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Structure of dihydroxyacetone phosphate dimethyl acetal, a stable dihydroxyacetone phosphate precursor, in the crystalline state

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Abstract—Crystal and molecular structures of four different salts of a dihydroxyacetone phosphate (DHAP) precursor, its dimethyl acetal [2,2-dimethoxy-1,3-propanediol phosphate, $C_5H_{13}O_7P$, $(MeO)_2$DHAP]: $(cha)_2[(MeO)_2DHAP]\cdot H_2O$ (**6a**), $(cha)[(MeO)_2DHAP]$ (**6b**), $Na_2[(MeO)_2DHAP]\cdot 5.75H_2O$ (**6c**) and $K_2[(MeO)_2DHAP]\cdot H_2O$ (**6d**), along with the cyclohexylammonium (cha) salt of its phenyl ester $(cha)[(MeO)_2DHAP(Ph)]$ (**6e**) are described. In the $(MeO)_2$DHAP mono- and dianions, slightly different orientation of the phosphate group in relation to the acetal carbon atom is observed, with a delicate tendency of phosphate group to be located *antiperiplanar* in the monoanions and *anticlinal* in the dianions. The 2,2-dimethoxy-1,3-propandiol moiety, $(MeO)_2$DHA, seems to be very rigid and its conformation is independent of phosphorylation, the ionization state of the inserted phosphate group and its additional substitution. The overall structures of the cyclohexylammonium (**6a**,**b**) and potassium salts (**6d**) have a double-layered architecture, while the sodium cation network in **6c** forms the system of channels, which are filled up with the $[(MeO)_2DHAP]^{2-}$ ions. The different architectures of **6c** and **6d** crystals result from the different ways in which the relevant dianions coordinate to sodium and potassium ions and affect also the hydrogen bonding system observed in **6c** and **6d** crystals.
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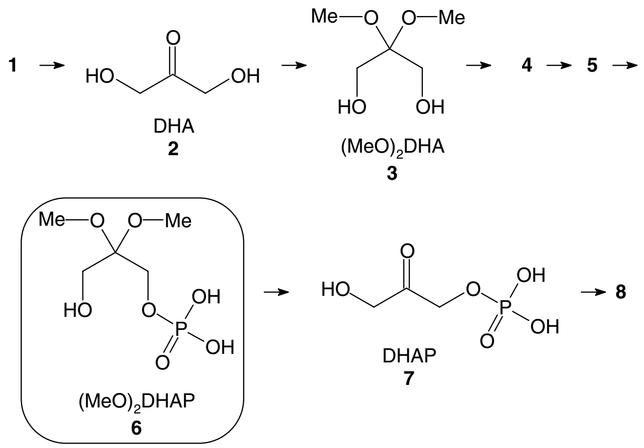
Keywords: Sugar phosphates; Dihydroxyacetone phosphate (DHAP) precursor; Dihydroxyacetone phosphate (DHAP) dimethyl acetal; Sodium, potassium coordination; O–H···O, N–H···O, C–H···O hydrogen bonds

1. Introduction

The crystal structure study of a stable dihydroxyacetone phosphate (DHAP) precursor, $(MeO)_2$DHAP, was undertaken as a continuation of our previous papers on the structural characterization of intermediates in the chemical pathway leading from the simplest ketose, dihydroxyacetone, DHA (**2**, Scheme 1) to its phosphate ester, DHAP (**7**).



Scheme 1. Chemical pathway leading from DHA to DHAP.

Our interest in small sugars and their phosphate esters results from the importance of these compounds, especially the role that DHAP plays in living cells. DHAP is one of the most important biochemical intermediates and acts as a substrate for at least 18 different enzymes, including triosephosphate isomerase, glycerol-3-phosphate dehydrogenase, dihydroxyacetone phosphate acyltransferase and several types of aldolases.[1,2]

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DHAP-dependent aldolases have been commonly used in the synthesis of synthetic sugars and related chiral compounds on a preparative scale. They accept a broad spectrum of aldehydes, but all of them are very specific for DHAP (the application of DHAP-dependent aldolases in asymmetric organic synthesis has been the subject of a number of reviews[3–8]). Dihydroxyacetone phosphate plays a crucial role in the main metabolic pathways, such as gluconeogenesis, fructose metabolism, the synthesis of triacylglycerols and phospholipids, glycerophosphate shuttle, and finally in glycolysis.[1,2]

Because DHAP itself is unstable and expensive, the usual strategy for preparing this compound is the chemical synthesis of a stable precursor, which may be stored indefinitely and which may be easily hydrolyzed to DHAP. Several stable DHAP precursors have been reported.[9,10] DHAP dimethyl acetal, $(MeO)_2$DHAP (**6** in Scheme 1) described herein, which is converted in nearly quantitative yield into DHAP by acidic hydrolysis, seems to be the most interesting and attractive. $(MeO)_2$DHAP was first synthesized by Ballou and Fisher[11] in 1956 and that was the first preparation of a

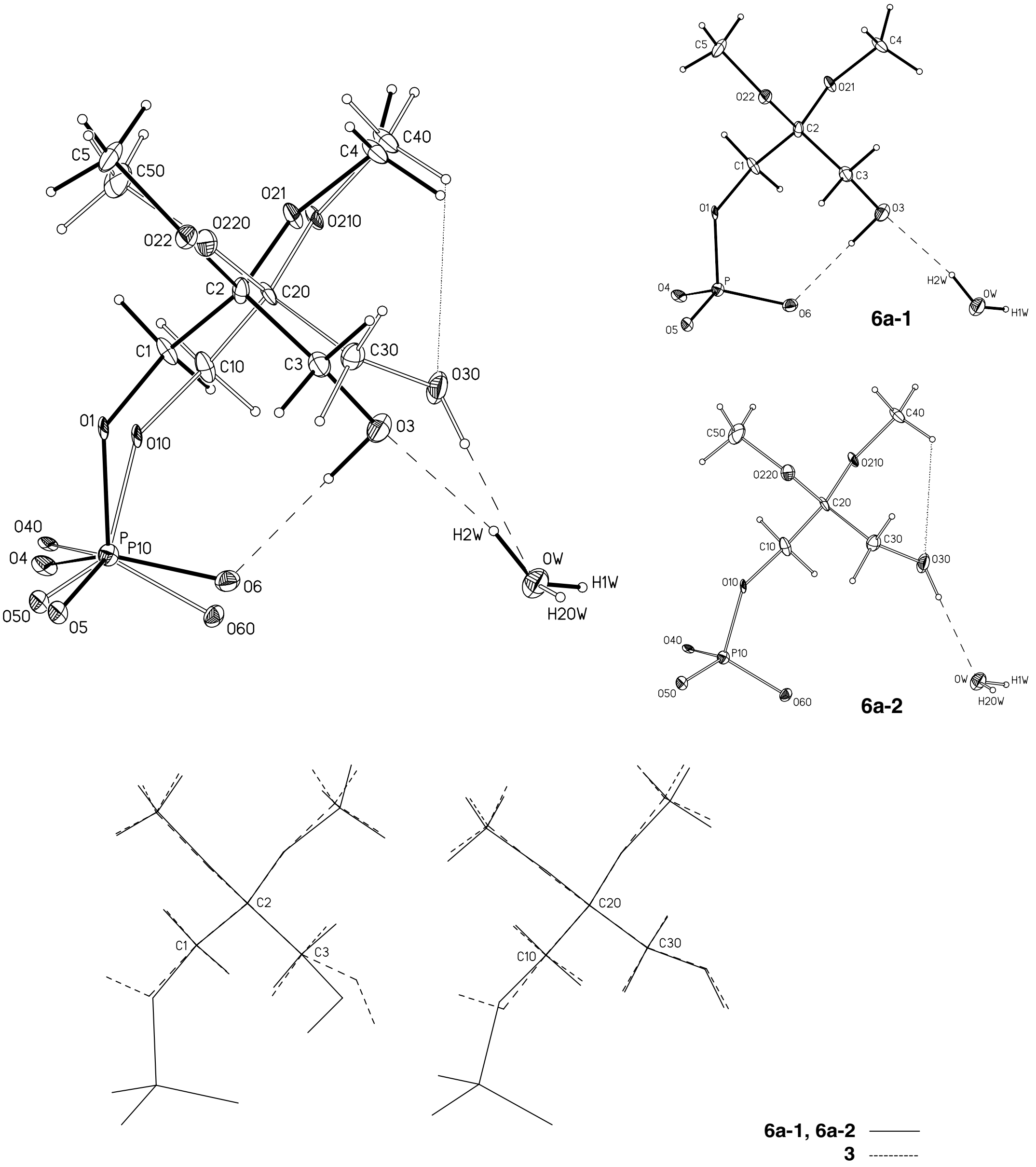

Figure 1. Top: the molecular structure and the atom-numbering scheme for the disordered $[(MeO)_2DHAP]^{2-}$ dianion in **6a** along with the separated anions: **6a-1** with s.o.f. = 0.548(10) (solid line) and **6a-2** with s.o.f. = 0.452(10) (open line). The O–H···O and C–H···O hydrogen contacts stabilizing the molecular structure are shown with dashed or dotted lines. Displacement ellipsoids are shown at 20% probability level. The H atoms are drawn as small circles of arbitrary radii. Bottom: the comparison of **6a-1** and **6a-2** molecular structures with $(MeO)_2$DHA (**3**); common reference points are the marked carbon atoms (C-1, C-2 and C-3).

stable DHAP precursor. The long and quite expensive synthesis requires the saponification and Pt-catalyzed hydrogenolysis of 3-acetoxy-2,2-dimethoxypropanol diphenylphosphate to obtain $(MeO)_2$DHAP. When carrying out this reaction, we have obtained **6e**, even when the catalyst amount and the reaction time has been extended (see Experimental section). Therefore, for our purposes we chose the synthetic procedure for **6** described by Ferroni et al.[10] and the conditions of **6**→**7** hydrolysis given by Ballou.[12] We then modified the DHA acetalization reaction[13] and isolated some additional intermediates, which will be described elsewhere. Recently, we have crystallized and determined the crystal and molecular structures of the compounds

Table 1. Principal interatomic distances (Å), valence angles (°) and torsion angles (°) in **6a**–**e** (standard deviations in parentheses)

	6a		**6b**	**6c**	**6d**	**6e**
	6a-1	**6a-2**				
Bond lengths						
P–O-1	1.638(5)		1.5961(10)	1.6207(6)	1.642(2)	1.608(2)
P–O-4	1.518(5)		1.5074(10)	1.5346(6)	1.517(2)	1.474(2)
P–O-5	1.515(5)		1.4929(10)	1.5221(6)	1.515(2)	1.491(2)
P–O-6	1.526(5)		1.5671(10)	1.5194(6)	1.514(2)	1.602(2)
O-1–C-1	1.443(5)		1.442(2)	1.4243(9)	1.425(3)	1.444(3)
O-21–C-2	1.420(6)		1.409(2)	1.4263(9)	1.403(3)	1.404(3)
O-21–C-4	1.438(7)		1.429(2)	1.4433(9)	1.430(4)	1.431(3)
O-22–C-2	1.414(6)		1.413(2)	1.4162(9)	1.431(3)	1.422(3)
O-22–C-5	1.430(7)		1.426(2)	1.4281(10)	1.438(4)	1.425(3)
O-3–C-3	1.420(7)		1.413(2)	1.4193(9)	1.422(3)	1.424(3)
C-1–C-2	1.519(6)		1.526(2)	1.5324(10)	1.538(4)	1.499(4)
C-2–C-3	1.519(7)		1.526(2)	1.5311(10)	1.533(4)	1.506(4)
Valence angles						
O-1–P–O-4	107.5(5)		109.19(6)	106.72(3)	107.05(12)	111.16(11)
O-1–P–O-5	102.6(5)		105.42(6)	102.82(3)	100.85(11)	104.29(11)
O-1–P–O-6	105.9(4)		106.06(6)	108.19(3)	107.76(11)	103.90(10)
O-4–P–O-5	113.7(5)		116.78(5)	111.40(3)	112.29(12)	119.88(11)
O-4–P–O-6	112.6(6)		110.33(5)	112.46(3)	113.43(12)	106.19(11)
O-5–P–O-6	113.6(5)		108.45(6)	114.45(3)	114.30(12)	110.37(11)
C-1–O-1–P	118.1(5)		118.90(8)	119.67(5)	120.2(2)	119.6(2)
C-2–O-21–C-4	114.9(7)		115.56(11)	114.46(6)	115.7(2)	115.7(2)
C-2–O-22–C-5	115.3(7)		115.10(12)	116.42(6)	117.0(2)	115.3(2)
O-1–C-1–C-2	109.8(5)		108.41(11)	107.52(6)	110.0(2)	107.6(2)
O-21–C-2–O-22	111.1(6)		111.83(11)	110.86(6)	112.6(2)	111.0(2)
O-21–C-2–C-1	102.8(5)		102.61(11)	104.44(6)	103.2(2)	103.7(2)
O-22–C-2–C-1	114.0(7)		113.39(11)	113.75(6)	111.6(2)	113.0(2)
O-21–C-2–C-3	112.7(7)		113.47(11)	112.94(6)	114.7(2)	113.4(2)
O-22–C-2–C-3	104.0(6)		103.83(11)	104.36(6)	102.2(2)	103.0(2)
C-1–C-2–C-3	112.6(6)		112.05(12)	110.73(6)	112.9(2)	113.0(3)
O-3–C-3–C-2	111.4(6)		111.12(13)	109.66(6)	113.5(2)	108.2(2)
Torsion angles						
O-4–P–O-1–C-1	−74(1)	−61(1)	−52.75(12)	−61.64(6)	−61.2(2)	−54.5(2)
O-5–P–O-1–C-1	166(1)	178(1)	−178.97(10)	−178.97(5)	−178.8(2)	175.0(2)
O-6–P–O-1–C-1	46(1)	59(1)	66.13(12)	59.59(6)	61.1(2)	59.3(2)
P–O-1–C-1–C-2	−124(1)	−149(1)	−175.68(9)	−155.91(5)	135.0(2)	171.1(2)
C-4–O-21–C-2–O-22	62(2)	61(3)	63.32(15)	63.63(8)	69.2(3)	61.1(3)
C-4–O-21–C-2–C-1	−175(2)	−176(3)	−174.82(12)	−173.48(6)	−170.3(2)	−177.2(2)
C-4–O-21–C-2–C-3	−54(2)	−56(3)	−53.72(16)	−53.09(8)	−47.0(3)	−54.2(3)
C-5–O-22–C-2–O-21	55(2)	60(2)	56.19(15)	53.47(8)	42.2(3)	65.5(3)
C-5–O-22–C-2–C-1	−60(2)	−56(2)	−59.25(15)	−63.87(8)	−73.3(3)	−50.5(3)
C-5–O-22–C-2–C-3	177(2)	−178(2)	178.90(12)	175.34(6)	165.8(2)	−172.8(2)
O-1–C-1–C-2–O-21	−177(1)	−169(1)	−171.61(11)	−178.34(5)	178.7(2)	−176.6(2)
O-1–C-1–C-2–O-22	−57(1)	−48(1)	−50.82(16)	−57.34(8)	−60.2(3)	−56.3(3)
O-1–C-1–C-2–C-3	61(1)	70(1)	66.33(15)	59.81(7)	54.2(3)	60.1(3)
O-3–C-3–C-2–O-21	−62(1)	−44(2)	−49.22(16)	−60.63(8)	−45.5(3)	−53.3(3)
O-3–C-3–C-2–O-22	178(1)	−165(1)	−170.85(10)	178.87(6)	−167.6(2)	−173.3(2)
O-3–C-3–C-2–C-1	54(1)	71(1)	66.41(15)	56.09(8)	72.4(3)	64.4(3)

Only one value of each bond length and valence angle for **6a-1** and **6a-2** positions are given due to geometrical restraints applied by SAME instruction.

occurring on the first four steps of the investigated pathway (**1–4** in Schemes 1 and 3 in the Experimental section).[13,14] The results of the structural investigations on three polymorphs of dihydroxyacetone in the dimeric form, DHA-dimer (**1a–c**), as well as in monomeric form, DHA (**2**), along with its dimethyl acetal, (MeO)$_2$DHA (**3**), have been published recently.[13] The present paper concerns the structure of DHAP dimethyl acetal, (MeO)$_2$DHAP (**6**), the phosphate ester of **3**. We describe herein two cyclohexylammonium salts of **6** (**6a**,**b**) as well as the sodium (**6c**) and potassium (**6d**) salts along with the cyclohexylammonium salt of its phenyl ester. Thus, the geometry of (MeO)$_2$DHAP and (MeO)$_2$DHAP(Ph) anions in **6a–e** will be compared with that of the phosphate-free molecule, (MeO)$_2$DHA (**3**), and the influence of (MeO)$_2$DHAP ionization state, additional substitution of the phosphate group, the chemical environment of the anions, as well as the arrangement in crystal lattice, will be discussed.

Table 2. Geometry of proposed hydrogen bonds and close C–H···O contacts for **6a**,**b**,**e** (Å, °)

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
*(cha)$_2$[(MeO)$_2$DHAP]·H$_2$O (**6a**)*				
O-3–H-3···O-6	0.97(8)	1.81(8)	2.752(11)	164(7)
O-30–H-30···O-W	0.86(12)	1.94(12)	2.746(6)	156(9)
O-W–H-1W···O-6^{i}	0.81(4)	1.84(4)	2.651(9)	173(3)
O-W–H-1W···O-60^{i}	0.81(4)	1.90(4)	2.709(11)	170(3)
O-W–H-2W···O-3	0.87(10)	1.92(10)	2.772(4)	165(7)
O-W–H-20W···O-W^{ii}	0.90(6)	1.84(6)	2.737(5)	175(7)
N-1–H-1N···O-4	0.95(3)	1.81(3)	2.761(14)	177(3)
N-1–H-1N···O-40	0.95(3)	1.80(4)	2.74(2)	169(3)
N-1–H-2N···O-5^{iii}	0.91(3)	1.78(4)	2.69(2)	179(3)
N-1–H-2N···O-50^{iii}	0.91(3)	1.92(4)	2.83(2)	171(3)
N-1–H-3N···O-5^{iv}	0.92(3)	1.92(3)	2.829(10)	172(2)
N-1–H-3N···O-50^{iv}	0.92(3)	1.78(3)	2.704(12)	178(3)
N-2–H-4N···O-4	0.91	1.75	2.64(2)	168
N-2–H-4N···O-40	0.91	1.76	2.65(2)	168
N-2–H-5N···O-6^{iii}	0.91	1.95	2.78(2)	151
N-2–H-5N···O-60^{iii}	0.91	1.89	2.75(2)	156
N-2–H-6N···O-W^{iii}	0.91	2.05	2.929(11)	163
N-3–H-7N···O-4	0.91	2.03	2.92(3)	165
N-3–H-7N···O-40	0.91	2.06	2.91(3)	157
N-3–H-8N···O-6^{iii}	0.91	1.82	2.70(3)	163
N-3–H-8N···O-60^{iii}	0.91	1.77	2.68(3)	175
N-3–H-9N···O-W^{iii}	0.91	1.77	2.67(2)	171
C-40–H-40B···O-30	0.98	2.60	3.13(4)	114
C-24–H-24A···O-210^{v}	0.99	2.42	3.38(2)	164
C-26–H-26A···O-30^{v}	0.99	2.25	3.212(8)	165
C-31–H-31···O-30^{v}	1.00	2.45	3.435(11)	167
C-33–H-33A···O-210^{v}	0.99	2.54	3.52(2)	170
*(cha)[(MeO)$_2$DHAP] (**6b**)*				
O-3–H-3···O-6^{v}	0.82(2)	2.00(2)	2.806(2)	169(2)
O-6–H-6···O-4^{vi}	0.76(2)	1.79(2)	2.545(2)	175(2)
N–H-1N···O-4^{vii}	0.90(2)	1.94(2)	2.833(2)	170(2)
N–H-2N···O-5	0.91(2)	1.86(2)	2.765(2)	169(2)
N–H-3N···O-5^{viii}	0.88(2)	1.92(2)	2.793(2)	175(2)
C-12–H-12A···O-3^{ix}	0.96(2)	2.68(2)	3.504(2)	145(2)
C-14–H-14A···O-3^{ix}	0.98(2)	2.64(2)	3.508(2)	147(2)
C-15–H-15A···O-21^{x}	0.97(2)	2.64(2)	3.419(2)	137(2)
*(cha)[(MeO)$_2$DHAP(Ph)] (**6e**)*				
O-3–H-3···O-5^{x}	0.74(2)	1.97(3)	2.706(3)	170(3)
N–H-1N···O-5^{xi}	0.91	1.93	2.824(3)	167
N–H-2N···O-4	0.91	1.85	2.712(3)	158
N–H-3N···O-21^{v}	0.91	2.66	3.064(3)	108
N–H-3N···O-3^{v}	0.91	1.90	2.808(3)	176
C-3–H-3A···O-4^{x}	0.99	2.61	3.416(3)	139
C-50–H-50···O-22^{xii}	0.95	2.55	3.444(4)	156
C-16–H-16A···O-4	0.99	2.65	3.351(4)	128

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, -y+3, -z+1$; (iii) $x, y-1, z$; (iv) $-x+1, y-1/2, -z+3/2$; (v) $-x+1, -y+1, -z+1$; (vi) $-x+1, -y, -z+1$; (vii) $x, y+1, z$; (viii) $-x+1, y+1/2, -z+3/2$; (ix) $x, -y+3/2, z+1/2$; (x) $x, -y+1/2, z+1/2$; (xi) $x, -y+1/2, z-1/2$; (xii) $x+1, y, z$.

2. Results and discussion

Crystal **6b** is composed of $[(MeO)_2DHAP]^-$ monoanions and cyclohexylammonium cations (cha^+), while **6a**,**c** and **6d** consist of $[(MeO)_2DHAP]^{2-}$ dianions, cha^+ or metal cations (sodium, potassium) and water molecules. Crystal **6e** is made up of $[(MeO)_2DHAP(Ph)]^-$ and cha^+ ions. The asymmetric units of **6a–e** consist of one anion each and the other components (cations and water molecules) in amounts relevant to their molecular formulas.

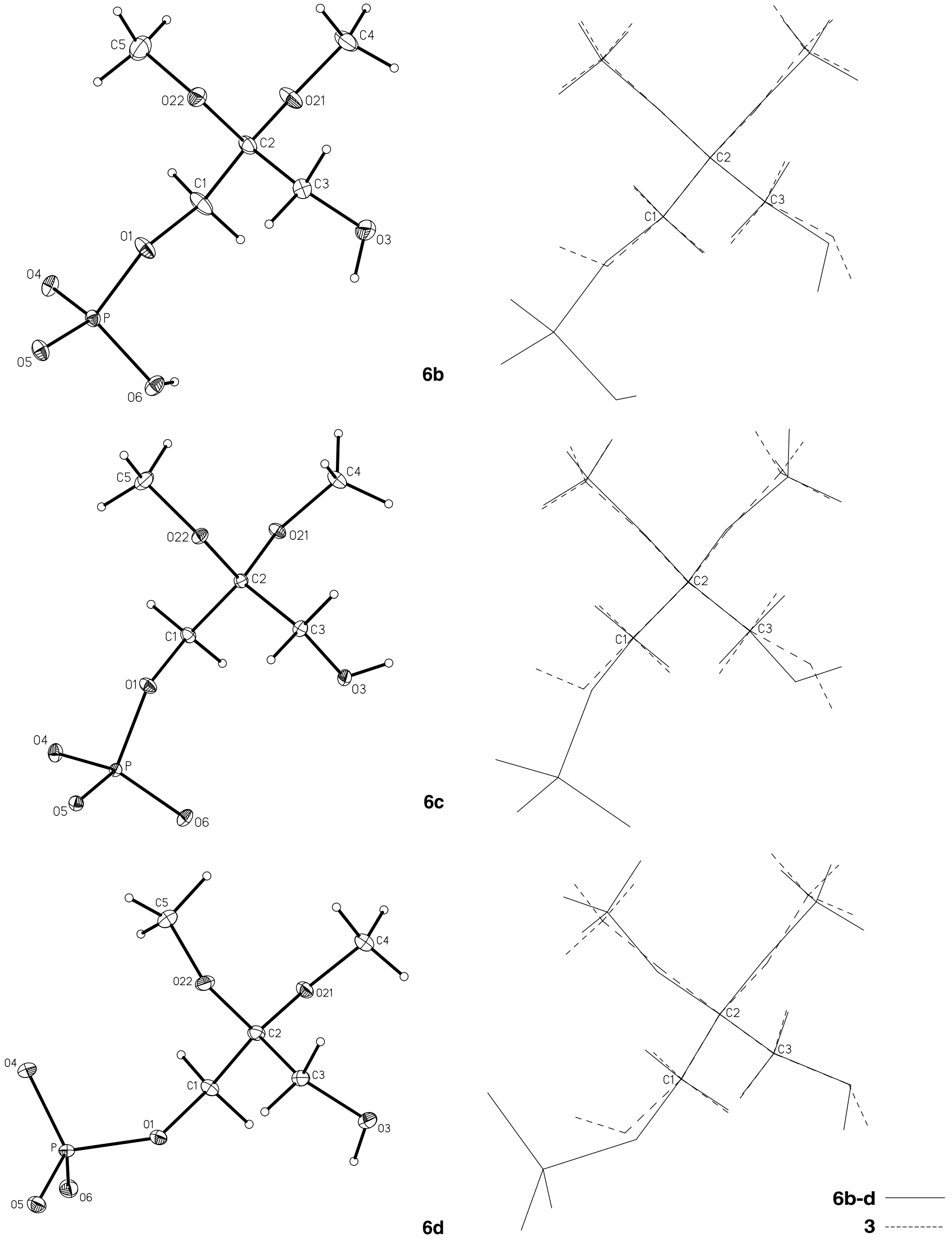

Figure 2. Left: the molecular structure and the atom-numbering scheme for the mono- or dianions: $[(MeO)_2DHAP]^-$ in **6b** and $[(MeO)_2DHAP]^{2-}$ in **6c** and **6d**. Displacement ellipsoids are shown at 30% probability level. The H atoms are drawn as small circles of arbitrary radii. Right: the comparison of the geometry of the respective anions with the geometry of $(MeO)_2DHA$ (**3**); the common reference points are the marked carbon atoms (C-1, C-2 and C-3).

2.1. Molecular geometry of the anions in 6a–e

The $[(MeO)_2DHAP]^{2-}$ anion in **6a** is disordered into two approximately equally occupied positions denoted as **6a-1**, with a site occupation factor (s.o.f.) of 0.548(10), and **6a-2** with a s.o.f = 0.452(10). Shown in Figure 1 are anions, **6a-1** and **6a-2**, which have different conformations with the main difference being the orientation of the phosphate group (P and P-10, respectively) in relation to the rest of the anion. The phosphate P atom in **6a-1** is oriented *anticlinal* (-*ac*) with relation to the C-2 atom and P-10 in **6a-2** is also oriented -*ac*, but very close to *ap* with respect to C-20 (for torsion angles see Table 1). The anion disorder is correlated with the disorder of water molecule, which occupies two different positions in the crystal and which forms two types of hydrogen bonds with the anions of different geometries and hydroxyl group orientations (Fig. 1). Different conformations of **6a-1** and **6a-2** are stabilized by different O–H···O hydrogen bonds. Especially interesting is the conformation observed in **6a-1** with a moderately strong intramolecular O-3–H-3···O-6 hydrogen bond formed between the hydroxyl and phosphate groups of the anion (see Table 2). In this case, the hydroxyl group acts as an acceptor of an additional intermolecular O-W–H-2W···O-3 bond from a water molecule with the same s.o.f. as for the **6a-1** anion. However, the O-30 hydroxyl group of **6a-2** is involved in intermolecular O-30–H-30···O-W hydrogen bond to the water molecule in the other site. It is possible that the molecular structure of **6a-2** anion is stabilized by intramolecular C-40–H-40B···O-30 hydrogen contact, also shown in Figure 1.

The overall structure of the anions in the remaining crystals reveals great similarities. The conformation of the $(MeO)_2DHAP$ mono- and dianions in **6b–d**, as well as that observed in the anion of the phenyl derivative, $[(MeO)_2DHAP(Ph)]^-$ (**6e**), is very similar. The hydroxyl groups are oriented *ap* in relation to O-22 in all **6b–e** anions, similar to that observed in **6a-1**, **6a-2** and **3**. The main difference within the **6b–e** series lies in slightly dissimilar orientations of the phosphate group with relation to the rest of the anion ($(MeO)_2DHA$ moiety). The molecular structures of the anions in **6b–e** along with the comparison of their geometry with the geometry of $(MeO)_2DHA$ (**3**) are shown in Figures 2 and 3. Principal geometric parameters (interatomic distances, bond angles and torsion angles) are given in Table 1.

As a matter of fact, the geometry of the non-phosphate part of the anions is the same in **6a–e** and is also very similar to that of dihydroxyacetone dimethyl acetal $(MeO)_2DHA$.[13] 2,2-Dimethoxy-1,3-propandiol moiety, $(MeO)_2DHA$–, seems to be very rigid and its conformation is independent of phosphorylation, ionization state of the inserted phosphate group and its additional substitution. The relevant C-4–O-21–C-2–O-22 and C-5–O-22–C-2–O-21 torsion angles reveal the *synclinal* (nearly *gauche*) orientation of the methyl groups (C-4 and C-5) in relation to the acetal O-22 and O-21 oxygen atoms. Similarly, as was observed in the structures of compounds **3**[13] and **4**,[14] the O-21–C-2–C-1 and O-22–C-2–C-3 bond angles are much smaller than the other bond angles with their vertex on the acetal C-2 atom. The conformation of the dihydroxyacetone acetal moiety may be described as a deformed swastika, as it was described in Ref. 13 for the $(MeO)_2DHA$ (**3**) molecule. Thus, it is very likely that the conformation of the non-phosphate part of the **6a–e** anions described here is determined and stabilized by the generalized anomeric

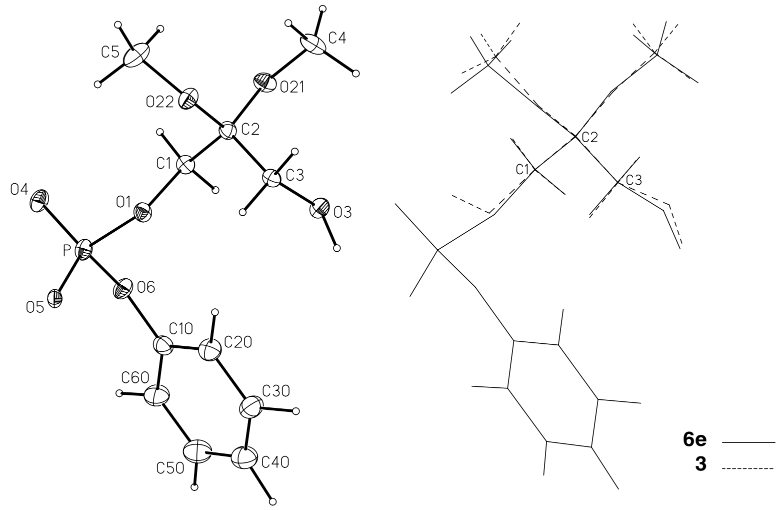

Figure 3. Left: the molecular structure and the atom-numbering scheme for the $[(MeO)_2DHAP(Ph)]^-$ monoanion in **6e**. Displacement ellipsoids are shown at 30% probability level. The H atoms are drawn as small circles of arbitrary radii. Right: the comparison of the anion geometry with the geometry of $(MeO)_2DHA$ (**3**); the common reference points are the marked carbon atoms. Selected interatomic distances and torsion angles not given in Table 1 (Å, °): O-6–C-10 1.386(3); O-1–P–O-6–C-10 72.2(2), O-4–P–O-6–C-10 −170.5(2), O-5–P–O-6–C-10 −39.1(2), P–O-6–C-10–C-20 −46.6(4).

effect, whose role in carbohydrate chemistry is well known. It should be emphasized here that the phosphorylation (phenylphosphorylation) of the $(MeO)_2DHA$ does not affect the conformation of the dihydroxyacetone acetal moiety.

As mentioned, the orientation of phosphate group in relation to the rest of the anion is different in **6a**–**e**. In the molecules with monoionized phosphate groups in $[(MeO)_2DHAP]^-$ (**6b**) and $[(MeO)_2DHAP(Ph)]^-$ (**6e**), the P atom is in *ap* orientation with respect to the acetal C-2 atom. However, the diionized phosphate groups in $[(MeO)_2DHAP]^{2-}$ in dipotassium (**6d**) and bis(cyclohexylammonium) (**6a-1** and **6a-2**) salts are *ac* oriented to the acetal C-2, whereas the value of relevant P–O-1–C-1–C-2 torsion angle in the disodium salt crystal, **6c** (−155.9(1)°) reveals *ap* but close to -*ac* conformation. Orientation of the terminal phosphate oxygen atoms is very similar in all the anions described: one of them (O-5) is always in *ap* conformation in relation to the C-1, and the others (O-4 and O-6) in ±*sc*.

In the phosphate group of **6a**–**e**, a deformation from the ideal tetrahedral shape is observed, especially in the O-4–P–O-5 angles in the monoanions, monoester **6b** and diester **6e**, in which the unprotonated O atoms are involved. The geometry of the diionized phosphate groups in the metal salts (**6c**,**d**) is very similar with O-1–P–O-5 bond angles adopting significantly smaller values than the other phosphate group angles.

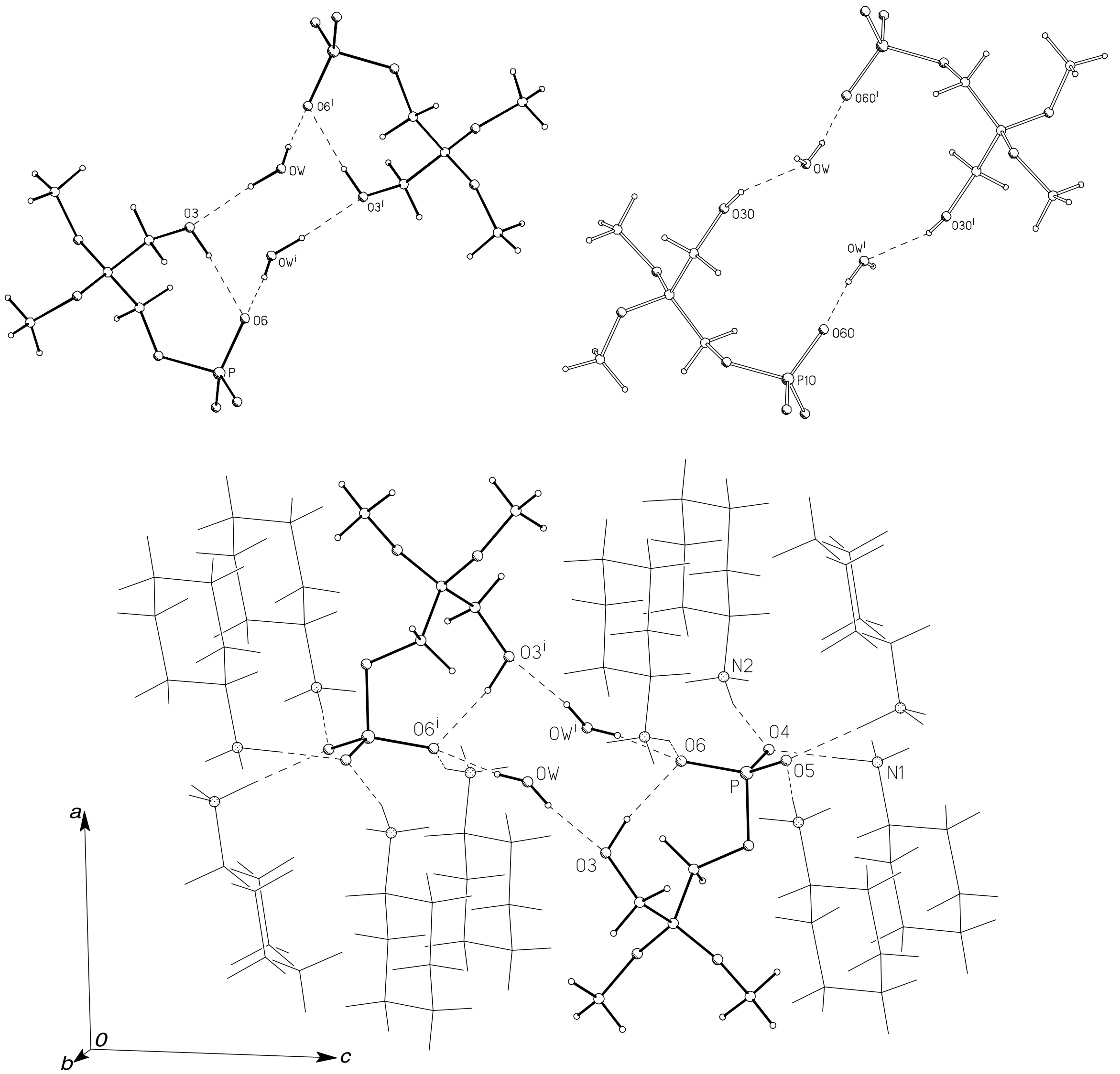

Figure 4. Top: centrosymmetric cyclic structures built up from **6a-1** (solid line) or **6a-2** (open line) anions and water molecules joined by O–H···O hydrogen bonds (dashed lines). Bottom: a packing diagram for **6a**, showing the arrangement of $[(MeO)_2DHAP]^{2-}$ anions, cha^+ cations and water molecules within the double-layer formed by O–H···O and N–H···O hydrogen bonds. Only one position of disordered anion (**6a-1**) and cha^+ cation (N2; shown with thin line) is shown for clarity. (Symmetry codes are listed in Table 2.)

The P–O-1 ester bonds in the monoesters **6a–d** are the longest among all the P–O bonds, whereas both ester bonds in the monoanion of the aliphatic–aromatic diester **6e** have similar values and the P–O-4 and P–O-5 bonds are over 0.1 Å shorter. The ester bond in **6c** is 1.621(1) Å, which is a typical value for diionized phosphate monoesters.[15] However, this bond in **6d** is over 0.02 Å longer (1.642(2) Å). The P–O(H) bond in the monoanion **6b** is about 0.03 Å shorter than the P–O(C) and over 0.06 Å longer than the remaining P–O bonds. P–O-4,5,6 bond values in the dianions **6a**,**c**,**d** are in the range of 1.514(2)–1.535(1) Å. Both the H atom in **6b** and the phenyl group in **6e** are located *synclinal* to the O-6 oxygen atoms.

2.2. Crystal packing and intermolecular interactions in cyclohexylammonium crystals: $(cha)_2[(MeO)_2DHAP]\cdot H_2O$ (6a), $(cha)[(MeO)_2DHAP]$ (6b) and $(cha)[(MeO)_2DHAP(Ph)]$ (6e)

The crystal structures of **6a**, **6b** and **6e** are stabilized mainly by a network of O–H···O and N–H···O hydrogen bonds (Table 2). The cha^+ cations, $[(MeO)_2DHAP]^{2-}$, $[(MeO)_2DHAP]^-$ or $[(MeO)_2DHAP(Ph)]^-$ anions, respectively, in **6a**, **6b** and **6e**, and water molecules (in **6a**) are linked with each other to form layers in the crystals. Adjacent anions are linked to each other directly (**6b** and **6e**) or through the water molecules (**6a**).

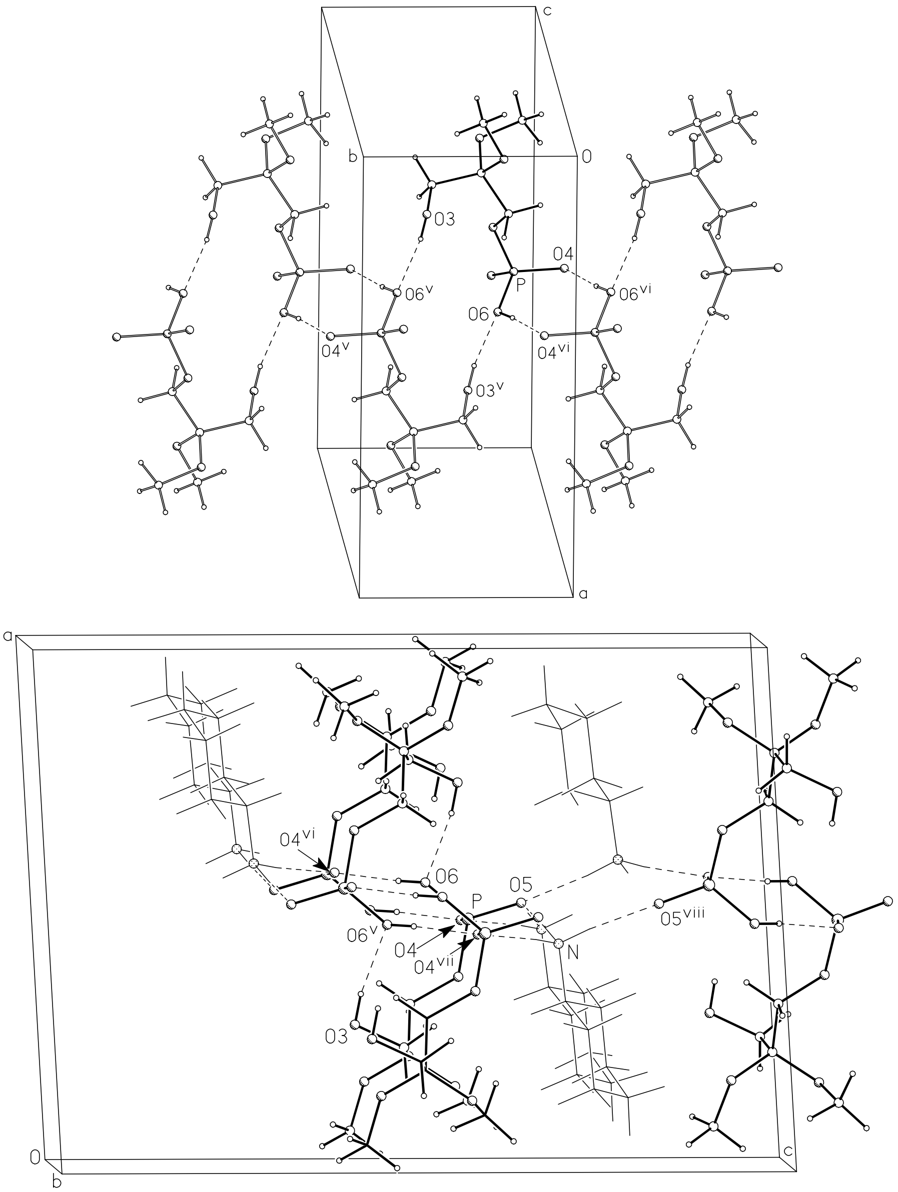

Figure 5. Top: arrangement of the monoanions in **6b**; ribbons (parallel to the *b*-axis) built up from the anions linked each other by O–H···O hydrogen bonds (dashed lines). Bottom: a packing diagram for **6b**, showing the arrangement of $[(MeO)_2DHAP]^-$ anions and cha^+ cations (shown with thin line) within the double layer formed by O–H···O and N–H···O hydrogen bonds. (Symmetry codes are listed in Table 2.)

The O–H···O hydrogen bonds formed between the adjacent anions and water molecules in **6a** result in dimeric, centrosymmetric structures shown in Figure 4, in which two anions (**6a-1** or **6a-2**) and two water molecules (with the respective occupancy factors) are involved. Such dimers are linked with cha^+ cations by the extensive network of N–H···O hydrogen bonds, in which all the phosphate O atoms are involved. As a result, double layers parallel to (1 0 0) plane are formed, the fragment of which is shown in Figure 4.

Every $[(\text{MeO})_2\text{DHAP}]^-$ monoanion in **6b** is linked with two adjacent anions by four O–H···O hydrogen bonds (i.e., by two with each). Two of the contacts (O-6–H-6···O-4^{vi} formed between the phosphate groups of the adjacent monoanions) are quite strong; the O···O distance is 2.545(2) Å (see Table 2). The two other hydrogen bonds (O-3–H-3···O-6^{v}, which link the hydroxyl and phosphate groups of the adjacent monoanions) are weaker. Due to these interactions, ribbons of the monoanions are formed in **6b** crystal along the *b* axis (Fig. 5). Adjacent ribbons at $z = 0$, 1/2, 1..., are separated by cha^+ cations, the protonated ammonium groups of which form N–H···O hydrogen bonds with the phosphate groups of the monoanions. Every cation is involved in two hydrogen contacts to one ribbon and one contact to another, and therefore plays the role of the linker between every two adjacent ribbons. This assembly of the anions and cations leads to the

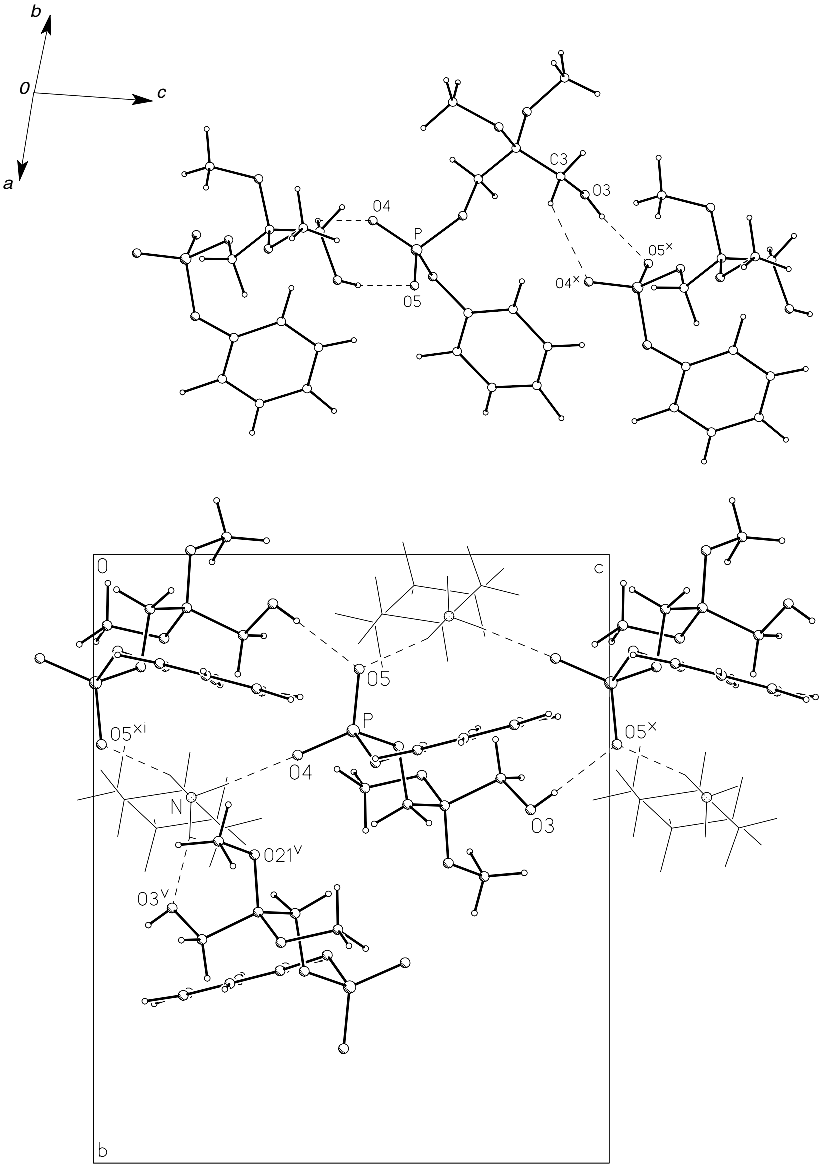

Figure 6. Top: chains of the $[(\text{MeO})_2\text{DHAP(Ph)}]^-$ monoanions in **6e** (parallel to the *c*-axis) linked each other by the O–H···O and C–H···O hydrogen bonds (dashed lines). Bottom: the arrangement of the anions and cha^+ cations (thin line) within the layer; viewed down the *a*-axis. (Symmetry codes are listed in Table 2.)

double-layer architecture of the crystal structure of **6b**. The fragment of such a layer parallel to the (1 0 0) plane is shown in Figure 5. The result of this arrangement of the individual ions in the crystal network is the aggregation of the hydrophilic and hydrophobic groups into two distinct regions in the crystal, which is the common feature of **6a** and **6b**.

The two adjacent $[(MeO)_2DHAP(Ph)]^-$ monoanions in **6e** are joined to each other by a O-3–H-3···O-5^x hydrogen bond formed between the hydroxyl group of one anion and the phosphate of another. That results in zigzag chains along the *c*-axis, the structure of which is additionally stabilized by hydrogen contacts of C–H···O type (Fig. 6, Table 2). Cyclohexylammonium cations are located between the zigzag chains occurring at $y = 1/4$, 3/4, and fill the void between them. This results in layers parallel to the (1 0 0) plane, built up from the anionic chains and cha$^+$ cations linked each other by the N–H···O hydrogen bonds, in which phosphate (O-3, O-4 and O-5) as well as one of the acetal oxygen atoms (O-21) play the role of acceptors (Fig. 6, Table 2).

2.3. The environment of the $[(MeO)_2DHAP]^{2-}$ ions and their arrangement in the crystals of the hydrated sodium and potassium salts: $Na_2[(MeO)_2DHAP]\cdot 5.75H_2O$ (6c) and $K_2[(MeO)_2DHAP]\cdot H_2O$ (6d)

The crystal of the potassium salt (**6d**) has a layer architecture similar to that observed in the cyclohexylammonium salts **6a**, **6b** and **6e**. However, in the sodium crystal (**6c**), the network of sodium cations forms a system of channels, which will be described later in this section.

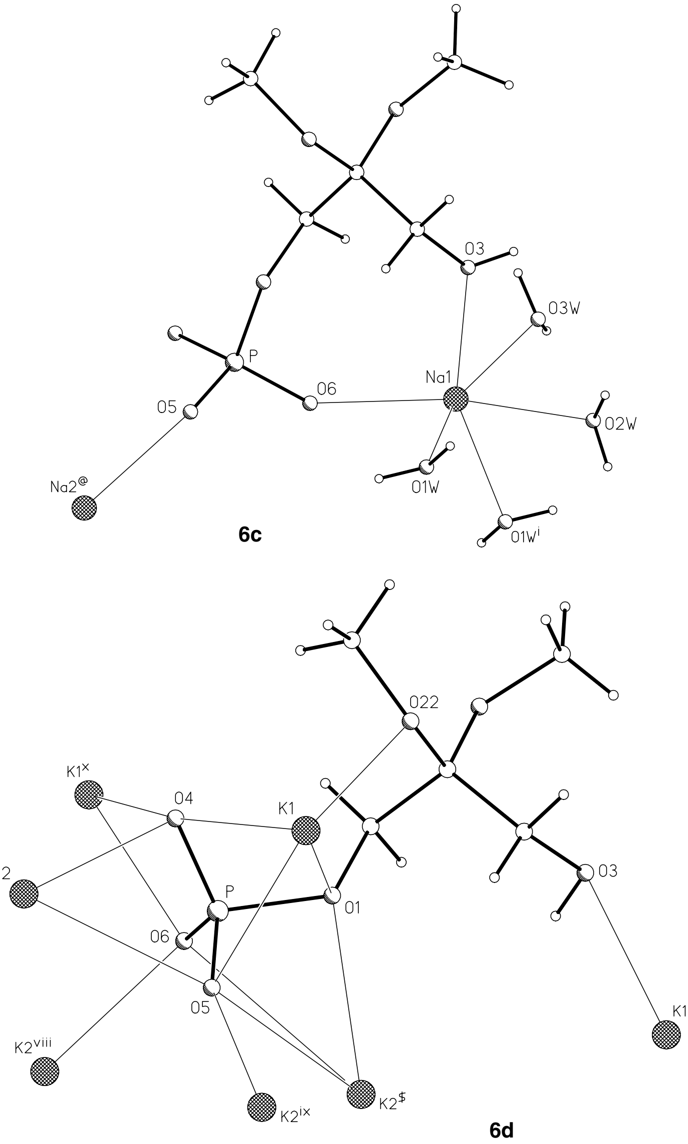

Figure 7. The environment of the $[(MeO)_2DHAP]^{2-}$ anions in sodium and potassium crystals, **6c** and **6d**. (Symmetry codes are listed in Table 3. Additional symmetry codes: (@) $y + 1/3$, $-x + y + 2/3$, $-z + 5/3$; (#) x, $-y + 1/2$, $z - 1/2$; ($) x, $-y + 3/2$, $z - 1/2$.)

Table 3. Coordination spheres of the sodium and potassium ions in **6c** and **6d** (M–O, Å) along with the shortest Na···Na and K···K distances (Å)

*$Na_2[(MeO)_2DHAP]\cdot 5.75H_2O$ (**6c**)*			
Na-1–O-3	2.3281(7)	Na-2–O-5^{ii}	2.4023(7)
Na-1–O-6	2.4720(7)	Na-2–O-2W	2.3074(8)
Na-1–O-1W	2.3980(9)	Na-2–O-3W	2.3770(8)
Na-1–O-2W	2.5392(8)	Na-2–O-4W	2.3982(7)
Na-1–O-3W	2.5696(9)	Na-2–O-5W	2.361(4)
Na-1–O-1W^{i}	2.3680(7)	Na-2–O-51W	2.327(3)
Na-1···Na-2	3.4600(6)	Na-2–O-52W	2.253(8)
Na-1···Na-1^{i}	3.3401(9)	Na-2–O-5W^{iii}	2.513(3)
		Na-2–O-51W^{iv}	2.629(6)
		Na-2–O-52W^{iii}	2.65(2)
		Na-2···Na-2^{iii,iv}	4.0067(7)
*$K_2[(MeO)_2DHAP]\cdot H_2O$ (**6d**)*			
K-1–O-1	2.943(2)	K-2–O-4	2.783(2)
K-1–O-22	2.787(2)	K-2–O-5	3.089(2)
K-1–O-4	2.893(2)	K-2–O-1^{vii}	2.947(2)
K-1–O-5	3.066(2)	K-2–O-5^{vii}	3.234(2)
K-1–O-4^{v}	3.170(3)	K-2–O-6^{vii}	3.361(2)
K-1–O-6^{v}	2.688(2)	K-2–O-5^{viii}	2.715(2)
K-1–O-3^{vi}	2.784(2)	K-2–O-6^{ix}	2.793(2)
K-1–O-W	2.640(2)	K-2–O-W	2.911(3)
K-1···K-2	4.185(2)	K-2–O-W^{x}	3.367(3)
		K-2···K-1^{viii}	3.983(2)

For Na-2 cation, the Na–O distances to all of the disordered water molecules (O-5W, O-51W and O-52W) are given.

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x-y+1/3, x-1/3, -z+5/3$; (iii) $-y+2/3, x-y+1/3, z+1/3$; (iv) $-x+y+1/3, -x+2/3, z-1/3$; (v) $x, y-1, z$; (vi) $x, -y+1/2, z+1/2$; (vii) $x, -y+3/2, z+1/2$; (viii) $-x+1, y+1/2, -z+1/2$; (ix) $-x+1, y-1/2, -z+1/2$; (x) $x, y+1, z$.

The different architectures of the **6c** and **6d** crystals result from differences in the way in which the relevant dianions coordinate to sodium and potassium ions and affect also the hydrogen bonding system observed in the **6c** and **6d** crystals.

The $[(MeO)_2DHAP]^{2-}$ anions in the sodium crystal (**6c**) coordinate to two crystallographically independent sodium ions in a manner as shown in Figure 7. Every dianion chelates one of the cations (Na1) with the phosphate (O-6) and hydroxyl (O-3) oxygen atoms and coordinates to the other sodium cation (Na2) in a monodentate way via the phosphate O-5 atom. However, there are as many as seven potassium ions in the close environment of every $[(MeO)_2DHAP]^{2-}$ anion in the potassium salt (**6d**). All of the terminal phosphate oxygen atoms are involved in coordination to the metal cations; two of them (O-4 and O-6) interact with three and the third one (O-5)—with four different potassium ions. Also the other oxygen atoms form coordination spheres of some potassium cations: ester O-1, hydroxyl O-3 and even acetal O-22 atom (Fig. 7, Table 3).

The coordination spheres of both sodium cations in **6c** (coordination number = 6) are completed by four (Na-1) or five[†] (Na-2) water molecules. The Na-1–O distances in Na-1 coordination polyhedron are in the range of 2.328(1)–2.570(1) Å, and Na-2–O for the other sodium cation are from 2.253(8) to 2.513(3) Å (Table 3).[‡] The O-1W water molecules act as linkers between two Na-1 atoms, O-5W coordinate to two Na-2 atoms, and O-2W and O-3W are the bridges between two independent Na-1 and Na-2 cations. As a result, the three-dimensional network of furcated sodium–water chains, building the system of channels along the *c*-axis, is formed in the crystal of **6c**. The channels and the fragment of the Na–water network is shown in Figure 8 and the shortest Na···Na distances within this network are listed in Table 3. The channels in **6c** are filled with $[(MeO)_2DHAP]^{2-}$ anions coordinating to the sodium cations (Fig. 9). The structural unit, from which every canal is built up, is 36-membered cyclic structure formed by 12 sodium ions bridged by 12 water molecules and 6 phosphate groups. Thus, the hydrophilic parts of the $[(MeO)_2DHAP]^{2-}$ anions build the backbone of the channels, while the hydrophobic parts protrude into their interior, which is shown in Figure 9. Na-1 atoms are involved in the building of the cyclic units, whereas Na-2 atoms build up the 'pillars' parallel to the *c*-axis, each of which join three adjacent cycles. The gaps occurring between the cyclic structures, arranged one above another along the *c*-axis, are filled with non-coordinat-

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[†] Two of the five water molecules in the coordination sphere of Na-2 are not fully occupied (O-5W and O-5W^{iii} with s.o.f. = 0.75). Therefore, the average number of water molecules in that coordination sphere is 4.5.

[‡] All the positions of disordered O-5W water molecule in the Na-2 coordination sphere have been taken into consideration.

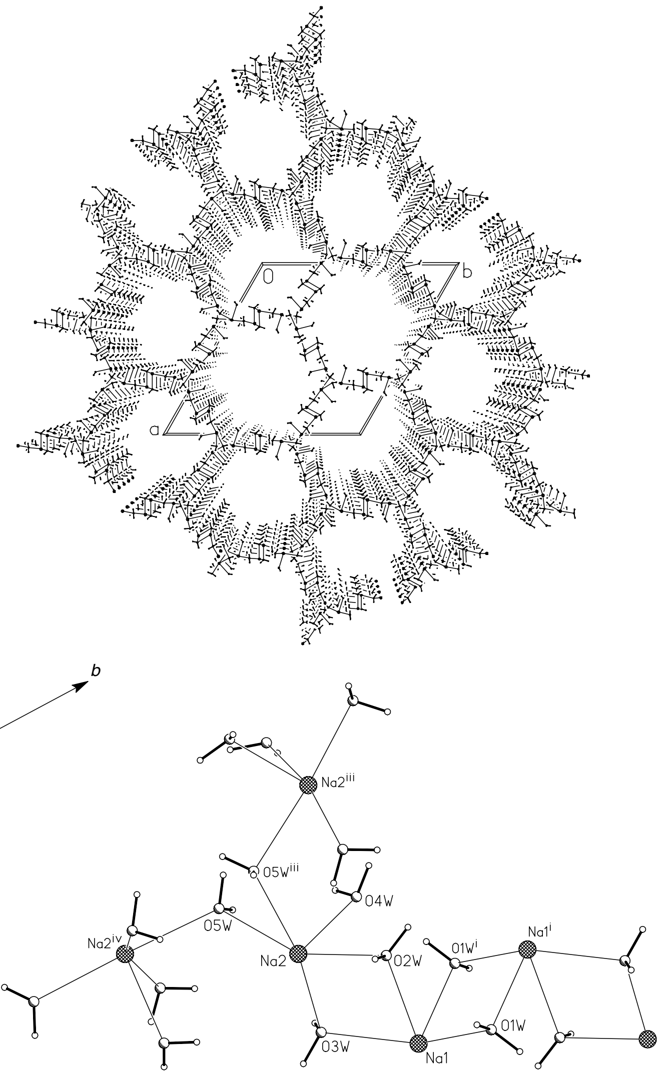


Figure 8. Top: channels in **6c** built up from sodium cations and water molecules coordinating to them; viewed down the *c*-axis. The $[(MeO)_2DHAP]^{2-}$ anions are omitted for clarity. Bottom: the network of furcated chains (built up from sodium cations and water molecules coordinating to them) forming the walls of the channels. Only the O-5W position of the disordered water molecule is shown for clarity. (Symmetry codes are given in Table 3.)

ing O-6W water molecules (six in each gap). These water molecules are involved in hydrogen bonding with $[(MeO)_2DHAP]^{2-}$ anions from adjacent cyclic units and play the role of linkers between them.

The crystal structure of **6c** is additionally stabilized by the O–H···O hydrogen bonds network, in which water molecules and phosphate oxygen atoms (O-4, O-5 and O-6) are mainly involved. Adjacent anions in every cyclic unit of the channel are joined to each other by moderately strong O-3–H-3···O-5^{ii} hydrogen bonds formed between their hydroxyl and phosphate groups, and additionally by two types of C–H···O contacts (Fig. 9). The geometric parameters of proposed hydrogen bonds are listed in Table 4.

In the potassium crystal (**6d**), each K1 cation (with coordination number = 8) is coordinated by three symmetry related $[(MeO)_2DHAP]^{2-}$ anions (one in a tetradentate manner, one bidentate and the other monodentate) and one water molecule. The coordination polyhedron of the K2 ion is built up from nine oxygen atoms from four symmetry related anions and two water molecules; one of the anions is tridentate, one bidentate, and two monodentate (Fig. 10). The K-1–O distances are in the range of 2.640(2)–3.170(3) Å, whereas the K-2–O interatomic distances are from 2.715(2) to 3.367(3) Å (Table 3).

The potassium cations along with the $[(MeO)_2DHAP]^{2-}$ anions and water molecules coordinating to them, form double layers parallel to the (1 0 0) plane (Fig. 11). The phosphate groups of the anions are mainly involved in building the double-layer backbone, while the acetal parts protrude into interlamellar spaces. The arrangement of the potassium ions within the double layer along with the K···K distances

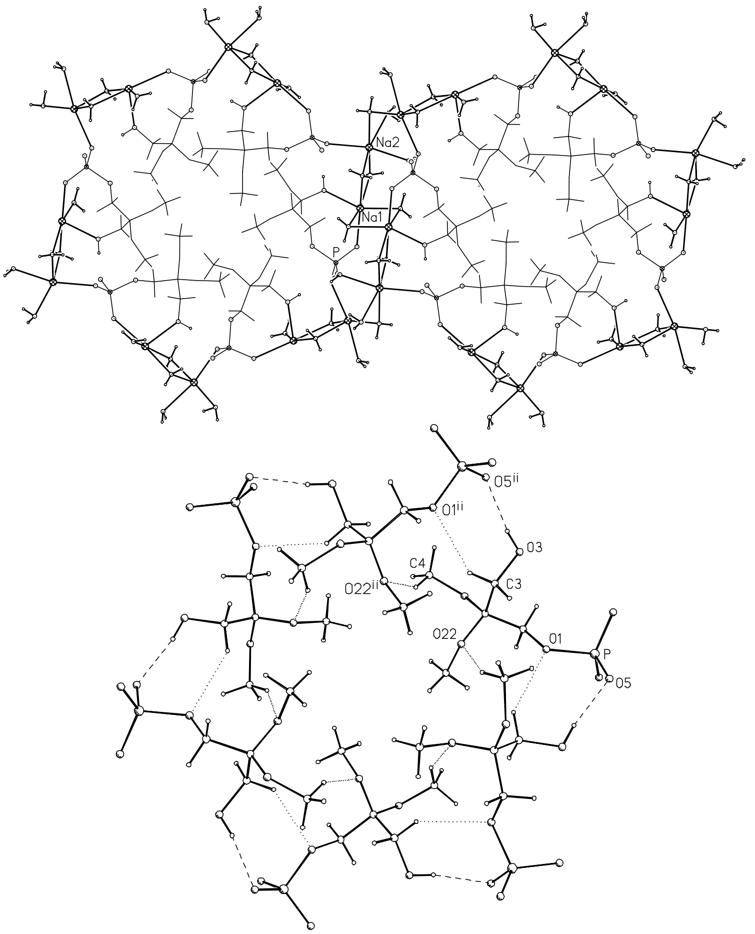


Figure 9. Top: two channels filled up with $[(MeO)_2DHAP]^{2-}$ anions (shown with thin line); viewed down the *c*-axis. Only the O-5W position of disordered water molecule is shown for clarity. Bottom: the anions within one cyclic unit joined each other by O-3–H-3⋯O-5^{ii} (dashed lines) and C-3–H-3A⋯O-1^{ii} and C-4–H-4B⋯O-22^{ii} (dotted lines) hydrogen bonds. (Symmetry codes are given in Table 4.)

are shown in Figure 11. The structure of the double layer is additionally stabilized by the network of moderately strong hydrogen bonds of O–H⋯O and C–H⋯O type, in which hydroxyl O-3 and phosphate O-4, as well as the water molecules are involved. Every $[(MeO)_2DHAP]^{2-}$ anion is joined with two other by O-3–H-3⋯O-4^{xv} and C-5–H-5B⋯O-3^{vii} hydrogen bonds to form chains shown in Figure 11. Adjacent chains from the opposite sides of the layer are linked through the water molecules, which act as donors of O–H⋯O bonds to the phosphate groups of the anions from the adjacent chains.

3. Conclusions

A stable DHAP precursor—its dimethyl acetal, $(MeO)_2DHAP$—was crystallized in the form of four different salts: bis(cyclohexylammonium) (**6a**), cyclohexylammonium (**6b**), disodium (**6c**) and dipotassium (**6d**). Additionally, the cyclohexylammonium salt of its phenyl ester (**6e**) was also obtained, which allowed us to establish the $(MeO)_2DHAP$ anion geometry in different ionization states (mono- and dianions), different chemical environments and arrangement mode in the crystal lattices, as well as different esterification states (mono- and diesters). On the basis of the X-ray structures presented, one may notice that the phosphate group of DHAP precursor shows a tendency to locate differently depending on its ionization state: *antiperiplanar* in the monoanions and *anticlinal* in the dianions. On the other hand, the 2,2-dimethoxy-1,3-propandiol moiety of the anions adopts a conformation that is quite rigid in solid state, regardless of the factors mentioned above.

The arrangement of the individual ions in the crystal network of all the $(MeO)_2DHAP$ salts presented (**6a**–**d**) results in aggregation of the hydrophilic and hydrophobic groups into two distinct regions in the crystals. The common feature of the cyclohexylammonium (**6a**,**b**) and potassium (**6d**) salts crystals is a double-layered architecture, however, sodium cation network in **6c** forms the system of channels, which are filled with the $[(MeO)_2DHAP]^{2-}$ ions. It is possible that such different architectures of the metal salts crystals result from a

Table 4. Geometry of proposed hydrogen bonds and close C–H···O contacts for **6c** and **6d** (Å, °)

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
*$Na_2[(MeO)_2DHAP]\cdot 5.75H_2O$ (**6c**)*				
O-3–H-3···O-5^{ii}	0.79(2)	1.92(2)	2.6986(8)	171(2)
O-1W–H-1W···O-6W^{xi}	0.82(2)	2.02(2)	2.8358(9)	173(2)
O-1W–H-2W···O-4W^{i}	0.83(2)	1.91(2)	2.7356(9)	172(2)
O-2W–H-3W···O-6^{i}	0.82(2)	2.01(2)	2.8224(9)	169(2)
O-2W–H-4W···O-4^{ii}	0.84(2)	2.02(2)	2.8291(9)	163(2)
O-3W–H-5W···O-6^{xii}	0.85(2)	1.95(2)	2.7972(9)	172(2)
O-3W–H-6W···O-6W	0.83(2)	2.07(2)	2.8965(10)	177(2)
O-4W–H-7W···O-5^{i}	0.82(2)	1.94(2)	2.7322(10)	163(2)
O-4W–H-8W···O-4^{xii}	0.85(2)	1.91(2)	2.7235(10)	162(2)
O-5W–H-9W···O-4^{xii}	0.84(7)	2.00(6)	2.813(6)	163(6)
O-51W–H-09W···O-4^{xiii}	0.77(8)	2.06(8)	2.784(3)	155(7)
O-6W–H-11W···O-4^{xiv}	0.85(2)	1.95(2)	2.7672(9)	162(2)
O-6W–H-12W···O-21	0.83(2)	1.99(2)	2.8235(9)	176(2)
C-3–H-3A···O-1^{ii}	0.97(2)	2.47(2)	3.2981(10)	143(1)
C-4–H-4B···O-22^{ii}	0.96(2)	2.52(2)	3.3828(12)	150(1)
*$K_2[(MeO)_2DHAP]\cdot H_2O$ (**6d**)*				
O-3–H-3···O-4^{xv}	0.92(5)	1.75(5)	2.646(3)	163(5)
O-W–H-1W···O-6^{vii}	0.86(4)	1.87(4)	2.703(3)	163(4)
O-W–H-2W···O-5^{ix}	0.82(6)	1.87(6)	2.689(3)	173(5)
C-3–H-3B···O-W^{xvi}	0.93(4)	2.65(4)	3.453(4)	144(3)
C-4–H-4C···O-21^{xvii}	0.95(5)	2.60(5)	3.452(4)	149(4)
C-4–H-4B···O-3	0.95(4)	2.56(4)	3.131(4)	118(3)
C-5–H-5B···O-3^{vii}	1.00(4)	2.47(4)	3.379(4)	151(3)

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x-y+1/3, x-1/3, -z+5/3$; (vii) $x, -y+3/2, z+1/2$; (ix) $-x+1, y-1/2, -z+1/2$; (xi) $x, y, z+1$; (xii) $-x+1, -y+1, -z+1$; (xiii) $y-1/3, -x+y+1/3, -z+4/3$; (xiv) $x-y+1/3, x-1/3, -z+2/3$; (xv) $x, -y+3/2, z-1/2$; (xvi) $x, -y+1/2, z-1/2$; (xvii) $-x+2, y-1/2, -z+1/2$.

different way in which the relevant dianions coordinate to the sodium and potassium ions.

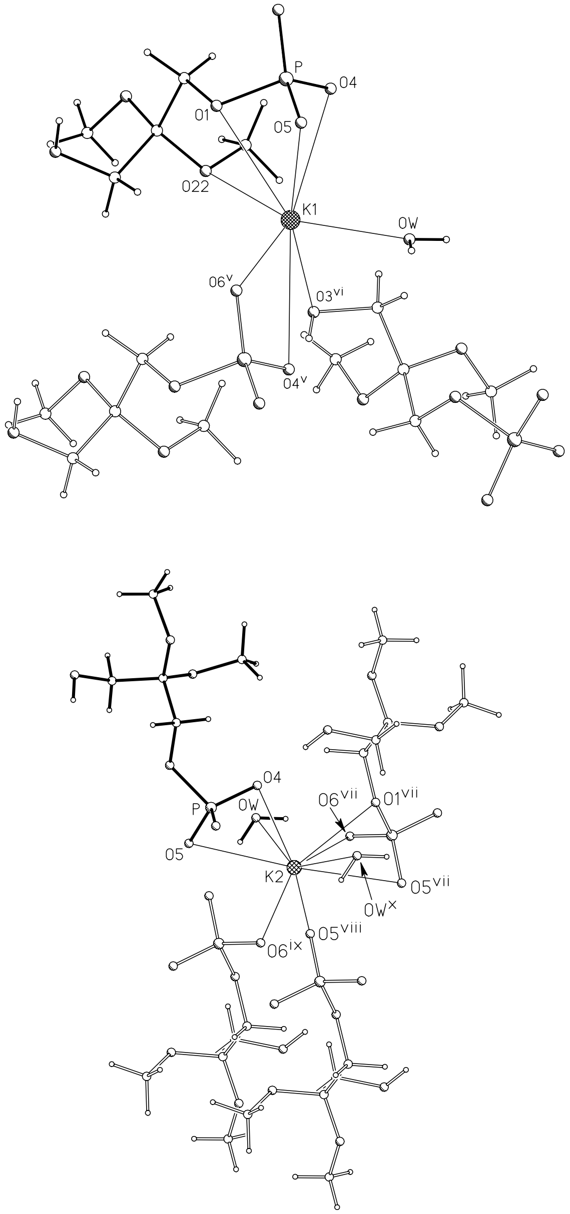


Figure 10. Coordination environment of two crystallographically independent potassium cations in **6d**. (Symmetry codes are given in Table 3.)

4. Experimental

4.1. Preparation of the compounds. Crystallization

$(cha)_2[(MeO)_2DHAP]\cdot H_2O$ (**6a**) and $(cha)[(MeO)_2DHAP(Ph)]$ (**6e**): Compound **6a** was synthesized according to the previously described procedure[10] in 60% yield. Compound **6e** was obtained during carrying out the synthesis of **6a** described by Ballou and Fischer.[11,12] Compound **6e** was produced as a product of the basic hydrolysis and incomplete hydrogenolysis, in the reaction shown in Scheme 2. Crystals of **6e** were obtained by the recrystallization of the synthesized compound from ethanol solution at 7 °C.

$(cha)[(MeO)_2DHAP]$ (**6b**), $Na_2[(MeO)_2DHAP]\cdot 5.75H_2O$ (**6c**) and $K_2[(MeO)_2DHAP]\cdot H_2O$ (**6d**): A water solution of compound **6a** (50 mg, 0.12 mmol in a minimal quantity of water) was passed through an ion-exchange column (Dowex 50-H^+) and 50 mg (0.12 mmol) of compound **6a** was added to the acidic eluant. The solution was evaporated under nitrogen stream yielding a syrup, which crystallized at 7 °C as large, colourless parallelepipeds. The sodium and potassium salts were prepared in an analogous way, with the difference that $NaHCO_3$ or $KHCO_3$ (in a molar ratio **6a**:$XHCO_3$ as 1:2) was added to the acidic eluant, instead of **6a** (Scheme 3).

4.2. Crystal structure determination

The crystallographic measurements for **6a**–**e** were performed on a *Kuma KM4CCD* automated four-circle diffractometer with the graphite–monochromatized MoK_α

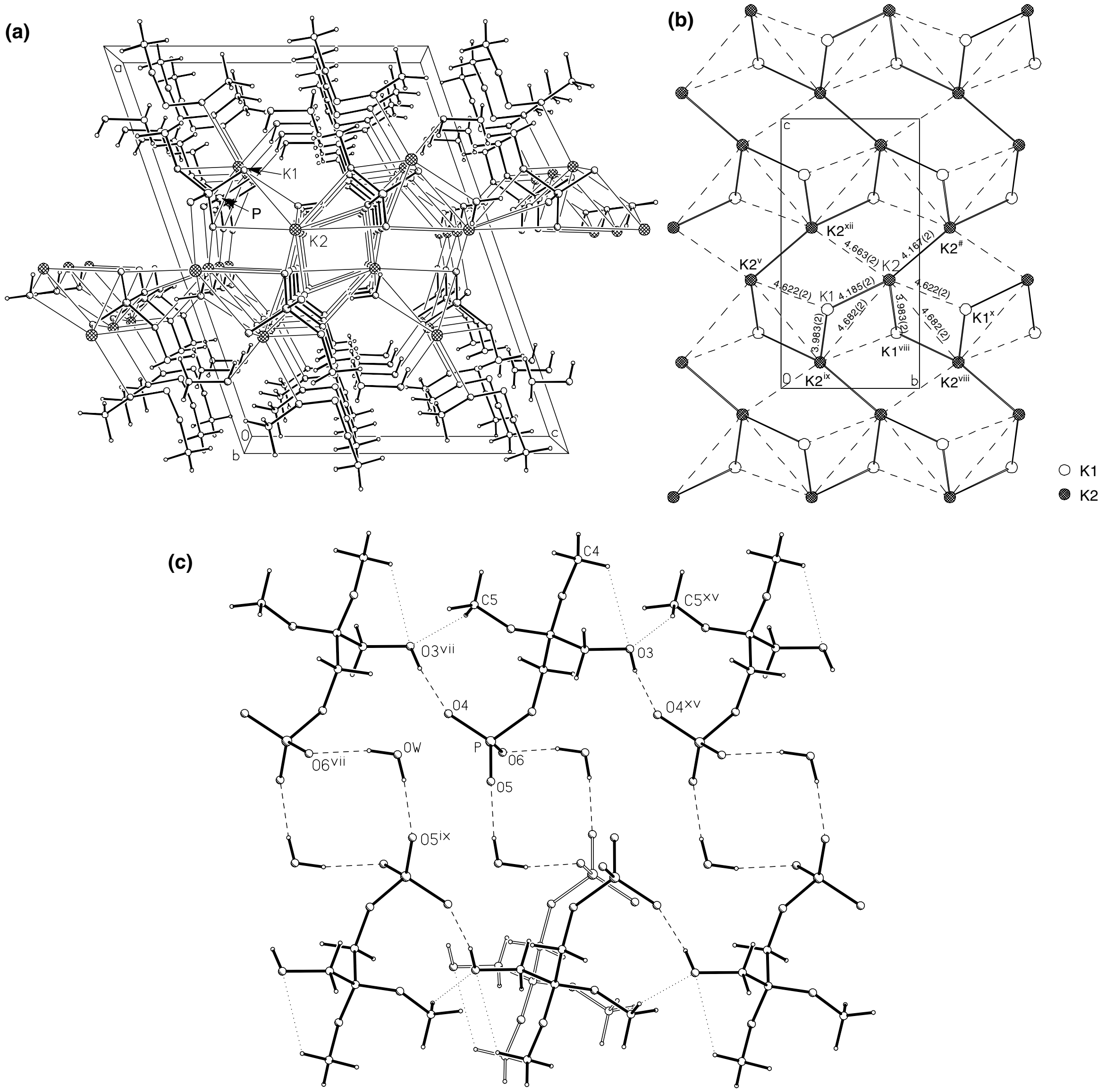
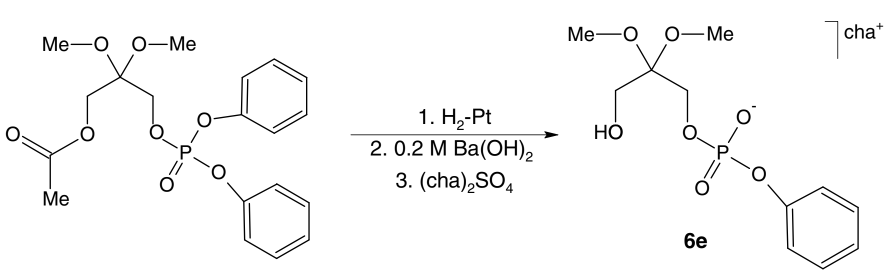
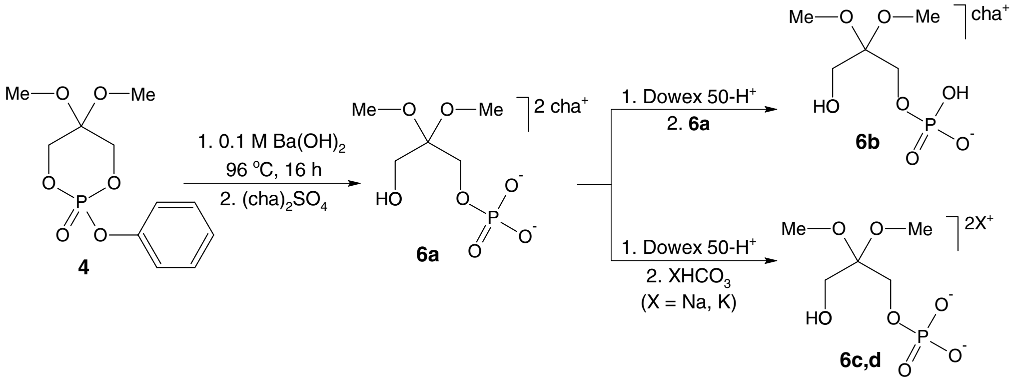


Figure 11. (a) A packing diagram for **6d**, viewed down the *b*-axis, showing the layer architecture. (b) The arrangement of the potassium ions within the double-layer with the K···K (Å) distances shown; viewed down the *a*-axis. (c) The arrangement of $[(MeO)_2DHAP]^{2-}$ anions and water molecules within the double layer in **6d**; viewed down the *b*-axis. The O-3–H-3···O-4^{xv} and C-5–H-5B···O-3^{vii} hydrogen bonds linking the anions and water molecules are shown with dashed and dotted lines. (Symmetry codes are given in Tables 3 and 4. Additional symmetry code: (#) $-x+1$, $-y+2$, $-z+1$.)



Scheme 2. Synthesis scheme for compound **6e**.

radiation. The data for the crystals were collected at 100(2) K using the *Oxford Cryosystems* cooler. All structures were solved by direct methods using *SHELXS-97*[16] and refined by a full-matrix least-squares technique



Scheme 3. Synthesis scheme for compounds **6a**–**d**.

using *SHELXL-97*[17] with anisotropic thermal parameters for all non-H atoms. A summary of the conditions for the data collection and the structure refinement parameters are given in Tables 5 and 6. The scattering

Table 5. Experimental data for **6a**–**c**

	(cha)$_2$[ANION]·H$_2$O (**6a**)	(cha)[ANION] (**6b**)	Na$_2$[ANION]·5.75H$_2$O (**6c**)
Crystal data			
Empirical formula	$C_{17}H_{41}N_2O_8P$	$C_{11}H_{26}NO_7P$	$C_5H_{22.5}Na_2O_{12.75}P$
Formula weight (g mol^{-1})	432.49	315.30	363.68
Crystal system, space group	Orthorhombic, *Pbca*	Monoclinic, $P2_1/c$	Trigonal, $R\bar{3}$
a (Å)	26.064(5)	13.314(3)	32.687(4)
b (Å)	6.354(3)	6.359(2)	
c (Å)	27.521(5)	18.619(4)	7.470(2)
β (°)		93.25(3)	
V (Å^3)	4558(2)	1573.8(7)	6912(2)
Z	8	4	18
D_{calc} (g cm^{-3})	1.261	1.331	1.573
μ (mm^{-1})	0.163	0.203	0.294
F(000)	1888	680	3447
Cell parameters—reflections No.	8737	6826	21547
Crystal size (mm)	0.70 × 0.15 × 0.15	0.45 × 0.15 × 0.15	0.63 × 0.30 × 0.16
Crystal colour	Colourless	Colourless	Colourless
Crystal form	Needle	Parallelepiped	Block
Data collection			
Diffractometer	Kuma KM4CCD	Kuma KM4CCD	Kuma KM4CCD
Monochromator	Graphite	Graphite	Graphite
Radiation type, wavelength, λ (Å)	MoK$_\alpha$, 0.71073	MoK_α, 0.71073	MoK$_\alpha$, 0.71073
T (K)	100(2)	100(2)	100(2)
θ range (°)	3.46–27.50	3.55–28.35	3.74–36.19
h, k, l range	$-33 \leqslant h \leqslant 33$	$-17 \leqslant h \leqslant 17$	$-52 \leqslant h \leqslant 54$
	$-8 \leqslant k \leqslant 4$	$-8 \leqslant k \leqslant 4$	$-52 \leqslant k \leqslant 53$
	$-34 \leqslant l \leqslant 34$	$-24 \leqslant l \leqslant 25$	$-12 \leqslant l \leqslant 9$
Measured reflections	28,014	10,218	39,006
Independent reflections	5094	3534	7194
Observed refl. ($I > 2\sigma(I)$)	3821	3017	6037
R_{int}	0.0548	0.0220	0.0283
Refinement			
Refinement on	F^2	F^2	F^2
Data/restraints/parameters	5094/44/494	3534/0/286	7194/1/307
$R(F_o^2 > 2\sigma(F_o^2))$	$R1 = 0.0703$	$R1 = 0.0337$	$R1 = 0.0291$
	$wR2 = 0.1125$	$wR2 = 0.0782$	$wR2 = 0.0722$
R (all data)	$R1 = 0.1027$	$R1 = 0.0435$	$R1 = 0.0394$
	$wR2 = 0.1243$	$wR2 = 0.0821$	$wR2 = 0.0766$
GooF = S	1.152	1.123	1.096
Weighting parameter a/b	0.0264/5.2967	0.0432/0.1435	0.0393/2.2739
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å^{-3})	0.27/−0.28	0.28/−0.34	0.53/−0.38

ANION = (MeO)$_2$DHAP.

$R1 = \sum \|F_o| - |F_c\| / \sum |F_o|$; $wR2 = \sqrt{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]}$ weighting scheme: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 6. Experimental data for **6d**,**e**

	$K_2[(MeO)_2DHAP]{\cdot}H_2O$ (**6d**)	(cha)[$(MeO)_2$DHAP(Ph)] (**6e**)
Crystal data		
Empirical formula	$C_5H_{13}K_2O_8P$	$C_{17}H_{30}NO_7P$
Formula weight (g mol^{-1})	310.32	391.39
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a (Å)	16.536(4)	11.161(3)
b (Å)	5.996(2)	14.557(4)
c (Å)	12.384(3)	12.375(3)
β (°)	108.92(3)	97.87(3)
V (Å^3)	1161.5(6)	1991.6(9)
Z	4	4
D_{calc} (g cm^{-3})	1.775	1.305
μ (mm^{-1})	0.977	0.175
F(000)	640	840
Cell parameters—reflection No.	8235	3015
Crystal size (mm)	0.38 × 0.27 × 0.02	0.25 × 0.05 × 0.05
Crystal colour	Colourless	Colourless
Crystal form	Plate	Needle
Data collection		
Diffractometer	Kuma KM4CCD	Kuma KM4CCD
Monochromator	Graphite	Graphite
Radiation type, wavelength, λ (Å)	MoK_α, 0.71073	MoK_α, 0.71073
T (K)	100(2)	100(2)
θ range (°)	3.29–29.99	3.26–25.00
h, k, l range	$-21 \leqslant h \leqslant 23$	$-13 \leqslant h \leqslant 13$
	$-8 \leqslant k \leqslant 7$	$-17 \leqslant k \leqslant 9$
	$-17 \leqslant l \leqslant 17$	$-14 \leqslant l \leqslant 14$
Absorption correction	Numerical	—
T_{min}/T_{max}	0.722/0.976	—
Measured reflections	15,177	13,020
Independent reflections	3366	3477
Observed refl. ($I > 2\sigma(I)$)	2778	1719
R_{int}	0.1233	0.0869
Refinement		
Refinement on	F^2	F^2
Data/restraints/parameters	3366/0/197	3477/0/243
$R(F_o^2 > 2\sigma(F_o^2))$	$R1 = 0.0614$	$R1 = 0.0507$
	$wR2 = 0.1582$	$wR2 = 0.0535$
R (all data)	$R1 = 0.0755$	$R1 = 0.1305$
	$wR2 = 0.1705$	$wR2 = 0.0582$
GooF = S	1.054	1.000
Weighting parameter a/b	0.1080/ 0.0	0.0/0.0
$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ^{-3})	1.09/−1.18	0.30/−0.27

$R1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR2 = \sqrt{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]}$ weighting scheme: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

factors were taken from Ref. 18. All figures were made using an *XP* program.[19]

(cha)$_2$[$(MeO)_2$DHAP]·H_2O (**6a**): The [$(MeO)_2$DHAP]$^{2-}$ anion and one of the cha$^+$ cations are disordered into two positions: approximately equally occupied for the anion (s.o.f. = 0.548(10) and 0.452(10)) and with occupation factors of 0.642(6) and 0.358(6) for cha$^+$. Additional disorder of water molecules is correlated with the disorder of the anion. Thus, in the model accepted, one of the H atoms from water molecule occupies two positions denoted as H-2W and H-20W with the occupation factors as for the two positions of the anion. In the refinement procedure, some geometrical parameters of two positions of the disordered anion, and of the disordered cation (equivalent bond distances and angles but not torsion angles) were restrained to be equal with the use of SAME instruction. The positions of pairs of the atoms: P and P-10, O-1 and O-10, O-5 and O-50, as well as C-4 and C-40, were refined with the same anisotropic displacement parameters (constrains were applied with EADP instruction). The hydroxyl H atoms of both anion positions, all the H atoms in the ordered cha$^+$ cation and in the water molecule were found in difference-Fourier maps and were refined isotropically. All the remaining H atoms, that is, those in the disordered cation, as well as methyl and methylene in the disordered anion, were included from geometry with the use of the proper HFIX instruction and were refined with $U_{iso}(H) = 1.2U_{eq}(C)$ (for CH_2) or $U_{iso}(H) = 1.5U_{eq}(C)$ (for CH_3 and NH_3^+). The extinction was also refined with the final extinction coefficient amounting 0.00093(16).

(cha)[(MeO)$_2$DHAP] (**6b**), K_2[(MeO)$_2$DHAP]·H_2O (**6d**) and (cha)[(MeO)$_2$DHAP(Ph)] (**6e**): The data for **6d** were numerically corrected for absorption with the use of *XPREP*.[20] One of the methylene H atoms in **6d** was refined with U_{iso}(H-1A) = U_{eq}(C-1). All H atoms in **6e** were found in difference Fourier maps. In the final refinement cycles, all N- and C-bonded H atoms were treated as riding atoms, with N–H distances of 0.91 Å, and C–H distances of 0.95–1.00 Å, and with U_{iso}(H) values of 1.2U_{eq}(C) for aromatic, CH and CH_2 groups H atoms, and 1.5U_{eq}(N,C) for NH_3^+ and methyl H atoms. The hydroxyl H-3 atom was refined isotropically. In **6b** and **6e**, the extinction was also refined; the final extinction coefficient was 0.0049(10) in **6b** and 0.00132(18) in **6e**.

Na_2[(MeO)$_2$DHAP]·5.75H_2O (**6c**): One of the water molecules is disordered into three positions denoted as O-5W, O-51W and O-52W. Initial refinement stages revealed that the sum of occupation factors of these positions is close to 0.75. Therefore, in the final refinement cycles, the s.o.f. for the individual positions were refined, but the sum of site occupation factors was restrained to be constant and equal to 0.75(1). In the model finally accepted, the s.o.f. for the respective positions were 0.38(2) for O-5W, H-9W, H-10W; 0.25(1) for O-51W, H-09W, H-01W and 0.12(2) for O-52W. The H atoms from disordered O-5W and O-51W positions were found in difference-Fourier maps and were refined with U_{iso}(H) = 1.5U_{eq}(O). Those from O-52W position were not even found.

Acknowledgements

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Supplementary data

The Cambridge Crystallographic Data Center (CCDC) contains the supplementary crystallographic data for this paper: (**6a**) (CCDC 289462), (**6b**) (CCDC 289463), (**6c**) (CCDC 289464), (**6d**) (CCDC 289465) and (**6e**) (CCDC 289466). These data may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Camridge CB2 1EZ, UK; fax +44 1223 336033, deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2005.12.003.

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