O1—P—O2	102.7 (1)	N1—C2—C1	108.5 (2)
O1—P—O3	108.6 (1)	N1—C2—C3	107.9 (2)
O1—P—O4	107.1 (1)	C1—C2—C3	114.8 (2)
O2—P—O3	113.8 (1)	C4—C3—C2	112.7 (2)
O2—P—O4	113.5 (1)	C6—C4—N2	106.2 (2)
O3—P—O4	110.4 (1)	C6—C4—C3	133.1 (2)
C1—O1—P	117.2 (2)	N2—C4—C3	120.7 (2)
C5—N2—C4	109.0 (2)	N3—C5—N2	109.0 (2)
C5—N3—C6	108.4 (2)	C4—C6—N3	107.4 (2)
O1—C1—C2	108.2 (2)		
O2—P—O1—C1	−166.0 (2)	O1—C1—C2—C3	64.3 (2)
O3—P—O1—C1	73.0 (2)	N1—C2—C3—C4	−173.1 (2)
O4—P—O1—C1	−46.2 (2)	C1—C2—C3—C4	65.7 (3)
P—O1—C1—C2	−164.7 (2)	C2—C3—C4—C6	15.1 (4)
O1—C1—C2—N1	−56.5 (2)	C2—C3—C4—N2	−164.4 (2)

Table 2. *Hydrogen-bonding geometry (Å, °) at 110 K*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H01···O5$^{\rm i}$	0.84 (3)	1.93 (3)	2.770 (3)	180 (3)
N1—H02···O4$^{\rm ii}$	0.87 (3)	1.90 (3)	2.732 (3)	159 (3)
N1—H03···O2$^{\rm iii}$	0.85 (4)	1.89 (4)	2.738 (3)	175 (3)
N2—H20···O2$^{\rm i}$	0.84 (3)	1.87 (3)	2.688 (3)	162 (3)
N3—H30···O3$^{\rm iv}$	0.89 (3)	1.71 (3)	2.594 (3)	171 (3)
O5—H51···O3	0.78 (4)	1.97 (4)	2.716 (3)	160 (4)
O5—H52···O7$^{\rm v}$	0.86 (4)	2.00 (4)	2.847 (3)	169 (4)
O6—H61···O4$^{\rm ii}$	0.80 (4)	1.94 (5)	2.711 (3)	161 (4)
O6—H62···O2	0.81 (5)	2.31 (5)	3.115 (3)	172 (4)
O7—H71···O8$^{\rm vi}$	0.87 (4)	1.87 (4)	2.729 (3)	167 (4)
O7—H72···O6$^{\rm vii}$	0.92 (4)	1.80 (4)	2.711 (3)	169 (3)
O8—H81···O7$^{\rm viii}$	0.82 (4)	2.04 (4)	2.823 (3)	161 (4)
O8—H82···O4	0.74 (4)	2.01 (4)	2.745 (3)	171 (4)
C5—H5···O8$^{\rm vii}$	0.94 (4)	2.58 (4)	3.210 (3)	124 (3)
C6—H6···O7$^{\rm i}$	0.97 (3)	2.66 (3)	3.556 (3)	154 (3)

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

(I) at 240 K

Crystal data

$C_6H_{12}N_3O_4P.4H_2O$
$M_r = 293.22$
Monoclinic
$P2_1$
$a = 9.359$ (7) Å
$b = 7.621$ (3) Å
$c = 9.367$ (6) Å
$\beta = 104.31$ (6)°
$V = 647.4$ (7) Å^3
$Z = 2$
$D_x = 1.504$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 8$–18°
$\mu = 0.250$ mm^{-1}
$T = 240$ (1) K
Plate
0.40 × 0.30 × 0.18 mm
Colourless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3994 measured reflections
3497 independent reflections
2704 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.022$
$\theta_{\rm max} = 30°$
$h = -13 \rightarrow 2$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.031$
$wR(F^2) = 0.078$
$S = 1.083$
3497 reflections
242 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.057P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.098$

$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.06 (8)

Table 3. *Hydrogen-bonding geometry (Å, °) at 240 K*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H01···O5$^{\rm i}$	0.80 (3)	1.97 (3)	2.772 (3)	176 (3)
N1—H02···O4$^{\rm ii}$	0.90 (3)	1.89 (3)	2.744 (3)	158 (3)
N1—H03···O2$^{\rm iii}$	0.87 (3)	1.86 (3)	2.732 (3)	178 (3)
N2—H20···O2$^{\rm i}$	0.87 (3)	1.86 (3)	2.687 (3)	160 (3)
N3—H30···O3$^{\rm iv}$	0.82 (3)	1.79 (3)	2.597 (3)	170 (3)
O5—H51···O3	0.79 (4)	1.94 (5)	2.724 (3)	173 (4)
O5—H52···O7$^{\rm v}$	0.82 (5)	2.06 (5)	2.860 (4)	165 (5)
O6—H61···O4$^{\rm ii}$	0.77 (5)	2.01 (5)	2.717 (3)	153 (5)
O6—H62···O2	0.80 (5)	2.38 (5)	3.174 (3)	175 (5)
O7—H71···O8$^{\rm vi}$	0.86 (4)	1.89 (4)	2.742 (3)	169 (3)
O7—H72···O6$^{\rm vii}$	0.88 (5)	1.87 (5)	2.713 (3)	159 (5)
O8—H81···O7$^{\rm viii}$	0.78 (4)	2.09 (4)	2.834 (3)	159 (4)
O8—H82···O4	0.76 (5)	2.05 (5)	2.748 (3)	154 (4)
C5—H5···O8$^{\rm vii}$	0.96 (4)	2.59 (4)	3.259 (3)	127 (3)
C6—H6···O7$^{\rm i}$	0.93 (3)	2.70 (3)	3.581 (3)	160 (3)

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

The same specimen was used for both data collections. Reflection counts for the two data collections are not comparable because the data were collected differently in the two experiments. The refinement was started for the diffraction data obtained at 110 K with the heavy-atom coordinates published by Suga & Okabe (1997). All H-atom positions were found from difference syntheses and refined isotropically. Note that the Suga & Okabe (1997) parameters are for the D enantiomer (although their figure shows the L enantiomer) and therefore their positional parameters were inverted to give the correct configuration. The structure refinement for data at 240 K was started with the parameters for all atoms obtained from the 110 K data. Note that at 110 K, the axial length a is longer than c, but at 240 K, the axial length a is shorter than c [as it is at 296 K according to Suga & Okabe (1997)]. Orthorhombic symmetry, consistent with the cell dimensions, can be excluded since it leads to an internal $R > 0.50$.

For both analyses, data collection: *Kuma KM*-4 *Users Guide* (Kuma Diffraction, 1989); cell refinement: *Kuma KM*-4 *Users Guide*; data reduction: *Kuma KM*-4 *Users Guide*; program used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1353). Services for accessing these data are described at the back of the journal.

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