Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Supercell and subcell description of the crystal structure of triammonium bis(*O*-phospho-L-serinate) trihydrate

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Received 26 April 2006
Accepted 20 June 2006

The X-ray diffraction pattern obtained for a crystal of triammonium bis(*O*-phospho-L-serinate) trihydrate at 100 K displays the presence of weak superstructure reflections with odd *l* indices. Omission of the superstructure reflections leads to orthorhombic Laue symmetry. The structure may be solved and refined in the space group $P2_12_12_1$ as an average structure omitting the weak reflections. The model reveals the presence of *O*-phospho-L-serinate monoanions, ammonium cations and partly disordered water molecules. The structure solution for the whole data set could be obtained only in the space group $P2_1$. There are two monoanions and two dianions of *O*-phospho-L-serinate per asymmetric unit, as well as six ordered ammonium cations and six water molecules.

1. Introduction

Elucidation of the nature of interactions of phosphorylated amino acids with cations would aid in understanding ion channel functions (Roman-Bravo *et al.*, 2004). It seems that such interactions are responsible for the highly selective transport of metal ions through ion channels. In the field of structural features depending on the environment of the phosphorylated amino acids, a number of X-ray crystal structures of potassium, sodium and ammonium salts of *O*-phosphoamino acids (L and DL forms) were investigated. It was found that there is no relationship between the ionization state of *O*-phosphoamino acids, especially *O*-phosphothreonine (PThr), and their conformations in the same cation environment (Bryndal & Lis, 2006). The aggregation of *O*-phosphoamino acid ions depends on a combination of O—H···O and N—H···O hydrogen bonds involving phosphate, carboxyl and ammonium groups. Usually, double layers of *O*-phosphoamino acid ions linked by N—H···O hydrogen bonds are formed, whereas the linkage by O—H···O hydrogen bonds generate chains or dimers. The presence of disordered solvent molecules or cations in some structures of *O*-phosphoamino acids results in an extensive hydrogen-bonding network (Bryndal *et al.*, 2003, 2004; Bryndal & Lis, 2006). On the other hand, weak superstructure reflections possibly connected with the hypersymmetry phenomenon were recorded for two other structures: the magnesium salt of L-PTyr and the dipotassium salt of L-PThr (Bryndal *et al.*, unpublished data).

We present here the structure solutions of triammonium bis(*O*-phospho-L-serinate) trihydrate and refinements that could be obtained for the data set with and without weak superstructure reflections. Differential scanning calorimetry (DSC) studies for this compound are described in §6.

doi:10.1107/S0108768106023573

Table 1
Crystal, data collection and refinement data for the average structure and whole data set structure solution of the title salt at 100 K.

	Whole data set	Average structure
Crystal data		
Chemical formula	$C_3H_7NO_6P\cdot C_3H_6NO_6P\cdot 3H_4N\cdot 3H_2O$	$C_6H_{13}N_2O_{12}P_2\cdot 3H_4N\cdot 3H_2O$
M_r	475.30	475.30
Cell setting, space group	Monoclinic, $P2_1$	Orthorhombic, $P2_12_12_1$
Temperature (K)	100 (2)	100 (2)
a, b, c (Å)	7.851 (3), 21.976 (5), 11.332 (4)	7.851 (3), 21.976 (5), 5.666 (2)
α, β, γ (°)	90.00, 90.00 (3), 90.00	90.00, 90.00, 90.00
V (Å^3)	1955.2 (11)	977.6 (6)
Z	4	2
D_x (Mg m^{-3})	1.615	1.615
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.31	0.31
Crystal form, colour	Plate, colourless	Plate, colourless
Crystal size (mm)	0.40 × 0.18 × 0.10	0.40 × 0.18 × 0.10
Data collection		
Diffractometer	Xcalibur PX	Xcalibur PX
Data collection method	ω	ω
Absorption correction	Numerical	Numerical
$T_{\min}$	0.888	0.888
$T_{\max}$	0.970	0.970
No. of measured, independent and observed reflections	49 395, 16 051, 9264	24 631, 5369, 4404
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.043	0.046
$\theta_{\max}$ (°)	38.6	38.5
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.087, 1.15	0.039, 0.103, 1.02
No. of reflections	16 051 reflections	5369 reflections
No. of parameters	619	184
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.004	<0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.41, −0.45	0.36, −0.42
Absolute structure	Flack (1983)	Flack (1983)
Flack parameter	0.03 (5)	−0.16 (8)

Computer programs used: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 1995–2003), *SHELXS*97 and *SHELXL*97 (Sheldrick, 1997), *DIAMOND* (Brandenburg & Putz, 2005).

Table 2
Temperature dependence of cell constants for the title crystal.

Temperature (K)	100	150	200	250
a (Å)	7.851 (3)	7.851 (2)	7.855 (2)	7.861 (2)
b (Å)	21.976 (5)	22.048 (4)	22.105 (4)	22.163 (4)
c (Å)	11.332 (4)	11.325 (3)	11.317 (3)	11.315 (3)
β (°)	90.00 (3)	90.04 (2)	90.05 (2)	90.06 (2)
V (Å^3)	1955.2 (11)	1960.3 (8)	1965.0 (8)	1971.3 (8)

Table 3
Statistical data for the diffraction pattern at 100 K.

	‘Strong’ reflections	‘Weak’ reflections	All reflections
No. of reflections	24 660	24 735	49 395
No. of independent reflections	8007	8044	16051
No. of observed ($I > 2\sigma$) reflections	6373	2891	9264
Average I/σ	22.53	4.69	18.05

2. Experimental

The crystals of the title compound were obtained by two methods. The first involves the reaction between L-PSer and ammonium hydrogen carbonate in aqueous solution in the molar ratio 1:1. Colourless plate crystals were grown from the solution by slow evaporation over a period of several months. The second method consists of the recrystallization of diammonium *O*-phospho-L-serinate dihydrate. The diammonium salt was prepared by reaction of L-PSer with ammonium hydrogen carbonate in aqueous solution in the molar ratio 1:2 (Bryndal, 2004). Diffraction data were collected on an Xcalibur PX κ-geometry diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The instrument was equipped with Oxford Cryosystems low-temperature devices. Roentgenographic measurements were carried out at room temperature and at 100 K, as well as at 150, 200 and 250 K. Crystal, data collection and refinement data for the average and whole data set structure solutions of the ammonium salt of L-PSer at 100 K are given in Table 1.[1] The temperature dependence of the cell constants for the title compound is shown in Table 2. The relevant statistical data describing the diffraction pattern at 100 K are given in Table 3.

The DSC measurement was carried out on a Perkin–Elmer DSC 7 device for a 9.770 mg sample with scanning rates of 10.0 and 20.0 K min^{-1}.

3. Structure solution and first refinement stages

The intensity distribution in the diffraction pattern suggested an orthorhombic crystal system. All reflections with odd l indices were weak. The observed systematic absences for the whole experimental data set led to space group $P2_12_12_1$. We were not able to obtain any structure solution in any of the space groups of the orthorhombic system. When the weak reflections were omitted, which meant halving the c cell constant, it was possible to obtain a chemically reasonable structure solution in space group $P2_12_12_1$ using direct methods (Table 1, right-hand column). The resulting structure model can be called the average structure.

We decided to attempt to find the crystal structure solution taking into consideration all the diffraction data. Additional measurements were carried out on two different crystals to check if a similar characteristic diffraction pattern, resulting in analogous diffraction data, could be obtained. In the first stage of the whole data-set structure solution it was assumed that

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: GP5011). Services for accessing these data are described at the back of the journal.

Table 4
$R_{\rm int}$ values for orthorhombic as well as monoclinic (three different unique axis choices) crystal system assumptions at 100 K.

The data are provided for three reflection sets: all reflections (denoted as 'A'), weak superstructure reflections ('W') and the data set with omitted weak superstructure reflections ('S').

Monoclinic									Orthorhombic		
a axis unique			*b* axis unique			*c* axis unique					
A	W	S	A	W	S	A	W	S	A	W	S
0.062	0.400	0.054	0.0490	0.220	0.0364	0.062	0.399	0.053	0.0630	0.409	0.0579

the structure is orthorhombic. As it was possible to obtain the average solution in the space group $P2_12_12_1$, the point group 222 was taken into consideration. This possibility could occur as a result of pseudotranslation along the *c* direction.

A unit cell with doubled *c* constant in comparison with the average structure was chosen. The coordinates of non-H atoms were taken from the average structure solution and transformed accordingly. However, the transformation was not direct, only approximate, so as to avoid singular matrix during refinement. The atoms not building up the PSer monoanions (L enantiomers) were all treated as N atoms. Isotropic displacement parameters were assumed. Thus, the introductory models in all space groups of 222 point symmetry were obtained for further refinement. However, none of these refinements gave successful results. Therefore, the specific symmetry in the diffraction pattern could not be elucidated by any model based on pseudotranslational symmetry in the crystal structure. This led us to the conclusion that the crystal system should be changed to the lower-symmetry monoclinic setting.

In the monoclinic system a unique axis along the largest cell constant was chosen using the lowest $R_{\rm int}$ criterion (Table 4) and the structure was solved in the space group $P2_1$ using direct methods. The model obtained contained four P atoms in the asymmetric unit. All non-H atoms were localized in the E map. The absolute configuration was assumed knowing that the substrate L-amino acid was enantiopure. The C- and N-bonded H atoms in the anions were positioned geometrically. At this stage the occurrence of H atoms bonded to O atoms of two phosphate groups (P1 and P2 groups) in the difference-Fourier map made it possible to distinguish between the two types of L-PSer anions: monoanions and dianions. The assignment was confirmed by the P—O bond-length differences. There are two monoanions and two dianions of PSer in the asymmetric unit. From electrostatic considerations this means that among the non-H atoms not involved in building up the anions there are six N atoms from the ammonium cations. The remaining atoms should be O atoms from water molecules.

All non-H atoms were assigned anisotropic displacement parameters. The model was refined using the full-matrix method in the *SHELXL97* program (Sheldrick, 1997). Restraints setting the N—H bond lengths in the PSer anions and the ammonium cations as well as O—H bond lengths in water molecules and the hydrogen phosphate groups were applied. In the difference-Fourier map, the highest peak lies in the middle of the P—O bond. The choice of monoclinic crystal system and the unique axis was verified by measurement of the cell constants as a function of temperature (Table 2). The data collected during each measurement led to a similar structure solution when the above-described considerations were applied.

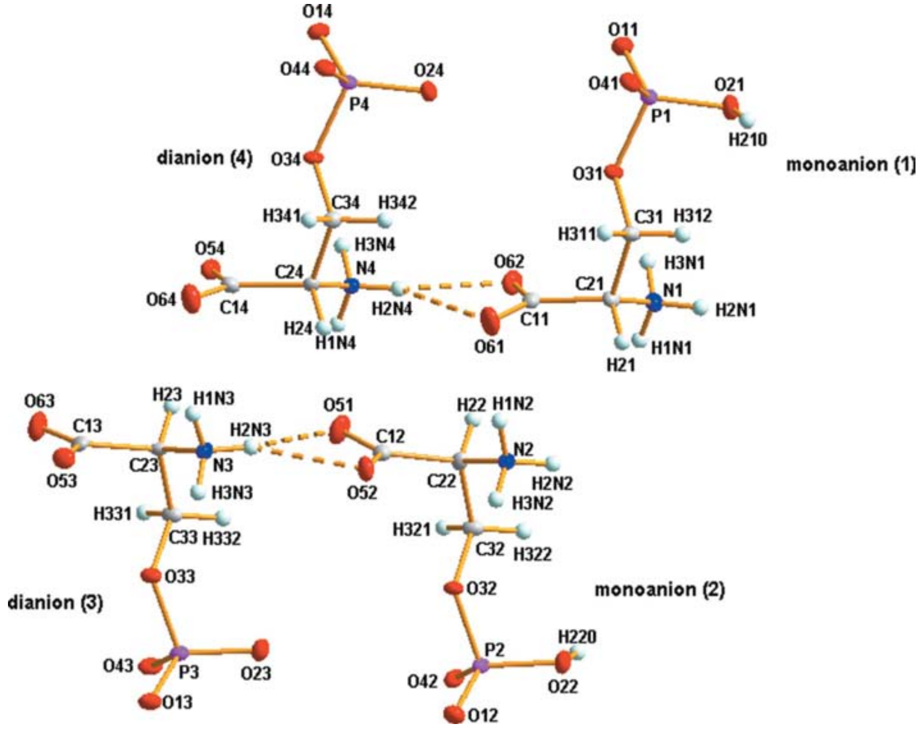

Figure 1
The PSer anions from the asymmetric unit, with the atom-labelling scheme, for the whole data set structure solution. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are depicted with dashed lines. The PSer monoanions and dianions are labelled with numbers used subsequently in the text.

4. Last stages of refinement and structure description

The asymmetric unit contains two monoanions [(1) and (2)] and two dianions of PSer [(3) and (4)] (Fig. 1). The geometric parameters summarized in Table 5 are in accordance with published data (Putkey & Sundaralingam, 1970; Bryndal & Lis, 2006). The analysis of the atom coordinates

Table 5
Selected geometric parameters for the title salt (whole data set solution) at 100 K.

Parameter	$n = 1$	$n = 2$	$n = 3$	$n = 4$
Bond lengths (Å)				
Pn—O1n	1.488 (2)	1.488 (2)	1.502 (2)	1.502 (2)
Pn—O4n	1.508 (2)	1.518 (2)	1.529 (2)	1.526 (2)
Pn—O2n	1.556 (2)	1.552 (2)	1.524 (2)	1.528 (2)
Pn—O3n	1.620 (2)	1.618 (2)	1.628 (2)	1.625 (2)
C21—Nn	1.489 (3)	1.493 (3)	1.486 (3)	1.492 (2)
Bond angles (°)				
O1n—Pn—O4n	117.2 (3)	116.8 (3)	114.3 (3)	114.2 (3)
O1n—Pn—O2n	111.0 (3)	111.4 (3)	114.5 (3)	114.4 (3)
O4n—Pn—O2n	109.4 (3)	104.7 (3)	109.9 (3)	110.2 (3)
O1n—Pn—O3n	104.6 (3)	107.8 (3)	103.4 (3)	103.4 (3)
O4n—Pn—O3n	108.0 (3)	107.8 (3)	107.3 (3)	106.8 (3)
O2n—Pn—O3n	105.9 (3)	106.0 (3)	106.8 (3)	107.0 (3)

proved that they are apparently related by some symmetry operations. Taking into consideration these operations the structure solution could not be reduced to orthorhombic symmetry. The operations are very accurate and a non-crystallographic twofold symmetry axis going through (−0.248, 0.675, 0) could be proposed. Similar symmetry elements are described by Zorky (1996) as a mark of hypersymmetry. In terms of Zorky's theory the crystal structure is a polysystem one. In order to describe it properly the theory should be generalized for heteromolecular structures.

The PSer monoanions form double chains of $P2_1$ symmetry along the *a* axis. The chains are not connected directly by hydrogen bonds; however, they form distinguishable layers perpendicular to the *c* axis. Within each chain characteristic motifs from Bernstein's considerations (Bernstein *et al.*, 1995) are present: $C(7)$ subchains as well as $R_3^2(13)$ rings. A similar analysis was performed recently for L-serine crystal structures under different pressures by Moggach *et al.* (2005).

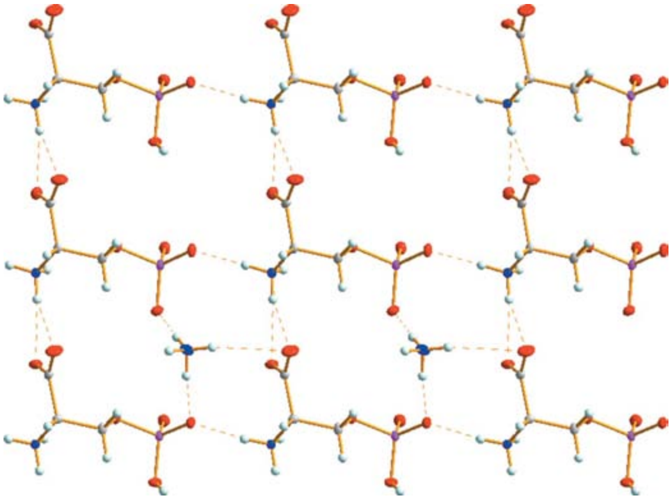

Figure 2
The PSer anionic layer in the whole data set crystal structure; view along [010] (dashed lines denote hydrogen bonds).

Table 6
Hydrogen-bonding geometry (Å, °) for the title salt (whole data set solution).

D—H···A	D—H	H···A	D···A	D—H···A
O21—H210···O3W^{i}	0.84	1.74	2.565 (2)	166
N1—H1N1···O41$^{\mathrm{ii}}$	0.91	1.87	2.777 (2)	178
N1—H2N1···O54$^{\mathrm{iii}}$	0.91	2.19	2.992 (2)	147
N1—H2N1···O64$^{\mathrm{iii}}$	0.91	2.28	3.118 (3)	152
N1—H3N1···O12$^{\mathrm{iv}}$	0.91	1.95	2.768 (2)	149
O22—H220···O1W^{iii}	0.84	1.74	2.566 (2)	170
N2—H1N2···O42$^{\mathrm{v}}$	0.91	1.87	2.777 (2)	174
N2—H2N2···O53$^{\mathrm{iii}}$	0.91	2.16	2.992 (3)	152
N2—H2N2···O63$^{\mathrm{iii}}$	0.91	2.33	3.140 (3)	149
N2—H3N2···O11$^{\mathrm{vi}}$	0.91	1.95	2.751 (2)	146
N3—H1N3···O43$^{\mathrm{v}}$	0.91	1.87	2.770 (2)	172
N3—H2N3···O52	0.91	2.25	3.064 (2)	149
N3—H2N3···O51	0.91	2.33	3.164 (3)	152
N3—H3N3···O14$^{\mathrm{ii}}$	0.91	2.00	2.794 (2)	145
N4—H1N4···O44$^{\mathrm{viii}}$	0.91	1.87	2.777 (2)	175
N4—H2N4···O62	0.91	2.23	3.070 (2)	154
N4—H2N4···O61	0.91	2.36	3.173 (2)	148
N4—H3N4···O13$^{\mathrm{viii}}$	0.91	2.01	2.781 (2)	142
N11—H11N···O52$^{\mathrm{viii}}$	0.91	1.92	2.820 (3)	170
N11—H21N···O43$^{\mathrm{viii}}$	0.91	1.99	2.891 (3)	170
N11—H31N···O12$^{\mathrm{viii}}$	0.91	1.98	2.831 (3)	160
N11—H41N···O34$^{\mathrm{ii}}$	0.91	2.24	3.098 (3)	160
N21—H12N···O11$^{\mathrm{x}}$	0.91	1.99	2.840 (3)	150
N21—H22N···O24$^{\mathrm{x}}$	0.91	1.99	2.876 (3)	160
N21—H32N···O62$^{\mathrm{ii}}$	0.91	1.92	2.824 (3)	170
N21—H42N···O33$^{\mathrm{ix}}$	0.91	2.28	3.125 (3)	150
N31—H13N···O13$^{\mathrm{ix}}$	0.91	1.83	2.738 (3)	170
N31—H23N···O53$^{\mathrm{viii}}$	0.91	1.94	2.827 (3)	160
N31—H33N···O31$^{\mathrm{ii}}$	0.91	2.38	3.103 (3)	140
N31—H33N···O62$^{\mathrm{ii}}$	0.91	2.50	3.028 (3)	120
N31—H43N···O24$^{\mathrm{ii}}$	0.91	1.89	2.794 (3)	170
N41—H14N···O54$^{\mathrm{ii}}$	0.91	1.92	2.819 (3)	170
N41—H24N···O14$^{\mathrm{x}}$	0.91	1.84	2.737 (3)	170
N41—H34N···O32$^{\mathrm{ix}}$	0.91	2.36	3.073 (3)	140
N41—H44N···O23$^{\mathrm{ix}}$	0.91	1.90	2.804 (3)	170
N51—H15N···O42	0.91	1.86	2.748 (3)	160
N51—H15N···O2W	0.91	2.61	3.151 (3)	120
N51—H25N···O5W	0.91	1.92	2.813 (3)	170
N51—H35N···O51$^{\mathrm{ii}}$	0.91	2.60	3.454 (3)	160
N51—H45N···O23	0.91	1.78	2.695 (3)	180
N61—H16N···O41$^{\mathrm{ii}}$	0.91	1.85	2.764 (3)	170
N61—H26N···O2W	0.91	1.91	2.804 (3)	160
N61—H36N···O61	0.91	2.57	3.396 (3)	150
N61—H46N···O24$^{\mathrm{ii}}$	0.91	1.84	2.702 (3)	160
O1W—H101···O43	0.86	1.87	2.727 (2)	170
O1W—H102···O4W	0.86	1.86	2.725 (3)	170
O2W—H201···O61$^{\mathrm{ii}}$	0.86	1.88	2.724 (3)	170
O2W—H202···O42	0.86	2.16	2.813 (2)	130
O2W—H202···O1W^{iii}	0.86	2.62	3.252 (3)	130
O3W—H301···O44	0.86	1.87	2.718 (2)	170
O3W—H302···O6W^{ii}	0.86	1.89	2.746 (3)	170
O4W—H401···O63	0.86	1.85	2.685 (3)	160
O4W—H402···O41$^{\mathrm{xi}}$	0.86	2.07	2.803 (2)	140
O5W—H501···O51	0.86	1.92	2.755 (3)	160
O5W—H502···O44$^{\mathrm{ii}}$	0.86	1.94	2.764 (2)	160
O6W—H601···O64	0.86	1.86	2.705 (3)	160
O6W—H602···O23$^{\mathrm{v}}$	0.86	1.95	2.770 (2)	160

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

The PSer dianions form double chains with pairs of anions related by non-crystallographic symmetry operations that consist of rotation and translation. It should be noted that individual chains have no pseudosymmetry elements.

According to the notation of Bernstein *et al.* (1995), within the chains $C(7)$ subchains and $R_3^3(13)$ rings are distinguishable, similar to those described for the PSer monoanions. The chains form layers perpendicular to the *c* axis similar to those in the monoanionic sublattice (Fig. 2). Analysis of monoanion–dianion contacts reveals that the layers are interconnected by hydrogen bonds involving H atoms from protonated amino groups of one layer and O atoms from carboxylate groups of the second layer (Fig. 3*a*). In each such contact each H atom from the protonated amino group participates in a bifurcated hydrogen bond in which two carboxylate O atoms are acceptors. Thus, a new structural motif is formed as monoanionic–dianionic layers perpendicular to *b*. Between these layers the channels are formed which contain ammonium cations and water molecules interconnected by hydrogen bonds and involved in hydrogen bonds with the PSer anions. The basic geometrical data for the hydrogen bonds are shown in Table 6.

5. Average structure solution

The average structure solution includes non-H atoms constituting one PSer anion (L enantiomer). Three other maxima were interpreted as two O atoms from two water molecules and one N atom from one ammonium cation. One water molecule was treated as disordered over two O-atom positions [the occupation factors are 0.56 (4) and 0.44 (4) for O81 and O82, respectively]. In order to account for the presence of two kinds of PSer anions it was necessary to introduce occupational disorder concerning the remaining ordered water molecule and an ammonium cation (Fig. 4). When the site is occupied by the water molecule there exists a PSer monoanion hydrogen bonded through the H atom protonating the phosphate group. On the other hand, when this site is occupied by the ammonium cation, a PSer dianion is present and is involved in an N—H···O hydrogen bond as an acceptor through the phosphate group. Therefore, it was necessary to assign the H atom protonating the PSer phosphate group position half occupancy. During average structure refinement, restraints were used to set the N—H and H···H distances in ammonium cations.

The average structure solution contains one PSer anion (which is a monoanion or a dianion depending on whether the site with occupational disorder is occupied by one ammonium cation or one water molecule), one ordered ammonium cation and one ordered water molecule in the asymmetric unit

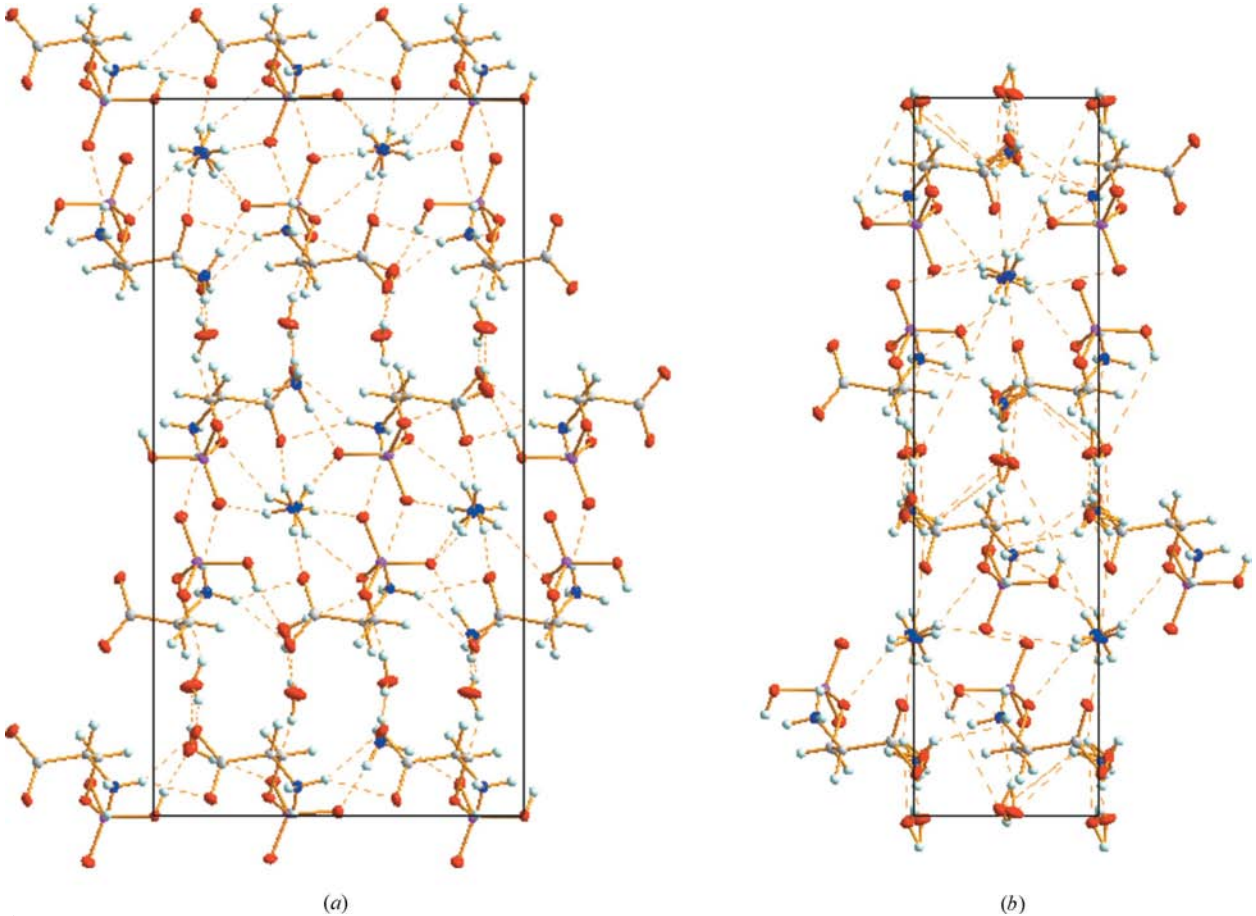

Figure 3
The crystal structure packing (view along [100]; dashed lines denote hydrogen bonds): (*a*) whole data set solution; (*b*) average solution. For the average solution, for clarity, only ammonium cations are drawn at sites displaying occupational disorder. Displacement ellipsoids are drawn at the 50% probability level.

(Fig. 4). In the PSer anion, the torsion angles O2—P—O3—C3 and P—O3—C3—C2 are 58.8 (1)° and −163.7 (1)°, respectively. The crystal structure consists of PSer anionic layers perpendicular to the *c* axis (Figs. 3*b* and 5). The channels between the layers contain ammonium cations and water molecules. The structure is stabilized by N—H···O and C—H···O hydrogen bonds.

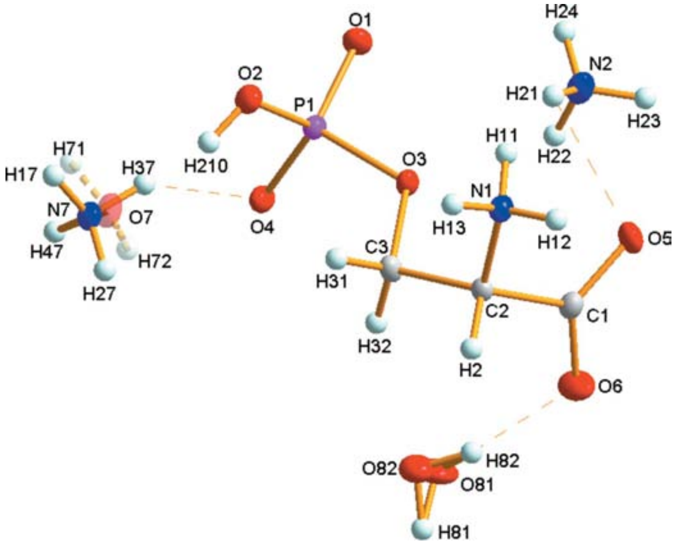

Figure 4
The asymmetric unit, with the atom-labelling scheme, for the average structure solution of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are depicted with dashed lines. The occupational disorder of one site switching between an ammonium cation and a water molecule, as well as the disordered H atom protonating the anion phosphate group, are indicated with different transparency.

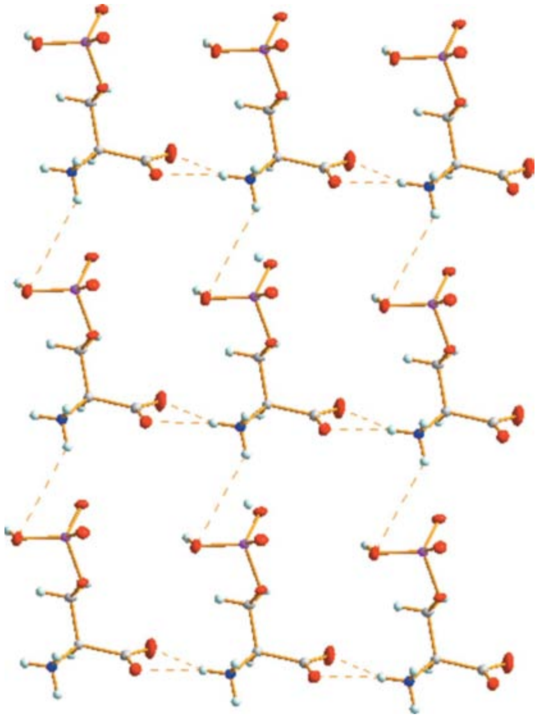

Figure 5
The PSer anionic layer formed in the average crystal structure packing (view along [001]; dashed lines denoted hydrogen bonds). All ammonium cations and water molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

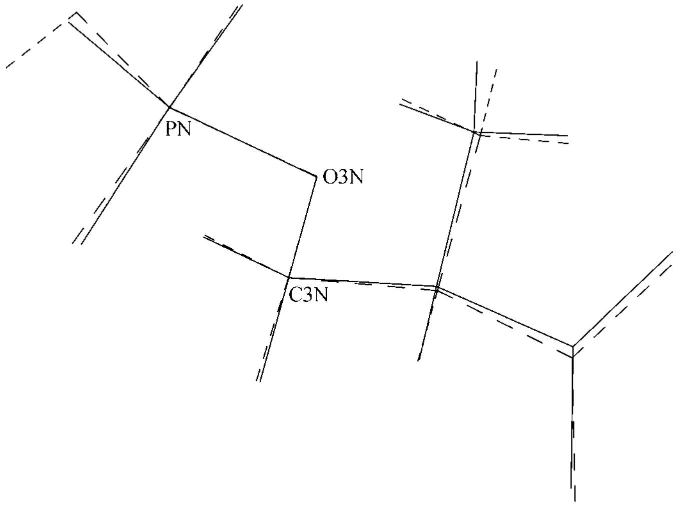

Figure 6
An overlap diagram of monoanion (2) and dianion (3) of PSer. The fitted atoms are labelled.

The average structure was easy to obtain because of the similarity in the conformations of the PSer monoanions and dianions (Fig. 6). As the most significant difference between these anions lies in the presence of an acidic H atom and the P—O bond lengths, it was possible to neglect the presence of two anionic sublattices in the space group $P2_12_12_1$.

6. Additional physicochemical measurements

For some L-PThr salts first-order phase transitions were detected (Bryndal, unpublished data). The weak superstructure reflections present in the diffraction pattern for the triammonium bis(*O*-phospho-L-serinate) trihydrate crystal allow the possibility that the structure could exist in a higher-symmetry form. If the energy barrier between two configurations – lower and higher symmetry – is low enough, a phase transition at higher temperatures could be expected (Igartua *et al.*, 1999). In order to check this possibility, a DSC measurement was carried out in the temperature range 77–298 K; in the resulting diagram no peaks or slopes as a mark of possible phase transitions could be noted.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Brandenburg, K. & Putz, H. (2005). *DIAMOND*, Release 3.0c. Crystal Impact GbR, Bonn, Germany.
Bryndal, I. (2004). PhD thesis, University of Wroclaw, Poland.
Bryndal, I. & Lis, T. (2006). *Z. Kristallogr.* **221**, 139–149.
Bryndal, I., Picur, B. & Lis, T. (2003). *J. Mol. Struct.* **647**, 295–310.
Bryndal, I., Picur, B. & Lis, T. (2004). *Z. Kristallogr.* **219**, 38–46.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Igartua, J. M., Aroyo, M. I., Kroumova, E. & Perez-Mato, J. M. (1999). *Acta Cryst.* B**55**, 177–185.

Moggach, S. A., Allan, D. R., Morrison, C. A., Parsons, S. & Sawyer, L. (2005). *Acta Cryst.* B**61**, 58–68.

Oxford Diffraction (1995–2003). *Xcalibur PX Software – CrysAlis CCD* and *CrysAlis RED*. Version 1.171. Oxford Diffraction Poland, Wrocław, Poland.

Putkey, E. F. & Sundaralingam, M. (1970). *Acta Cryst.* B**26**, 782–789.

Roman-Bravo, P., Lopez-Cardoso, M. & Garcia, P. G. (2004). *Chem. Commun.* **17**, 1940–1941.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Gőttingen, Germany.

Zorky, P. N. (1996). *J. Mol. Struct.* **374**, 9–28.