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

Katarzyna Ślepokura*

Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie St., 50-383 Wrocław, Poland

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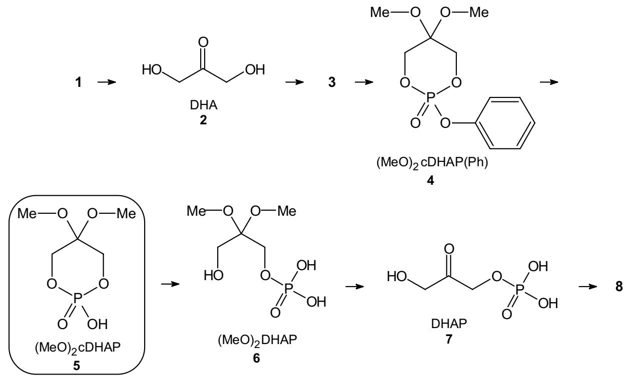
Abstract—The six-membered cyclic phosphate diester, 5,5-dimethoxy-2-oxo-1,3,2-dioxaphosphorinane-2-ol, the dimethyl acetal of cyclic dihydroxyacetone phosphate, $(MeO)_2$cDHAP, was obtained by the isolation of an intermediate in the basic hydrolysis of the cyclic triester derivative. The compound had been isolated in the form of the crystalline cyclohexylammonium (cha) salts: (cha)[$(MeO)_2$cDHAP]·$3H_2O$ (**5a**) and (cha)[$(MeO)_2$cDHAP]·H_2O (**5b**), which were then converted into the free acid: (H_5O_2)[$(MeO)_2$cDHAP] (**5c**) and then into a series of different salts: Na[$(MeO)_2$cDHAP]·$2H_2O$ (**5d**), K[$(MeO)_2$cDHAP]·$1.5H_2O$ (**5e**), K[$(MeO)_2$cDHAP]·$0.5H_2O$ (**5e′**), Ca[$(MeO)_2$cDHAP]$_2$·$2H_2O$ (**5f**), CaK[$(MeO)_2$cDHAP]$_3$·$2H_2O$ (**5g**) and NH_4[$(MeO)_2$cDHAP] (**5h**). The synthesis of the compounds, their crystallization and crystal structures determined by X-ray crystallography are described. The most interesting structural feature observed in **5a**–**g** anions in the crystalline state is the chair conformation of the P/O/C/C/C/O 1,3,2-dioxaphosphorinane ring, which is generally not flattened, in contrast to the deformations often observed in the analogous aryl derivatives (also in $(MeO)_2$cDHAP(Ph); Ślepokura, K.; Lis, T. *Acta Crystallogr. Sect. C* **2004**, *60*, o315–o317). However, the anion in crystal **5h** is disordered and exists in two conformations, 76% of which is the skew, *S*, conformation, not observed so far in the compounds of related structure.

Keywords: Cyclic phosphates; cDHAP; Cyclic dihydroxyacetone phosphate dimethyl acetal; 1,3,2-Dioxaphosphorinane ring; X-ray crystal structure

1. Introduction

The synthesis and structural investigations of cyclic dihydroxyacetone phosphate (cDHAP) dimethyl acetal [$(MeO)_2$cDHAP, **5**] were undertaken as a continuation of our previous work on the structural characterization of the intermediates on the chemical pathway leading from the simplest ketose, dihydroxyacetone (DHA, **2**), to its phosphate ester, dihydroxyacetone phosphate (DHAP, **7**, Scheme 1).

DHAP (**7**) is one of the most important biochemical intermediates of high importance for all living cells. It 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] The DHAP-dependent aldolases have been commonly used in the synthesis of synthetic sugars and related chiral



Scheme 1. Chemical pathway leading from DHA to DHAP.

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* Tel.: +48 071 3757338; e-mail addresses: slep@eto.wchuwr.pl; slep@o2.pl

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compounds on a preparative scale. They accept a broad spectrum of aldehydes, but all of them are very specific to DHAP. (For a review of the application of DHAP-dependent aldolases in asymmetric organic synthesis, see Refs. 3–8.) Dihydroxyacetone phosphate plays a crucial role in the main metabolic pathways, such as gluconeogenesis, fructose metabolism, synthesis of triacylglycerols and phospholipids, glycerophosphate shuttle and finally in glycolysis.[1]

The cyclic form of DHAP (cDHAP) became interesting very recently as a new molecule of biological importance.[9] In general, six-membered cyclic phosphate esters are the constituents of a number of biologically important molecules, for example, the precursor Z of molybdenum cofactor (molybdopterin)[10] or cyclic nucleotides, like cAMP. Occurring in living organisms, small cyclic phosphates of cDHAP-like structure have simultaneously attracted attention very recently when their biological activity as signalling molecules had been suggested. For example, a strong and rapid protein phosphorylation in cells, induced by 1,3-cyclic glycerophosphate and its synthetic analogues (Chart 1) at the micromolar concentration range, was observed. These cyclic phosphates were also found to induce neuronal differentiation in PC12 cells and elevate the state of differentiation in human breast cancer cells.[11] It is to be mentioned here that cyclic glycerophosphates can be formed by enzymatic degradation of phospholipids. 1,3-Cyclic glycerophosphate is naturally formed in the action of phospholipase C on phosphatidyl glycerol, and it is actually the active residue in cAMP.

There are several popular methods for the chemical synthesis of six-membered acidic cyclic phosphates, for example, phosphorylation of the proper 1,3-diol with $POCl_3$, or phosphorylation of the diol with $(ArO)POCl_2$ and subsequent selective catalytic hydrogenolysis (H_2/Pt–C) of the synthesized neutral triester aryl derivative (like **4** in Scheme 1; Ar = Ph). It is known that prolonged alkaline treatment of the neutral triester precursor also leads to the cyclic diester, but this method is usually applied for the non-cyclic monoester production (like **6** in Scheme 1). Ferroni et al., whose synthetic procedure was the basis of the synthesis presented here, obtained the linear monoester **6** (stable DHAP precursor) in a direct 16-hour-long basic hydrolysis of the neutral compound **4**.[12] They presume the formation of cyclic diester **5** in the first stage of this reaction; nevertheless, the dimethyl acetal of cDHAP was not isolated. When carrying out this reaction, we have isolated intermediate **5** and found the method of partial basic hydrolysis as a fast, easy and convenient procedure for the synthesis of $(MeO)_2$cDHAP, the precursor of cDHAP. The compound was isolated in the form of its stable cyclohexylammonium (cha) salt trihydrate, (cha)[$(MeO)_2$cDHAP]·$3H_2O$ (**5a**), and then recrystallized to give (cha)[$(MeO)_2$cDHAP]·H_2O (**5b**), and easily converted into the free acid: (H_5O_2)[$(MeO)_2$cDHAP] (**5c**) and then into the other salts **5d**–**h**.

Previously, we have reported the crystal and molecular structures of the series of the compounds occurring on the first four and the sixth step of the investigated pathway (**1a**–**c**, **2a**–**c** **3**, **4** and **6a**–**e** in Scheme 1).[13–15] Among other things the results of the structural investigations on the phenyl derivative of the compound presented here, $(MeO)_2$cDHAP(Ph) (**4**), have been published.[14] The present paper concerns the synthesis and the structure of six-membered cyclic phosphate diester, 5,5-dimethoxy-2-oxo-1,3,2-dioxaphosphorinane-2-ol, the dimethyl acetal of cyclic dihydroxyacetone phosphate, $(MeO)_2$cDHAP (**5**) in the form of the crystalline cyclohexylammonium (cha) salts: (cha)[$(MeO)_2$cDHAP]·$3H_2O$ (**5a**) and (cha)[$(MeO)_2$cDHAP]·H_2O (**5b**), the free acid: (H_5O_2)[$(MeO)_2$cDHAP] (**5c**) and other salts: Na[$(MeO)_2$cDHAP]·$2H_2O$ (**5d**), K[$(MeO)_2$cDHAP]·$1.5H_2O$ (**5e**), K[$(MeO)_2$cDHAP]·$0.5H_2O$ (**5e′**), Ca[$(MeO)_2$cDHAP]$_2$·$2H_2O$ (**5f**), CaK[$(MeO)_2$cDHAP]$_3$·$2H_2O$ (**5g**) and NH_4[$(MeO)_2$cDHAP] (**5h**). Thus, the geometry of the [$(MeO)_2$cDHAP]$^-$ anions occurring in the nine different salts (with both organic and inorganic cations), especially the conformation of the P/O/C/C/C/O 1,3,2-dioxaphosphorinane ring, will be compared with that of the phenyl derivative, $(MeO)_2$cDHAP(Ph) (**4**), and the influence of Ph substituent, the chemical environment of the anions, as well as the arrangement in the crystal lattice, will be discussed.

Among the cyclic phosphates with six-membered rings, two classes of compounds seem to be the most interesting: 3′:5′-cyclic nucleotides and cyclic phosphates of small organic compounds (Chart 1) of structures related to that of the $(MeO)_2$cDHAP presented here. In the cyclic nucleotides, only one from about 20 structures deposited with the Cambridge Structural Database[16] exists in non-chair conformation (but in skew, *S*). However, solution studies have shown that not chair, but just skew conformation is preferred, and therefore may be important in cellular media.[17] Cyclic phosphates of small compounds structurally related to the ones presented here in general exist in chair conformation in solid state. Skew or boat conformation has been never observed in these compounds containing the tetra-bonded phosphorus atom. However, skew

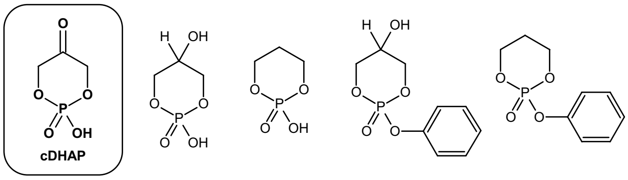


Chart 1. Structures of cyclic dihydroxyacetone phosphate (cDHAP) along with its analogues: glycerol and 1,3-propandiol cyclic phosphates and phenylphosphates.

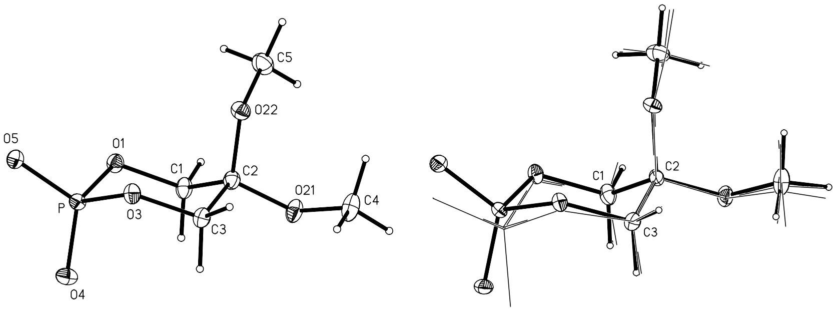
conformation is often observed in penta-bonded phosphorus-containing compounds. Therefore, from the structural point of view, searches for the small cyclic phosphates in non-chair conformation may be of great importance.

2. Results and discussion

Crystals of cyclohexylammonium salts, **5a** and **5b**, are composed of $[(MeO)_2cDHAP]^-$ monoanions, cyclohexylammonium cations (cha^+) and water molecules. Crystals of **5c** and **5h** consist of $[(MeO)_2cDHAP]^-$ and $H_5O_2^+$ or NH_4^+ ions. Crystals of **5d**–**g** are built up from the same $[(MeO)_2cDHAP]^-$ anions and water molecules coordinating to metal cations (Na^+, K^+ and/or Ca^{2+}). The asymmetric units of **5a**–**h** consist of the anions and the other components (cations and water molecules) in amounts relevant to their molecular formulas, except for **5e** (anion:K:H_2O is 2:3:3) and for **5f**, the asymmetric unit of which is composed of one $[(MeO)_2cDHAP]^-$ ion, half Ca^{2+} (located on a twofold axis) and one water molecule. The water molecule in **5e′** is located on a twofold axis. The two crystallographically independent anions in **5e**, as well as three anions in **5g**, will be denoted in the text as **5e-1**, **5e-2**, **5g-1**, **5g-2** and **5g-3**.

2.1. Molecular geometry of the anions in 5a–g

The overall structure of the $[(MeO)_2cDHAP]^-$ anions in crystals **5a**–**g** reveals great similarities (Fig. 1). The six-membered 1,3,2-dioxaphosphorinane ring (P/O1/C1/C2/C3/O3) adopts the chair (*C*) conformation slightly distorted towards an envelope (*E*), which is reflected in the values of dihedral angles between the least-squares plane through the four central atoms of the ring (O1, O3, C1 and C3) and the O1/P/O3 and C1/C2/C3 planes (angles φ_1 and φ_2). It is to be noted here that this flattening of the ring at the P atom is much smaller than that observed in the molecule of the phenyl derivative,



5a

5g-1,2,3

Figure 1. The molecular structure of the $[(MeO)_2cDHAP]^-$ anion in **5a** showing the atom numbering scheme along with the comparison of the geometry of three crystallographically independent anions in **5g** (**5g-1**: thick line, **5g-2**,**3**: thin line; the common reference points are C1, C2, C3). Displacement ellipsoids are shown at the 40% probability level.

Table 1. The values of φ_1, φ_2 and the Cremer–Pople puckering parameters for P/O1/C1/C2/C3/O3 rings in $[(MeO)_2cDHAP]^-$ anions in **5a**–**g** along with the relevant values for the phenyl derivative $(MeO)_2cDHAP(Ph)$, **4**

		φ_1(°)	φ_2(°)	$\lvert\varphi_2-\varphi_1\rvert$ (°)	Cremer–Pople parameters[a]		
					Q (Å)	Θ (°)	Φ (°)
$(cha)[(MeO)_2cDHAP]\cdot 3H_2O$ (**5a**)		47.3(1)	50.8(1)	**3.6**	0.573(1)	178.4(1)	234(4)
$(cha)[(MeO)_2cDHAP]\cdot H_2O$ (**5b**)		48.2(1)	50.3(1)	**2.1**	0.577(1)	177.5(1)	199(2)
$(H_5O_2)[(MeO)_2cDHAP]$ (**5c**)		45.4(1)	52.5(1)	**7.1**	0.569(1)	176.3(1)	321(2)
$Na[(MeO)_2cDHAP]\cdot 2H_2O$ (**5d**)		47.5(1)	50.5(2)	**3.0**	0.576(2)	176.3(2)	233(2)
$K[(MeO)_2cDHAP]\cdot 1.5H_2O$ (**5e**)	**5e-1**	47.0(2)	53.0(4)	**6.0**	0.585(4)	176.4(4)	275(6)
	5e-2	47.3(2)	54.4(4)	**7.1**	0.598(4)	178.3(4)	309(12)
$K[(MeO)_2cDHAP]\cdot 0.5H_2O$ (**5e′**)		49.9(1)	51.4(2)	**1.5**	0.598(2)	176.5(2)	202(4)
$Ca[(MeO)_2cDHAP]_2\cdot 2H_2O$ (**5f**)		51.0(1)	49.2(1)	**1.8**	0.595(2)	174.1(2)	177(2)
$CaK[(MeO)_2cDHAP]_3\cdot 2H_2O$ (**5g**)	**5g-1**	40.0(1)	56.0(2)	**16.0**	0.566(2)	169.9(2)	356(2)
	5g-2	48.4(1)	51.0(3)	**2.6**	0.584(2)	175.6(2)	245(3)
	5g-3	48.9(2)	50.3(3)	**1.4**	0.582(2)	176.0(2)	213(3)
$NH_4[(MeO)_2cDHAP]$ (**5h**)	Skew	—	—	—	0.783(5)	88.1(3)	90(1)
	Chair	—	—	—	0.66(1)	170(1)	301(6)
$(MeO)_2cDHAP(Ph)$ (**4**)		35.9(1)	51.8(2)	**15.9**	0.514(2)	167.5(2)	349(1)

[a] Cremer–Pople parameters are also given for two conformations (skew and chair) of the disordered anion in **5h**.

Table 2. Principal interatomic distances (Å, °), valence angles (°) and torsion angles (°) in **5a**–**g** and **5h** anion in skew (*S*) conformation (standard deviations in parentheses)

	5a	**5b**	**5c**	**5d**	**5e**		**5e′**	**5f**	**5g**			**5h** (*S*)
					5e-1	**5e-2**			**5g-1**	**5g-2**	**5g-3**	
P–O1	1.5990(10)	1.6068(7)	1.5913(9)	1.616(2)	1.624(3)	1.627(3)	1.625(2)	1.6213(10)	1.599(2)	1.609(2)	1.605(2)	1.623(6)
P–O3	1.5986(9)	1.6040(7)	1.5911(10)	1.619(2)	1.589(3)	1.622(3)	1.616(2)	1.6008(10)	1.605(2)	1.600(2)	1.611(2)	1.603(2)
P–O4	1.4888(10)	1.4964(8)	1.5079(9)	1.498(2)	1.504(3)	1.470(3)	1.481(2)	1.4840(10)	1.487(2)	1.493(2)	1.490(2)	1.484(2)
P–O5	1.4952(10)	1.4833(7)	1.4952(9)	1.474(2)	1.468(3)	1.490(3)	1.481(2)	1.4786(10)	1.485(2)	1.485(2)	1.487(2)	1.476(2)
O1–C1	1.446(2)	1.4419(11)	1.449(2)	1.434(2)	1.436(5)	1.444(5)	1.444(3)	1.442(2)	1.435(3)	1.441(3)	1.437(3)	1.430(8)
O21–C2	1.410(2)	1.4147(11)	1.415(2)	1.417(2)	1.422(5)	1.421(5)	1.428(3)	1.418(2)	1.408(3)	1.421(3)	1.412(3)	1.406(4)
O21–C4	1.436(2)	1.4358(12)	1.440(2)	1.433(3)	1.425(5)	1.424(6)	1.430(4)	1.431(2)	1.435(3)	1.432(3)	1.436(3)	1.403(5)
O22–C2	1.413(2)	1.4110(11)	1.407(2)	1.415(2)	1.395(5)	1.392(5)	1.413(3)	1.407(2)	1.417(3)	1.414(3)	1.402(3)	1.481(6)
O22–C5	1.431(2)	1.4276(12)	1.433(2)	1.432(3)	1.426(5)	1.424(5)	1.438(3)	1.445(2)	1.439(3)	1.428(3)	1.438(3)	1.444(7)
O3–C3	1.447(2)	1.4420(11)	1.454(2)	1.441(2)	1.453(5)	1.440(5)	1.441(3)	1.445(2)	1.448(3)	1.445(3)	1.443(3)	1.441(4)
C1–C2	1.530(2)	1.5296(13)	1.535(2)	1.524(3)	1.513(6)	1.517(6)	1.530(4)	1.531(2)	1.520(3)	1.526(3)	1.527(3)	1.495(6)
C2–C3	1.530(2)	1.5312(12)	1.540(2)	1.532(2)	1.540(6)	1.529(6)	1.523(4)	1.535(2)	1.524(3)	1.521(3)	1.522(3)	1.522(4)
O1–P–O3	102.58(5)	102.25(4)	104.68(6)	101.04(7)	101.4(2)	101.0(2)	100.58(11)	100.72(5)	103.02(8)	101.77(8)	101.47(8)	99.8(2)
O1–P–O4	110.75(5)	109.35(4)	109.05(5)	108.72(7)	108.4(2)	111.2(2)	109.48(11)	108.47(6)	110.35(9)	107.19(9)	110.19(9)	103.9(2)
O1–P–O5	106.15(5)	107.26(4)	107.37(5)	109.11(8)	108.2(2)	107.2(2)	105.46(11)	107.64(5)	107.26(9)	108.44(9)	106.12(9)	115.3(2)
O3–P–O4	110.27(5)	109.53(4)	109.26(5)	108.76(8)	109.2(2)	111.1(2)	109.23(11)	109.50(5)	110.55(9)	110.65(9)	109.44(9)	111.4(2)
O3–P–O5	108.07(5)	108.14(4)	108.42(5)	107.11(7)	107.7(2)	105.4(2)	109.11(11)	108.32(6)	107.29(9)	107.38(9)	107.62(9)	106.4(2)
O4–P–O5	117.86(6)	119.00(4)	117.31(6)	120.38(8)	120.3(2)	119.3(2)	121.01(12)	120.40(6)	117.36(9)	119.90(10)	120.32(9)	118.6(2)
P–O1–C1	115.23(8)	115.24(6)	115.22(7)	114.6(1)	113.9(3)	114.2(3)	114.9(2)	114.30(8)	116.9(2)	113.8(2)	115.1(2)	113.3(5)
C2–O21–C4	115.77(10)	115.55(7)	115.44(9)	114.8(2)	115.8(3)	115.6(4)	114.8(2)	116.21(11)	114.4(2)	114.9(2)	116.1(2)	114.7(3)
C2–O22–C5	115.47(10)	115.50(7)	115.66(9)	116.0(2)	115.9(4)	116.2(3)	116.6(2)	115.08(11)	115.0(2)	115.7(2)	115.9(2)	113.3(4)
P–O3–C3	115.70(7)	114.97(5)	115.86(7)	117.2(1)	118.2(3)	116.5(3)	114.4(2)	114.42(8)	118.8(2)	116.1(2)	114.9(2)	115.6(2)
O1–C1–C2	110.40(10)	110.30(7)	109.59(8)	110.7(2)	110.1(4)	110.3(4)	109.3(2)	111.15(11)	110.5(2)	110.0(2)	109.7(2)	108.5(4)
O21–C2–O22	112.43(10)	112.27(7)	112.74(11)	111.9(2)	112.9(3)	112.4(4)	111.2(2)	112.05(10)	112.4(2)	111.1(2)	112.7(2)	109.1(3)
O21–C2–C1	103.56(9)	103.99(7)	103.70(8)	104.2(2)	103.6(4)	104.1(4)	104.4(2)	103.25(10)	104.0(2)	104.1(2)	103.6(2)	112.6(3)
O22–C2–C1	113.42(10)	113.85(7)	113.63(9)	113.4(2)	114.6(4)	114.1(4)	113.9(2)	114.19(11)	113.4(2)	113.5(2)	113.6(2)	108.9(4)
O21–C2–C3	111.25(10)	110.45(7)	111.03(9)	111.4(2)	110.5(4)	110.8(4)	111.9(2)	110.90(11)	113.1(2)	111.2(2)	111.2(2)	112.2(3)
O22–C2–C3	105.62(10)	105.40(7)	105.31(9)	104.8(2)	104.4(4)	105.7(4)	104.8(2)	105.75(11)	105.3(2)	106.7(2)	104.7(2)	102.1(3)
C1–C2–C3	110.72(10)	111.01(7)	110.57(10)	111.4(2)	111.0(4)	109.8(4)	110.8(2)	110.84(11)	108.7(2)	110.5(2)	111.2(2)	111.3(3)
O3–C3–C2	110.92(10)	111.30(7)	110.62(9)	110.3(2)	108.6(4)	109.2(4)	111.4(2)	110.91(11)	108.8(2)	111.5(2)	111.7(2)	109.4(3)
O3–P–O1–C1	55.00(9)	55.98(6)	53.19(8)	55.9(2)	55.3(3)	54.4(3)	58.2(2)	58.40(9)	46.6(2)	57.2(2)	57.6(2)	−37.0(4)
O4–P–O1–C1	−62.66(9)	−60.04(7)	−63.64(9)	−58.4(2)	−59.6(3)	−63.5(4)	−56.7(2)	−56.52(10)	−71.4(2)	−59.0(2)	−58.3(2)	−152.2(4)
O5–P–O1–C1	168.30(8)	169.63(6)	168.29(8)	168.6(2)	168.3(3)	164.5(3)	171.6(2)	171.72(8)	159.6(2)	170.2(2)	170.0(2)	76.4(5)
O1–P–O3–C3	−53.96(9)	−54.90(6)	−51.04(8)	−54.1(2)	−53.8(3)	−54.3(3)	−56.3(2)	−58.79(9)	−46.6(2)	−53.9(2)	−54.9(2)	−32.5(3)
O4–P–O3–C3	64.04(10)	61.00(6)	65.65(9)	60.2(2)	60.5(3)	63.6(3)	58.8(2)	55.35(10)	71.3(2)	59.7(2)	61.5(2)	76.7(2)
O5–P–O3–C3	−165.84(8)	−167.89(6)	−165.40(8)	−168.3(2)	−167.2(3)	−165.8(3)	−166.9(2)	−171.60(9)	−159.6(2)	−167.7(2)	−166.1(2)	−152.7(2)
P–O1–C1–C2	−59.69(12)	−59.58(8)	−59.58(11)	−61.8(2)	−62.7(4)	−62.1(4)	−61.7(3)	−59.96(12)	−58.7(2)	−63.0(2)	−61.4(2)	74.2(6)
P–O3–C3–C2	57.70(12)	58.24(8)	55.61(11)	56.4(2)	56.7(5)	59.8(4)	59.8(3)	60.83(13)	56.8(2)	56.3(2)	57.5(2)	68.1(3)
C4–O21–C2–O22	53.82(15)	47.45(10)	58.08(13)	65.6(2)	56.8(5)	56.8(5)	59.2(3)	56.22(15)	54.3(3)	59.9(3)	53.7(3)	55.0(5)
C4–O21–C2–C1	176.63(11)	170.98(7)	−178.58(11)	−171.5(2)	−178.7(4)	−179.2(4)	−177.5(2)	179.55(12)	177.4(2)	−177.6(2)	177.0(2)	176.1(4)
C4–O21–C2–C3	−64.41(14)	−69.87(9)	−59.82(14)	−51.3(2)	−59.8(5)	−61.3(5)	−57.6(3)	−61.69(15)	−64.9(3)	−58.7(3)	−63.5(3)	−57.4(4)
C5–O22–C2–O21	63.95(13)	66.67(10)	60.63(14)	61.9(2)	67.9(5)	65.0(5)	69.8(3)	56.39(15)	69.1(2)	68.3(2)	64.4(3)	61.3(5)
C5–O22–C2–C1	−53.12(14)	−51.14(10)	−57.00(15)	−55.6(2)	−50.4(5)	−53.2(5)	−47.9(3)	−60.55(15)	−48.5(3)	−48.6(3)	−53.1(3)	−62.0(5)
C5–O22–C2–C3	−174.54(10)	−173.04(7)	−178.15(12)	−177.3(2)	−172.0(4)	−174.0(4)	−169.2(2)	177.32(11)	−167.3(2)	−170.5(2)	−174.6(2)	−179.8(4)
O1–C1–C2–O21	175.75(10)	174.32(7)	177.69(9)	177.4(2)	178.9(4)	179.6(3)	177.2(2)	172.88(10)	−176.5(2)	177.5(2)	175.5(2)	91.0(5)
O1–C1–C2–O22	−62.10(13)	−63.20(9)	−59.56(12)	−60.7(2)	−57.6(5)	−57.5(5)	−61.4(3)	−65.21(14)	−54.0(3)	−61.6(3)	−61.9(3)	−147.9(4)
O1–C1–C2–C3	56.42(14)	55.54(9)	58.60(11)	57.2(2)	60.3(5)	60.9(5)	56.5(3)	54.09(14)	62.8(2)	58.1(3)	55.9(3)	−36.1(6)
O3–C3–C2–O21	−170.03(9)	−170.07(6)	−171.31(9)	−169.6(2)	−169.7(3)	−173.2(4)	−172.4(2)	−168.30(10)	−175.6(2)	−169.4(2)	−169.6(2)	−157.1(3)
O3–C3–C2–O22	67.70(12)	68.45(8)	66.36(12)	69.2(2)	68.5(4)	64.7(5)	67.0(3)	70.02(13)	61.2(2)	69.3(2)	68.4(2)	86.3(3)
O3–C3–C2–C1	−55.45(13)	−55.26(9)	−56.77(11)	−53.7(2)	−55.4(5)	−58.8(5)	−56.3(3)	−54.23(14)	−60.6(2)	−54.4(3)	−54.7(3)	−29.8(5)

$(MeO)_2$cDHAP(Ph).[14] The values of φ_1 and φ_2, along with the Cremer–Pople puckering parameters for the $[(MeO)_2cDHAP]^-$ anions in crystals **5a**–**g**, as well as for the phenyl derivative (**4**), are given in Table 1.

Values of $|\varphi_2 - \varphi_1|$ given in Table 1 clearly show that the flattening of the dioxaphosphorinane ring is negligible in almost all of the $[(MeO)_2cDHAP]^-$ anions in **5a**–**g**, and the conformation of the rings may be described as close to an ideal chair. Only in one of three crystallographically independent anions in $CaK[(MeO)_2cDHAP]_3{\cdot}2H_2O$, **5g-1** (Fig. 1), the deformation of P/O1/C1/C2/C3/O3 ring is more distinct and is comparable to that observed in the phenyl derivative $(MeO)_2$cDHAP(Ph) (**4**). However, it is probable that the differences in the geometry of **5g-1**,**2**,**3** result from the close chemical environment of the respective anions, which will be discussed later.

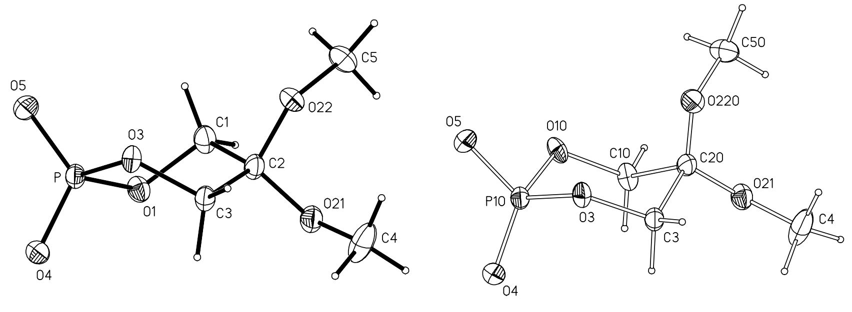
The selected geometrical parameters for the $[(MeO)_2cDHAP]^-$ anions in **5a**–**h** are given in Table 2. In the phosphate group, a deformation from the ideal tetrahedral shape is observed, especially in the endocyclic O1–P–O3 and exocyclic O4–P–O5 bond angles, which are, respectively, the smallest (about 102° on average) and the largest (about 119°) from all the O–P–O angles. On the whole, the differences in the values of endo- and exocyclic O–P–O angles are correlated with the differences in the P–O bond lengths. In all the presented anions, endocyclic ester P–O bonds (P–O1 and P–O3) are over 0.1 Å longer than the exocyclic P–O4 and P–O5 bonds.

The geometry of the dihydroxyacetone acetal moiety was analyzed in detail for the linear, non-cyclic compounds: dihydroxyacetone dimethyl acetal, $(MeO)_2$DHA (**3**)[13] and the series of five different salts of its phosphate and phenylphosphate derivatives, $(MeO)_2$DHAP and $(MeO)_2$DHAP(Ph) (**6**).[15] The crystal structure of the cyclic compound, a phenyl derivative of the compound presented here, $(MeO)_2$cDHAP(Ph) (**4**), was also reported.[14] It was shown that in the non-cyclic compounds **3** and **6**, the 2,2-dimethoxy-1,3-propandiol moiety, $(MeO)_2$DHA–, seems to be very rigid, and its conformation (described as deformed swastika-like) is independent of phosphorylation, the ionization state of the inserted phosphate group, or its additional substitution. It is very likely that such conformation of the dihydroxyacetone acetal moiety in the non-cyclic compounds is determined and stabilized by the generalized anomeric effect, whose role in carbohydrate chemistry is well known.

The dihydroxyacetone acetal moiety in the cyclic compounds **4** and **5** is forced by the cyclization, and therefore it is somewhat different than in the non-cyclic analogues. However, some common features with compounds **3** and **6** are observed: the relevant C4–O21–C2–O22 and C5–O22–C2–O21 torsion angles reveal the synclinal (nearly gauche) orientation of the methyl groups (C4 and C5) in relation to the acetal O22 and O21 oxygen atoms. Similarly, as was observed in the structures of compounds **3**, **4** and **6**, the O21–C2–C1 and O22–C2–C3 bond angles are much smaller than the other angles with their vertex on the acetal C2 atom.

2.2. Molecular geometry of the anions in 5h

The $[(MeO)_2cDHAP]^-$ anion in the ammonium salt **5h** is disordered into two positions with two different conformations of the P/O1/C1/C2/C3/O3 ring, the skew, *S*, and the chair, *C*, which are shown in Figure 2 and in Table 1. Site occupation factors determined for the two conformations (0.762(9) for *S* and 0.238(9) for *C*) reveal that as much as 76% of the anions in the crystal of ammonium salt exist in *S* conformation, which has not been observed so far in the six-membered cyclic phosphates of small compounds structurally related with that presented here. It is to mention here that C4 and C5 methyl groups in the higher occupied *S* position of the anion are in synclinal orientation in relation to the acetal O22 and O21 oxygen atoms, just like it was observed in the previously mentioned compounds **3**, **4**, **5a**–**g** and **6**.



76% in skew conformation

24% in chair conformation

Figure 2. The molecular structure of the disordered $[(MeO)_2cDHAP]^-$ anion in **5h** showing the atom numbering schemes of the separate anions, with different skew, *S* (full line; s.o.f. = 0.762(9)) and chair, *C* (open line; s.o.f. = 0.238(9)) conformations. The two anions occupy the same site in the asymmetric unit of **5h** in an approximate 3:1 ratio. Displacement ellipsoids are shown at the 20% probability level.

2.3. Crystal packing and intermolecular interactions in the crystals of cyclohexylammonium salts: (cha)[$(MeO)_2$cDHAP]·$3H_2O$ (5a) and (cha)[$(MeO)_2$cDHAP]·H_2O (5b), oxonium (H_5O_2)[$(MeO)_2$cDHAP] (5c) and ammonium NH_4[$(MeO)_2$cDHAP] (5h)

The crystal structure of oxonium salt **5c** is stabilized mainly by the network of O–H···O hydrogen bonds. The crystal packing of anhydrous ammonium salt **5h** is dominated by N–H···O contacts. In cyclohexylammonium salts **5a** and **5b** an important role is played by hydrogen bonds of the N–H···O type, which, in combination with O–H···O interactions, build the crystal lattices. Water molecules, NH_4^+ or cha$^+$ cations act as donors of these hydrogen bonds, and the role of acceptors is played mainly by exocyclic phosphate oxygen atoms O4 and O5, rarely by water molecules and only once by endocyclic phosphate oxygen atom O1. Additionally, the crystal structures of **5a–c** and **5h** are also stabilized by C–H···O interactions. The geometrical parameters of the proposed hydrogen bonds and close contacts are given in Table 3.

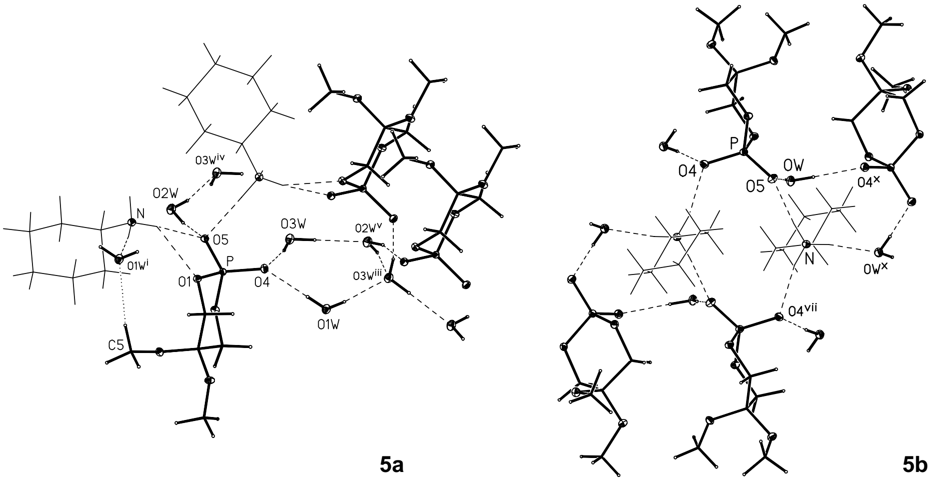
Table 3. Geometry of proposed hydrogen bonds and close C–H···O contacts for **5a–c** and **5h** (Å, °)

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
(cha)[$(MeO)_2$cDHAP]·$3H_2O$ (**5a**)				
N–H1N···O1	0.96(2)	2.55(2)	3.097(2)	116(2)
N–H1N···O5	0.96(2)	1.94(2)	2.890(2)	173(2)
N–H2N···O1W$^{\mathrm{i}}$	0.87(2)	1.98(2)	2.829(2)	167(2)
N–H3N···O5$^{\mathrm{ii}}$	0.92(2)	1.93(2)	2.856(2)	175(2)
O1W–H1W···O4	0.86(3)	1.90(3)	2.755(2)	177(2)
O1W–H2W···O3W$^{\mathrm{iii}}$	0.84(3)	2.00(3)	2.830(2)	171(2)
O2W–H3W···O3W$^{\mathrm{iv}}$	0.87(3)	1.91(3)	2.773(2)	169(2)
O2W–H4W···O5	0.89(3)	1.94(3)	2.814(2)	165(2)
O3W–H5W···O4	0.88(3)	1.88(3)	2.748(2)	170(2)
O3W–H6W···O2W$^{\mathrm{v}}$	0.87(3)	1.86(3)	2.730(2)	176(2)
C1–H1B···O2W$^{\mathrm{vi}}$	0.99(2)	2.71(2)	3.238(2)	114(2)
C3–H3B···O22$^{\mathrm{vii}}$	0.98(2)	2.50(2)	3.473(2)	175(2)
C4–H4A···O3$^{\mathrm{vii}}$	0.99(2)	2.69(2)	3.419(2)	130(2)
C4–H4B···O21$^{\mathrm{viii}}$	0.97(2)	2.47(2)	3.338(2)	150(2)
C5–H5C···O1W$^{\mathrm{i}}$	0.97(2)	2.54(2)	3.503(2)	170(2)
C11–H11···O3W$^{\mathrm{ix}}$	0.98(2)	2.67(2)	3.643(2)	175(2)
C12–H12B···O3$^{\mathrm{i}}$	1.00(2)	2.67(2)	3.489(2)	139(2)
(cha)[$(MeO)_2$cDHAP]·H_2O (**5b**)				
N–H1N···O4$^{\mathrm{vii}}$	0.91(2)	1.95(2)	2.830(2)	162(2)
N–H2N···O5	0.95(2)	1.82(2)	2.765(2)	172(2)
N–H3N···OW$^{\mathrm{x}}$	0.94(2)	1.86(2)	2.774(2)	164(2)
OW–H1W···O5	0.87(2)	1.90(2)	2.764(2)	175(2)
OW–H2W···O4$^{\mathrm{x}}$	0.83(2)	1.97(2)	2.799(2)	174(2)
C3–H3B···O22$^{\mathrm{viii}}$	0.96(2)	2.59(2)	3.548(2)	172(1)
C4–H4B···O22$^{\mathrm{viii}}$	0.97(2)	2.69(2)	3.576(2)	152(2)
C5–H5B···O21$^{\mathrm{x}}$	0.97(2)	2.72(2)	3.282(2)	117(1)
C11–H11···OW$^{\mathrm{xi}}$	0.97(2)	2.58(2)	3.348(2)	137(1)
(H_5O_2)[$(MeO)_2$cDHAP] (**5c**)				
O2W···H3W···O1W	1.21(3)	1.23(3)	2.437(2)	173(3)
O1W–H1W···O5$^{\mathrm{xii}}$	0.89(2)	1.72(2)	2.602(2)	176(2)
O1W–H2W···O4	0.91(3)	1.69(3)	2.608(2)	177(3)
O2W–H4W···O5$^{\mathrm{iv}}$	0.84(3)	1.79(3)	2.616(2)	167(3)
O2W–H5W···O4$^{\mathrm{xiii}}$	0.95(2)	1.63(2)	2.580(2)	178(3)
C3–H3B···O21$^{\mathrm{xiv}}$	0.91(2)	2.58(2)	3.417(2)	154(2)
C4–H4B···O2W$^{\mathrm{xv}}$	0.93(2)	2.73(2)	3.653(2)	169(2)
NH_4[$(MeO)_2$cDHAP] (**5h**)				
N–H1N···O4	1.02(5)	1.79(5)	2.785(4)	163(4)
N–H2N···O5$^{\mathrm{ii}}$	1.11(4)	1.70(4)	2.806(4)	173(3)
N–H3N···O5$^{\mathrm{xvi}}$	0.98(5)	1.90(5)	2.826(4)	158(4)
N–H4N···O4$^{\mathrm{xvii}}$	0.94(5)	1.96(5)	2.878(4)	163(4)
C1–H1B···O21$^{\mathrm{xviii}}$	0.98	2.68	3.641(6)	168
C10–H10A···O21$^{\mathrm{xviii}}$	0.98	2.63	3.61(2)	172

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

The overall packing schemes in the crystal lattices of hydrated cyclohexylammonium salts **5a** and **5b** are similar. The cations and anions are arranged in a way leading to the aggregation of their hydrophilic and hydrophobic groups into distinct regions in the crystals. The hydrophilic parts of the ions are linked by the N–H···O hydrogen bonds, which is illustrated in Figure 3. The voids formed between the organic cations and anions are filled by the water molecules, which participate in hydrogen bonds of cha$^+$···H_2O···anion (and anion···H_2O···anion in **5b**) type. The water molecules in **5a** are involved in additional H_2O···H_2O and H_2O···anion interactions formed between four adjacent water molecules and one phosphate O4 atom (Fig. 3). This gives rise to $R_5^3(10)$ motifs linking the adjacent [(MeO)$_2$cDHAP]$^-$ anions. Each of such rings is connected by the hydrogen bonds with three different anions.

The crystals of oxonium (**5c**) and ammonium (**5h**) salts have layered architectures, and their structures are stabilized mainly by O–H···O (in **5c**) and N–H···O (in **5h**) hydrogen bonds. The H^+ dissociated from the cyclic phosphate group is involved in Zundel ion formation, $H_5O_2{}^+$ ([H_2O···H···OH_2]$^+$),[18] with both H_2O···H^+ distances equal and amounting to 1.21(3) i 1.23(3) Å, and with O···O distance being characteristic for a very strong hydrogen bond (2.437(2) Å). $H_5O_2{}^+$ cations are located close to the phosphate groups of [(MeO)$_2$cDHAP]$^-$ anions. The hydrogen bonds of O–H···O type formed between the Zundel cations and phosphate exocyclic O4 and O5 atoms give rise to layers parallel to (001) plane in the **5c** crystal, which is shown in Figure 4. The



5a **5b**

Figure 3. Arrangement of [(MeO)$_2$cDHAP]$^-$ anions, cha$^+$ cations and water molecules in the cyclohexylammonium salts crystals **5a** and **5b**. O–H···O and N–H···O hydrogen bonds are drawn with dashed lines, C–H···O with dotted line. The cha$^+$ are shown with thin line for clarity. Symmetry codes are listed in Table 3.

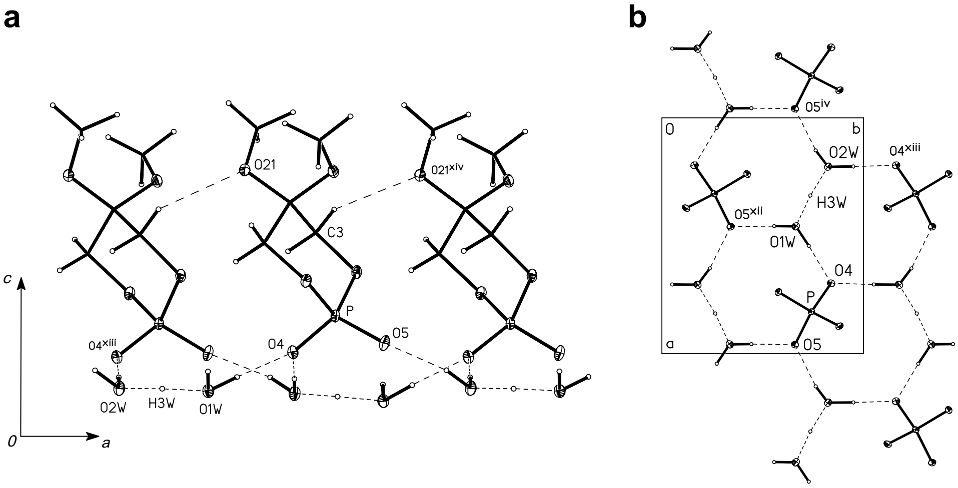


Figure 4. The layers in **5c** formed by the $H_5O_2{}^+$ and [(MeO)$_2$cDHAP]$^-$ ions joined to each other by the O–H···O and C–H···O hydrogen bonds (dashed lines). Viewed down the *b*-axis (a) and *c*-axis (b; only the phosphate groups of the anions are shown for clarity). Symmetry codes are given in Table 3.

adjacent anions within the layer are additionally linked to each other by C3–H3B···O21^{xiv} contacts, which also stabilize the layer structure (Fig. 4, Table 3). Very weak C–H···O interactions may also be observed between the methyl groups from one layer and the $H_5O_2^+$ cations from the adjacent (C4–H4B···O2W^{xv}).

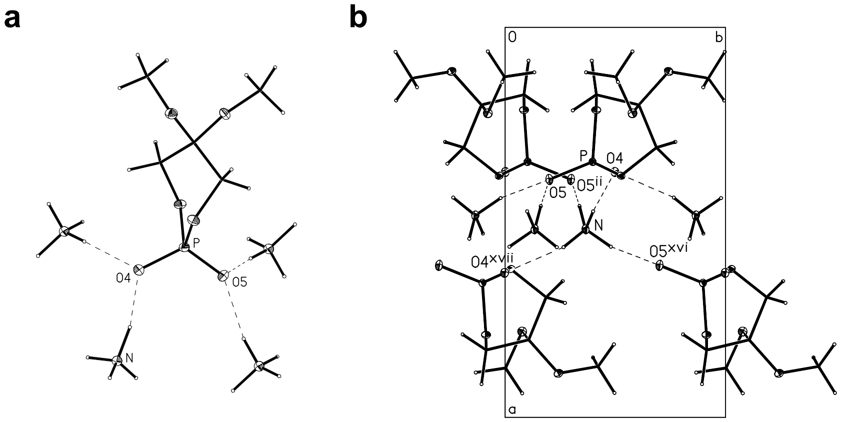


Figure 5. The crystal packing in **5h**: four symmetry-related ammonium cations in the close environment of the $[(MeO)_2cDHAP]^-$ anion (a), and the fragment of the double-layer formed by the cations and anions joined with each other by the N–H···O hydrogen bonds (b). Only anions in skew conformation (s.o.f. = 0.762(9)) are shown. Symmetry codes are listed in Table 3.

Table 4. Coordination spheres of the sodium, potassium and calcium ions in **5d**–**g** (M–O, Å) along with the shortest M···M distances (Å)

Na[(MeO)$_2$cDHAP]·2H$_2$O (**5d**)			
Na–O5	2.428(2)	Na–O1W^{ii}	2.436(2)
Na–O5^{i}	2.360(2)	Na–O2W^{i}	2.499(2)
Na–O1W	2.406(2)	Na···Na^{i,ii}	3.282(1)
Na–O2W	2.406(2)		
K[(MeO)$_2$cDHAP]·1.5H$_2$O (**5e**)			
K1–O221	2.978(3)	K2–O51	2.641(3)
K1–O31	2.830(4)	K2–O222	2.859(3)
K1–O51	3.323(3)	K2–O32	2.967(3)
K1–O51^{iii}	2.914(3)	K2–O42^{v}	3.026(3)
K1–O42^{iv}	2.847(3)	K2–O52^{v}	2.847(3)
K1–O52^{v}	2.665(3)	K2–O1W	2.821(4)
K1–O1W^{iii}	2.732(5)	K2–O2W	2.724(4)
K1–O2W^{v}	2.795(4)	K2···K1^{iii}	4.117(2)
K1···K2	4.429(2)	K2···K1^{vi}	4.143(2)
K[(MeO)$_2$cDHAP]·0.5H$_2$O (**5e′**)			
K–O1	2.836(2)	K–OW	2.854(2)
K–O5	2.850(2)	K···K^{iii}	3.694(2)
K–O4^{vii}	2.633(2)	K···K^{ix}	4.154(2)
K–O5^{viii}	2.705(2)	K···K^{viii,x}	4.844(2)
K–O5^{iii}	2.768(2)		
Ca[(MeO)$_2$cDHAP]$_2$·2H$_2$O (**5f**)			
Ca–O4,O4^{xi}	2.259(1)	Ca–OW,OW^{xi}	2.383(1)
Ca–O5^{viii,xii}	2.337(1)	Ca···Ca^{iii,xii}	5.643(1)
CaK[(MeO)$_2$cDHAP]$_3$·2H$_2$O (**5g**)			
Ca–O41	2.325(2)	K–O221^{xiii}	2.807(2)
Ca–O51^{xiii}	2.330(2)	K–O31^{xiii}	2.784(2)
Ca–O42	2.309(2)	K–O41	3.045(2)
Ca–O52^{xiv}	2.354(2)	K–O51	2.731(2)
Ca–O53	2.346(2)	K–O52^{xv}	3.135(2)
Ca–O1W	2.353(2)	K–O13	2.732(2)
Ca···K	4.040(2)	K–O53	3.093(2)
Ca···K^{xiii}	3.994(1)	K–O2W	2.734(2)

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

In the crystal of ammonium salt (**5h**), the double layers parallel to the (1 0 0) plane are observed. The double layers are formed by NH_4^+ cations and the organic anions linked with each other by the N–H···O hydrogen bonds (Fig. 5, Table 3). The phosphate exocyclic O4 and O5 atoms of each $[(MeO)_2cDHAP]^-$ anion act as acceptors of two N–H···O contacts from two, symmetry-related ammonium cations. Therefore, there are four NH_4^+ cations located in the close environment of each anion.

2.4. The environment of the $[(MeO)_2cDHAP]^-$ ions and their arrangement in the crystals of the hydrated sodium, potassium, calcium and calcium–potassium salts: Na[(MeO)$_2$cDHAP]·2H$_2$O (5d), K[(MeO)$_2$cDHAP]·1.5H$_2$O (5e), K[(MeO)$_2$cDHAP]·0.5H$_2$O (5e′), Ca[(MeO)$_2$cDHAP]$_2$·2H$_2$O (5f) and CaK[(MeO)$_2$cDHAP]$_3$·2H$_2$O (5g)

The characteristics of the crystal packing diagrams of **5d–g** are double layers built up from the organic anions

Table 5. Geometry of proposed hydrogen bonds and close C–H···O contacts for **5d–g** (Å, °)

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
Na[(MeO)$_2$cDHAP]·2H$_2$O (**5d**)				
O1W–H1W···O4$^{\mathrm{viii}}$	0.81(4)	1.97(4)	2.761(2)	165(3)
O1W–H2W···O22	0.73(3)	2.21(3)	2.941(2)	174(3)
O2W–H3W···O3$^{\mathrm{ii}}$	0.82(3)	2.10(3)	2.891(2)	162(3)
O2W–H4W···O4$^{\mathrm{xvi}}$	0.85(3)	1.94(3)	2.789(2)	174(3)
C1–H1A···O21$^{\mathrm{iii}}$	0.97(2)	2.58(2)	3.440(2)	149(2)
C3–H3A···O1W$^{\mathrm{x}}$	0.96(2)	2.65(2)	3.407(2)	136(2)
C3–H3B···O4$^{\mathrm{xvii}}$	0.95(2)	2.56(2)	3.497(3)	169(2)
C4–H4C···O4$^{\mathrm{xvii}}$	0.91(3)	2.69(3)	3.449(3)	142(3)
K[(MeO)$_2$cDHAP]·1.5H$_2$O (**5e**)				
O1W–H1W···O3W$^{\mathrm{xviii}}$	0.87(6)	1.93(6)	2.781(6)	166(6)
O1W–H2W···O32$^{\mathrm{xii}}$	0.81(5)	2.48(5)	3.116(5)	136(4)
O2W–H3W···O41$^{\mathrm{xviii}}$	0.69(5)	2.10(5)	2.785(4)	174(7)
O2W–H4W···O3W$^{\mathrm{iii}}$	1.01(5)	1.82(5)	2.822(6)	168(5)
O3W–H5W···O52$^{\mathrm{xix}}$	0.83(5)	1.97(5)	2.787(5)	165(5)
O3W–H6W···O41	0.81(5)	1.92(5)	2.705(5)	164(6)
C11–H11A···O212$^{\mathrm{xx}}$	0.99	2.54	3.519(6)	170
C41–H41C···O41$^{\mathrm{xxi}}$	0.98	2.48	3.437(6)	166
C51–H51B···O42$^{\mathrm{iv}}$	0.98	2.52	3.287(6)	135
C52–H52B···O11	0.98	2.54	3.213(6)	126
K[(MeO)$_2$cDHAP]·0.5H$_2$O (**5e′**)				
OW–H1W···O4$^{\mathrm{iii}}$	0.80(3)	2.02(3)	2.816(2)	169(4)
C1–H1A···O22$^{\mathrm{viii}}$	0.99	2.53	3.472(4)	160
C3–H3B···O21$^{\mathrm{xxii}}$	0.99	2.64	3.390(4)	133
C5–H5A···O22$^{\mathrm{viii}}$	0.98	2.68	3.346(4)	125
C5–H5C···O3$^{\mathrm{viii}}$	0.98	2.65	3.524(4)	148
Ca[(MeO)$_2$cDHAP]$_2$·2H$_2$O (**5f**)				
OW–H1W···O21$^{\mathrm{x}}$	0.84(2)	2.00(2)	2.836(2)	175(2)
OW–H2W···O1$^{\mathrm{xvii}}$	0.82(2)	1.99(2)	2.794(2)	166(2)
C3–H3B···O22$^{\mathrm{xxiii}}$	0.92(2)	2.60(2)	3.523(2)	176(2)
C5–H5C···O5$^{\mathrm{xvi}}$	0.99(2)	2.50(2)	3.230(2)	130(2)
C5–H5C···OW$^{\mathrm{vii}}$	0.99(2)	2.62(2)	3.519(2)	151(2)
CaK[(MeO)$_2$cDHAP]$_3$·2H$_2$O (**5g**)				
O1W–H1W···O43	0.77(3)	2.07(3)	2.793(3)	157(3)
O1W–H2W···O2W$^{\mathrm{xxiv}}$	0.83(3)	1.92(3)	2.734(3)	166(3)
O2W–H3W···O42$^{\mathrm{xxv}}$	0.76(3)	2.29(3)	2.981(3)	152(3)
O2W–H4W···O43$^{\mathrm{xiii}}$	0.92(3)	1.94(3)	2.835(3)	163(3)
C11–H11A···O213$^{\mathrm{xiii}}$	0.97(3)	2.48(2)	3.049(3)	118(2)
C41–H41B···O43$^{\mathrm{xxvi}}$	1.00(3)	2.61(3)	3.605(4)	172(2)
C51–H51A···O223$^{\mathrm{xxv}}$	0.97(2)	2.42(3)	3.358(3)	162(2)
C32–H32A···O53	1.00(2)	2.47(3)	3.409(3)	156(2)
C43–H43C···O223$^{\mathrm{xxvii}}$	0.95(3)	2.56(3)	3.298(3)	134(2)
C53–H53B···O32$^{\mathrm{xv}}$	0.96(3)	2.71(3)	3.437(4)	133(2)

Symmetry codes: (ii) $-x+1/2, y-1/2, -z+1/2$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, y, z-1$; (vii) $x, y-1, z$; (viii) $x, -y+1, z-1/2$; (x) $x, -y+1, z+1/2$; (xii) $-x+1, -y+1, -z+2$; (xiii) $-x+3/2, y-1/2, -z+1/2$; (xv) $x-1/2, -y-1/2, z-1/2$; (xvi) $x, -y, z-1/2$; (xvii) $x, y+1, z$; (xviii) $-x+1, y+1/2, -z+3/2$; (xix) $-x+1, y-1/2, -z+3/2$; (xx) $-x, -y+1, -z+1$; (xxi) $x, -y+1/2, z-1/2$; (xxii) $x, -y+2, z+1/2$; (xxiii) $-x+1/2, -y+1/2, -z+1$; (xxiv) $x+1/2, -y-1/2, z+1/2$; (xxv) $-x+3/2, y+1/2, -z+1/2$; (xxvi) $-x+2, -y, -z+1$; (xxvii) $-x+1, -y, -z+1$.

and water molecules coordinating to the metal cations (Table 4). The overall structures of the layers are similar in all the salts presented here. Their interior is filled with metal cations and the [(MeO)$_2$cDHAP]$^-$ anions are located on both sides of the double layers, locating their phosphate groups inward (towards the metal ions) and the methoxy groups to the interlayer exterior. The result of such arrangement of the individual components in the crystal networks is the aggregation of the hydrophilic and hydrophobic groups into two distinct regions in crystals **5d**–**g**. The crystal structures are additionally stabilized by the networks of O–H···O and C–H···O hydrogen bonds, of the geometrical parameters given in Table 5.

In the crystal of sodium salt **5d**, each Na$^+$ ion is coordinated by two symmetry-related [(MeO)$_2$cDHAP]$^-$ anions and by four water molecules. However, the same organic anion is coordinated (by its exocyclic phosphate O5 atom) to two different sodium cations in a manner as shown in Figure 6. The Na–O distances in sodium coordination polyhedron (of a geometry of distorted octahedron) are in the range of 2.360(2)–2.499(2) Å (Table 4). The anions as well as water molecules coordinate simultaneously to two adjacent sodium cations, which leads to polymeric chains along the *b*-axis, with Na···Na distances of 3.282(1) Å (Fig. 6). The structure of the chain is stabilized by O–H···O and C–H···O hydrogen bonds involving both water molecules, phosphate endo- and exocyclic (O3 and O4) oxygen atoms as well as the acetal O22 (Table 5). The adjacent chains are joined with each other by the O–H···O interactions formed between water molecules from the one chain and phosphate, exocyclic O4 atoms from another (O1W–H1W···O4^{viii} and O2W–H4W···O4^{xvi}). These hydrogen bonds, in combination with the C–H···O contacts, give rise to double layers parallel to the (1 0 0) plane.

Quite different is the coordination manner in the crystals of two potassium salts K[(MeO)$_2$cDHAP]·1.5H$_2$O (**5e**) and K[(MeO)$_2$cDHAP]·0.5H$_2$O (**5e′**). Two crystallographically independent [(MeO)$_2$cDHAP]$^-$ anions in **5e** coordinate to the metal cations by the endo- and exocyclic phosphate oxygen atoms (O31, O51 in **5e-1** and O32, O42, O52 in **5e-2**), as well as by the acetal O atoms (O221 in **5e-1** and O222 in **5e-2**) (Fig. 7). However, only phosphate O atoms (exocyclic O4 and O5 and endocyclic O1) coordinate to the potassium cations in **5e′** (Fig. 7). The coordination spheres of the three different K$^+$ ions in **5e** and **5e′** are also different: the coordination numbers of two crystallographically independent metal cations in **5e**, K1 and K2, and the K atom in **5e′** are 8, 7 and 6, respectively (Fig. 8, Table 4). The polyhedron of atom K1 is built up from six oxygen atoms from four different organic anions and two O atoms from water molecules, and that of K2 is formed by five oxygen atoms from three different [(MeO)$_2$cDHAP]$^-$ anions and two from water molecules. The coordination environment of K$^+$ ion in **5e′** is composed of five oxygen atoms from four different organic anions and one from a water molecule (Fig. 8, Table 4). It is to be mentioned here that some of the oxygen atoms coordinate to two or even three different potassium cations simultaneously (Fig. 7): O5 in **5e-1** and **5e′** coordinates to three K atoms, O4 and O5 in **5e-2** coordinates to two different K$^+$. Packing diagrams revealing the differences in the overall structures of **5e**

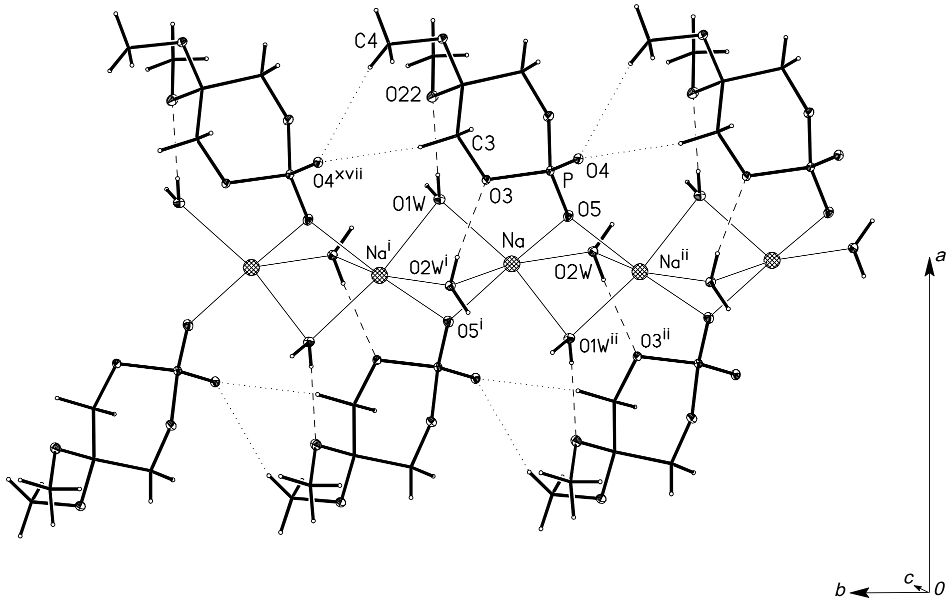


Figure 6. Polymeric chains along the *b*-axis formed by the coordination of [(MeO)$_2$cDHAP]$^-$ anions and water molecules to sodium cations in **5d**. O–H···O and C–H···O hydrogen interactions stabilizing the chain structure are shown with dashed and dotted lines, respectively. Symmetry codes are listed in Tables 4 and 5.

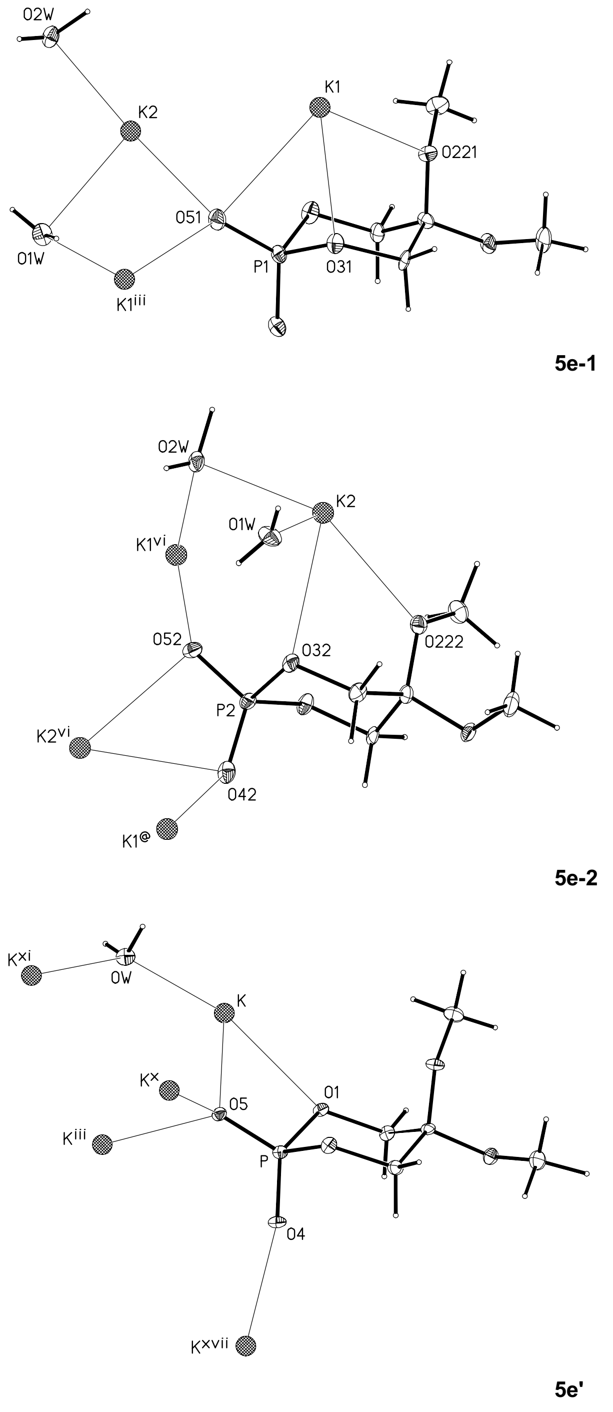


Figure 7. The environment of the $[(MeO)_2cDHAP]^-$ anions in potassium salts: two crystallographically independent anions **5e-1** and **5e-2** in $K[(MeO)_2cDHAP]{\cdot}1.5H_2O$ (**5e**) and one anion in $K[(MeO)_2cDHAP]{\cdot}0.5H_2O$ (**5e′**). Displacement ellipsoids are shown at the 30% probability level. The metal cations are shown as circles of arbitrary radii. Symmetry codes are given in Tables 4 and 5. (@) *x*, *y*, *z* + 1.

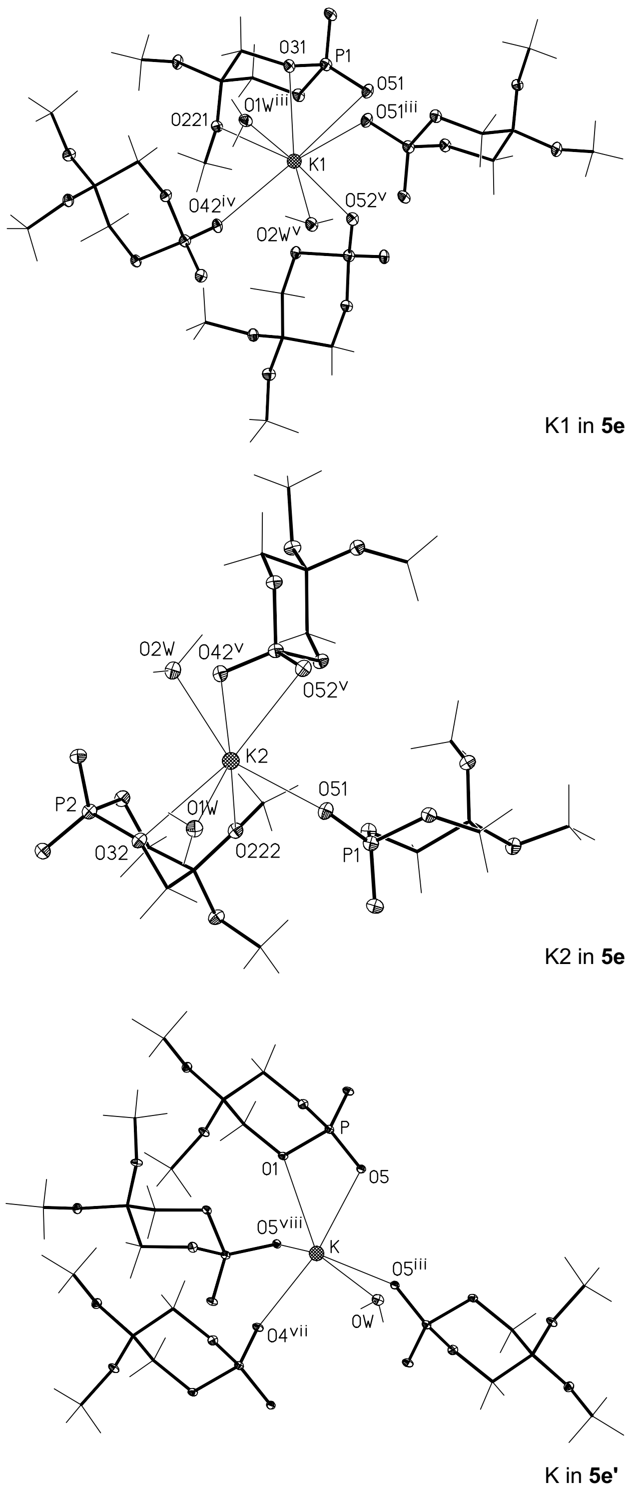


Figure 8. Coordination environment of two crystallographically independent K1 and K2 in $K[(MeO)_2cDHAP]{\cdot}1.5H_2O$ (**5e**) and one K^+ ion in $K[(MeO)_2cDHAP]{\cdot}0.5H_2O$ (**5e′**). Symmetry codes are given in Table 4.

and **5e′** crystals are shown in Figure 9. K–O and K···K distances are listed in Table 4.

The $[(MeO)_2cDHAP]^-$ anions in the calcium salt **5f** coordinate to the metal cation by both exocyclic oxygen atoms O4 and O5. To every Ca^{2+} ion (located on a two-fold axis) coordinate four organic anions (two of them by the O4 atoms, two others by O5) and two water molecules. The geometry of coordination polyhedron is close to octahedral with the Ca–O distances from 2.259(1) to 2.383(1) Å (Table 4). Every [(MeO)$_2$-cDHAP]$^-$ anion is coordinated to two adjacent calcium cations (by its O4 atom to one of them and by O5 to another) in a manner as shown in Figure 10. This results in polymeric chains along the *c*-axis of the **5f** crystal, with the Ca···Ca distances of 5.643(1) Å. Their structure is stabilized by OW–H1W···O21^{x} hydrogen bonds formed between water molecules and acetal oxygen atoms (symmetry codes and geometry of proposed hydrogen bonds are given in Table 5). Furthermore, the water molecules are also involved in hydrogen bonding with the phosphate endocyclic O1 atoms of the anions from different, symmetry-related chains (OW–H2W···O1^{xvii}). Additionally, the adjacent chains are joined with each other by the weak interactions of C–H···O type. All this gives rise to a double-layered architecture for the **5f** crystal, with the layers parallel to the (1 0 0) plane.

In the crystal of mixed, calcium–potassium salt **5g**, each from three crystallographically independent [(MeO)$_2$cDHAP]$^-$ anions coordinates to the metal cation in a different manner, as shown in Figure 11. The anions denoted as **5g-2** and **5g-3** utilize two phosphate oxygen atoms (**5g-2**: O42, O52, and **5g-3**: O13, O53) to coordinate to both K$^+$ and Ca^{2+}. However, the **5g-1** anion coordinates by as many as four different O atoms, three phosphate and one acetal: O31, O41, O51 and O221. Such differences observed in the chemical environments of the three anions and the way they coordinate to the metal centres may be the reason of the differences in deformation of the chair conformation

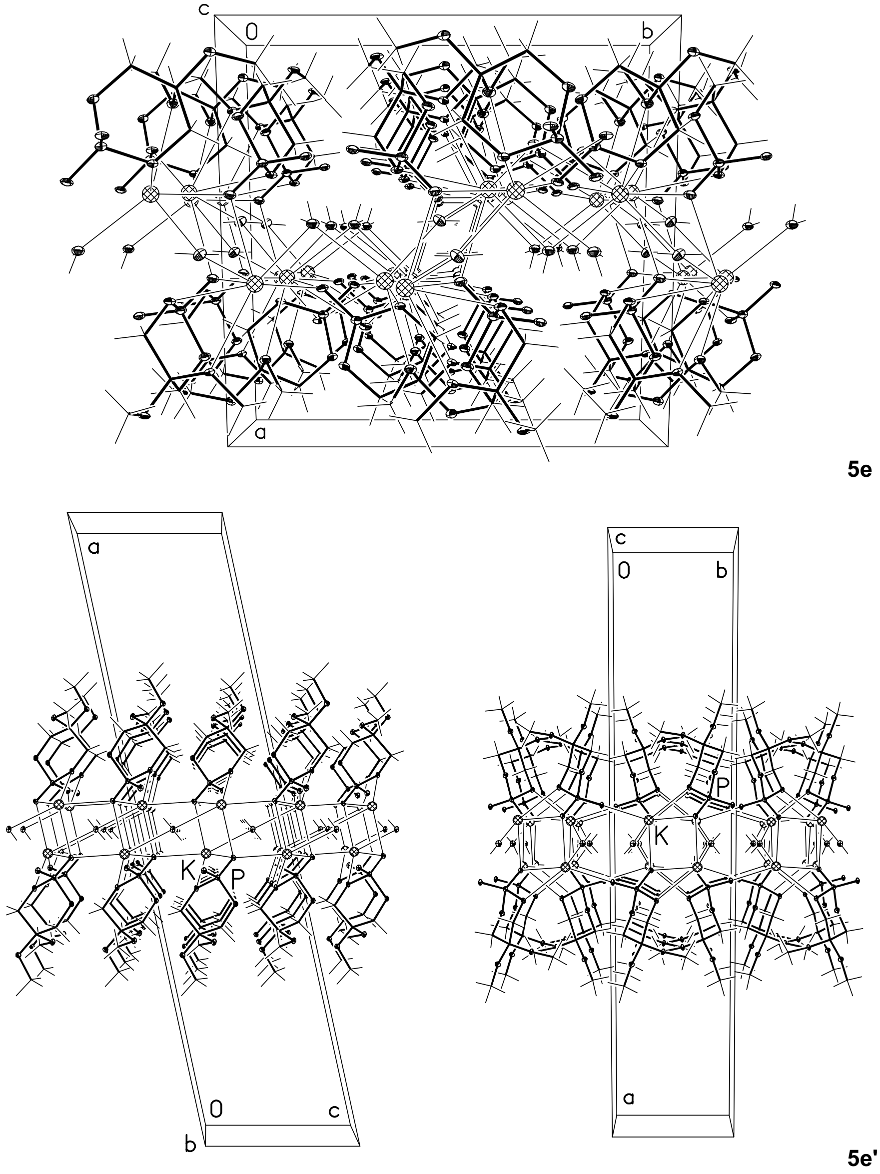


Figure 9. Packing diagrams for the potassium salts crystals: **5e** (viewed down the *c*-axis) and **5e′** (viewed down the *b*-axis and *c*-axis), showing the layer architecture of the crystals. Non-coordinating to K$^+$ ions O3W water molecules in **5e** are omitted for clarity.

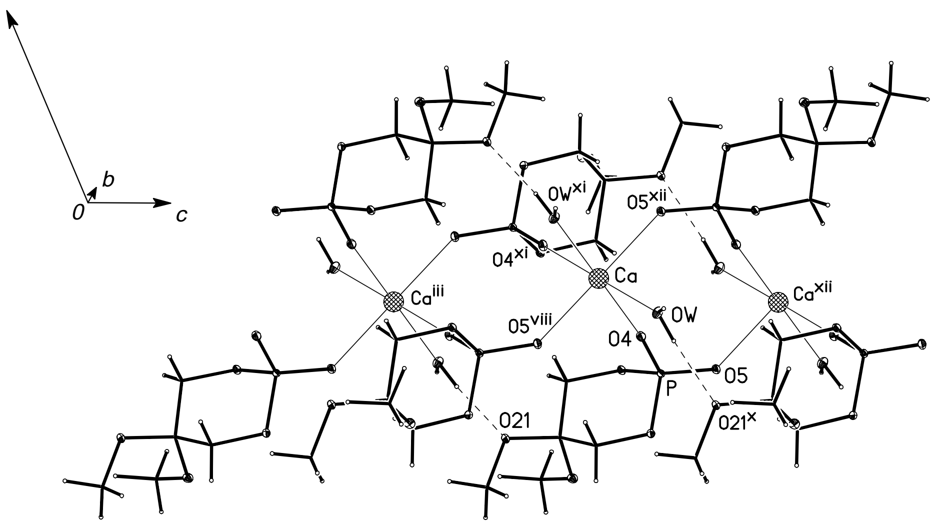


Figure 10. Polymeric chains along the *c*-axis formed by the coordination of $[(MeO)_2cDHAP]^-$ anions and water molecules to calcium cations in **5f**. OW–H1W···O21^x hydrogen bonds stabilizing the chain structure are shown with dashed lines. Symmetry codes are listed in Tables 4 and 5.

of six-membered 1,3,2-dioxaphosphorinane ring (P/O1/C1/C2/C3/O3), discussed earlier.

Each Ca^{2+} ion in the **5g** crystal is coordinated by five organic anions (two symmetry-related **5g-1**, two **5g-2** and one **5g-3**) and one water molecule. The K^+ ion is coordinated by four $[(MeO)_2cDHAP]^-$ anions (**5g-2**, **5g-3** and two symmetry-related **5g-1**) and by one water molecule. All the five organic anions in the environment of calcium cation act as monodentate ligands for Ca^{2+}. However, three of four anions coordinating the potassium cation chelate K^+ in a bidentate manner. The Ca–O distances in a slightly deformed octahedral coordination sphere of calcium cation are in the range of 2.309(2)–2.354(2) Å (Table 4, Fig. 12), while the K–O distances in the coordination polyhedron of potassium cation (coordination number = 8) are from 2.731(2) to 3.135(2) Å (Table 4).

The adjacent Ca^{2+} and K^+ ions, along with the coordinating $[(MeO)_2cDHAP]^-$ anions, are arranged in the chains parallel to the *b*-axis in the crystal of **5g** (Fig. 13a). The Ca···K and Ca···K^{xiii} distances within the chain are almost equal and amount to 4.040(2) and 3.994(1) Å. The **5g-1** and **5g-3** anions coordinate to a single $[Ca\cdots K]_n\cdots Ca$ chain, while the **5g-2** anions fulfill a function as linkers between two adjacent chains. This gives rise to layers parallel to the $(10\bar{1})$ plane of **5g**, the simplified structure of which (with **5g-1**,**3** omitted) is shown in Figure 13b.

3. Conclusions

The dimethyl acetal of cyclic dihydroxyacetone phosphate, $(MeO)_2cDHAP$, the cDHAP precursor, was synthesized and crystallized in the form of nine different salts with both organic and inorganic cations: (cha)$[(MeO)_2cDHAP]\cdot 3H_2O$ (**5a**), (cha)$[(MeO)_2cDHAP]\cdot H_2O$ (**5b**), $(H_5O_2)[(MeO)_2cDHAP]$ (**5c**), $Na[(MeO)_2cDHAP]\cdot 2H_2O$ (**5d**), $K[(MeO)_2cDHAP]\cdot 1.5H_2O$ (**5e**), $K[(MeO)_2cDHAP]\cdot 0.5H_2O$ (**5e′**), $Ca[(MeO)_2cDHAP]_2\cdot 2H_2O$ (**5f**), $CaK[(MeO)_2cDHAP]_3\cdot 2H_2O$ (**5g**) and $NH_4[(MeO)_2cDHAP]$ (**5h**). This allowed us to discuss the geometry of $[(MeO)_2cDHAP]^-$ anions in detail, mainly the conformation of the P/O/C/C/C/O 1,3,2-dioxaphosphorinane ring, and compare it with that of the phenyl derivative, $(MeO)_2cDHAP(Ph)$ (**4**). In addition, the chemical environment of the anions, as well as the arrangement mode in the crystal lattices, was also presented. The X-ray structures reported for all the nine compounds revealed that the dioxaphosphorinane ring in **5a**–**g** exists in the chair conformation, in generally only slightly flattened, in contrast to the deformations observed in the analogous phenyl derivative **4**. However, the anion in **5h** is disordered and exists in two conformations, 76% of which are in the skew conformation, which has never been observed so far in compounds of related structure.

The arrangement of the individual ions in the crystal networks of all the nine $(MeO)_2cDHAP$ salts presented here (**5a**–**h**) results in aggregation of the hydrophilic and hydrophobic groups into two distinct regions in the crystals similar to that which was observed in the crystals of the acyclic analogue, **6a**–**e**. The characteristic of the crystal packing mode of **5a**–**h** is the layer architecture, with well-defined double layers formed in the salts with inorganic cations, **5d**–**g**.

Five different crystals of the salts containing inorganic cations: sodium **5d**, potassium **5e**, **5e′**, calcium **5f** and calcium and potassium together **5g**, allowed us to establish the characteristics of the coordination of

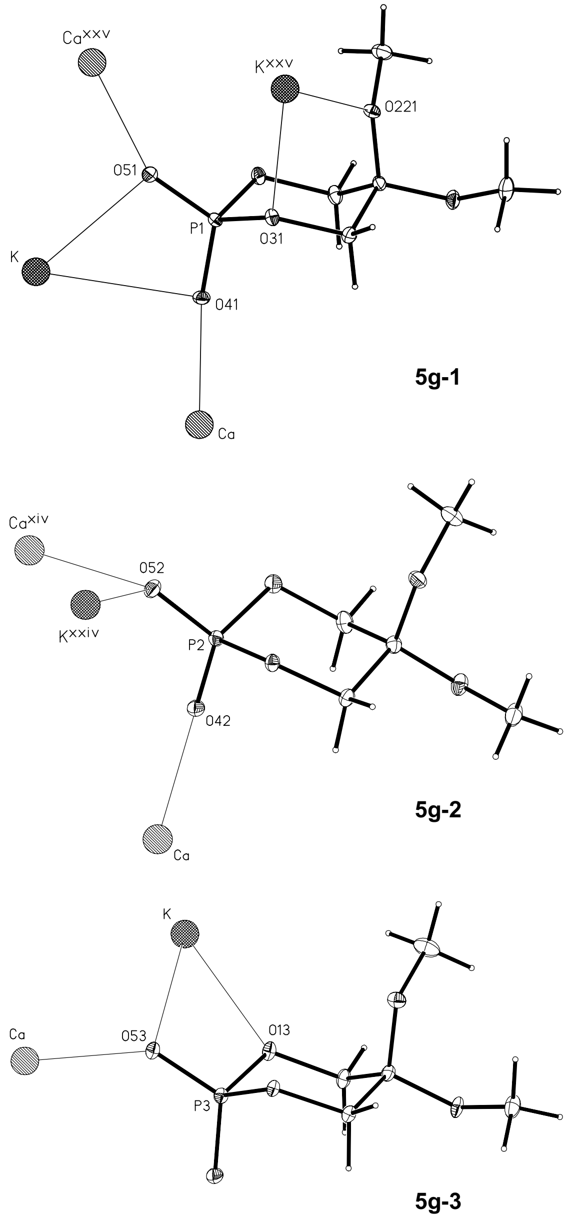


Figure 11. The environment of the three crystallographically independent $[(MeO)_2cDHAP]^-$ anions in calcium–potassium salt **5g**. Displacement ellipsoids are shown at the 30% probability level. The metal cations are shown as circles of arbitrary radii. Symmetry codes are given in Tables 4 and 5.

$[(MeO)_2cDHAP]^-$ anions depending on the metal cation. It is evident that the coordination mode is similar in both the sodium and calcium environment (**5d**,**f**,**g**), where only exocyclic phosphate O atoms are involved, and polymeric chains, linked together to form layers, are observed (as in **5d**,**f**). There are only two metal cations in the close environment of the anions in **5d**,**f**. In the case of potassium-containing salts **5e**,**e′**,**g**, the coordination mode is much more complex, and usually involves three or four cations bonded to the anions. All that is reflected in the quantity and type of a single anion oxygen atoms acting in bonding to the cations: only one or two exocyclic phosphate O atoms coordinating to sodium and calcium, respectively, in the **5d**, and **5f**,**g** crystals, compared to three O atoms in **5e′**, and as much as four (both exo-, endocyclic and even acetal O atoms) coordinating to K^+ in **5e** and **5g**. Additionally, it is worth mentioning that the respective $[(MeO)_2cDHAP]^-$ anions act as monodentate groups for both Na^+ and Ca^{2+} (also in the calcium–potassium salt, **5g**), whereas they chelate K^+ ions with two or even three O atoms in both potassium **5e**, **5e′**, and calcium–potassium salts (anions **5g-1**, **5g-3**). Such significantly higher affinity of the $[(MeO)_2cDHAP]^-$ anions to potassium cations, compared with the other metal ions, is similar to that observed in the non-cyclic analogue, $[(MeO)_2DHAP]^{2-}$, which coordinates to only two Na^+ and to as much as seven different K^+ ions.[15]

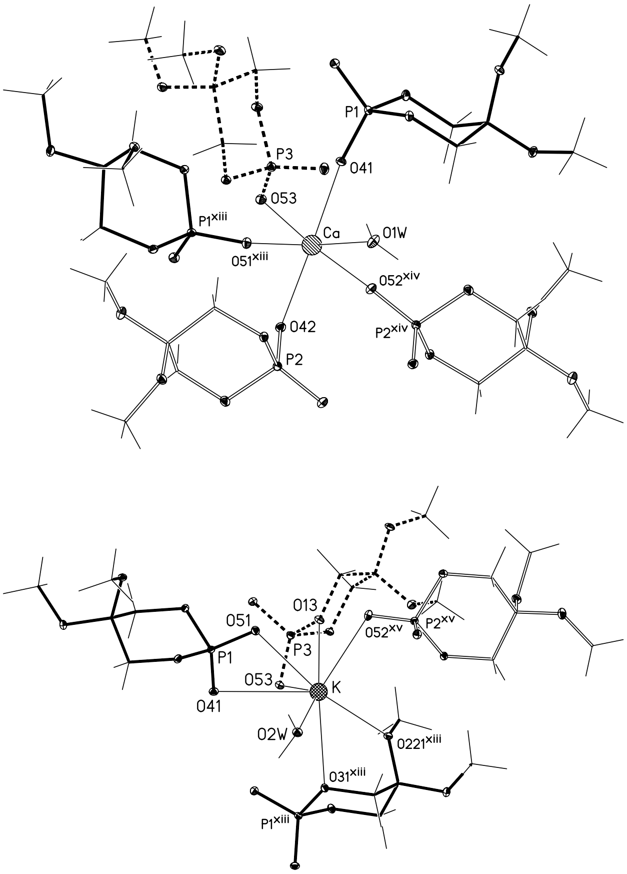


Figure 12. Coordination environment of calcium and potassium cations in $CaK[(MeO)_2cDHAP]_3 \cdot 2H_2O$ (**5g**). Three crystallographically independent anions are drawn with different line types: **5g-1**, solid; **5g-2**, open; **5g-3**, solid dashed. Symmetry codes are given in Table 4.

4. Experimental

4.1. General experimental procedures

$Ba(OH)_2 \cdot 8H_2O$ (Avocado) was recrystallized from water before use (if necessary). N_2 was passed through the

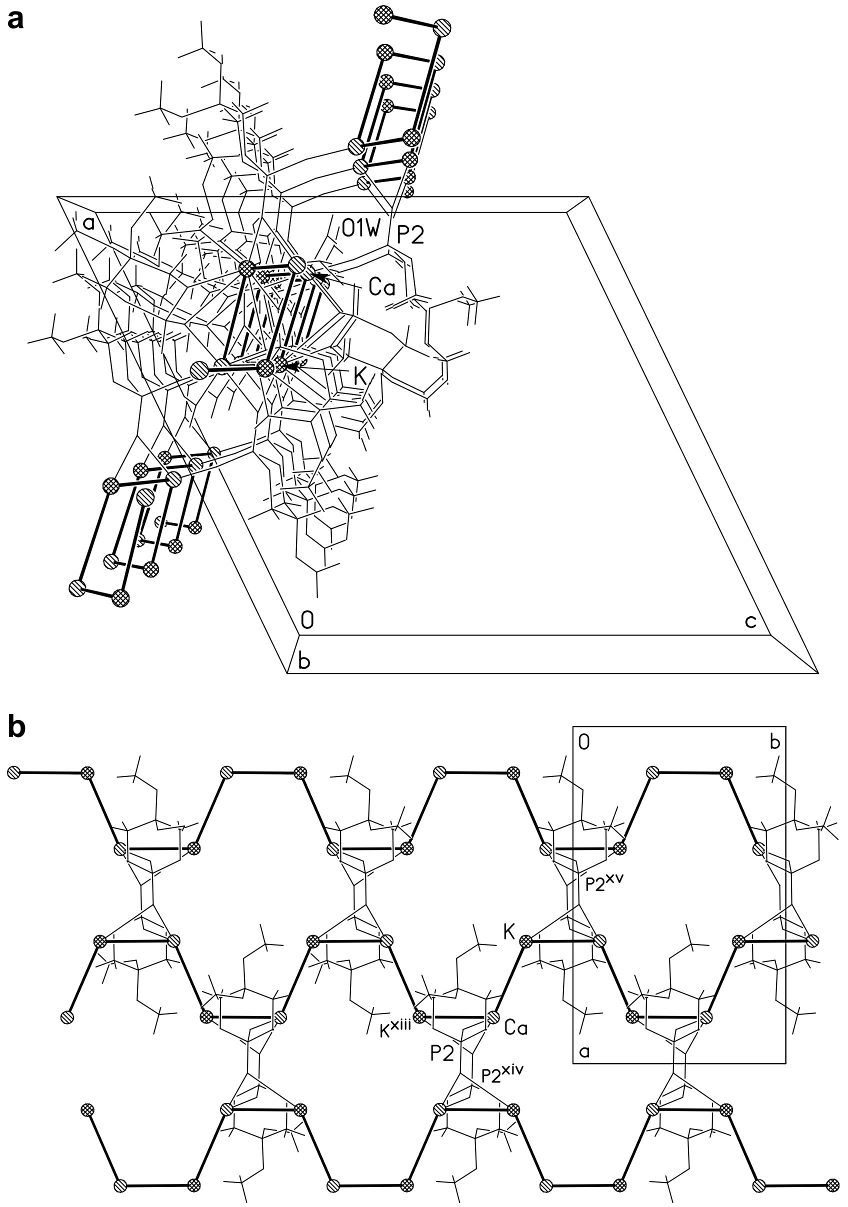


Figure 13. (a) A packing diagram for **5g**, viewed down the *b*-axis, showing the layer architecture and the chains built up from the alternate arrangement of the Ca^{2+} and K^+ ions, **5g-1**, **5g-2** and **5g-3** $[(MeO)_2cDHAP]^-$ ions and water molecules coordinating to them. (b) The arrangement of the metal cations within the layer parallel to $(10\bar{1})$ plane, along with the **5g-2** anions joining the adjacent three chains into the layer. The remaining anions and water molecules are omitted for clarity. Symmetry codes are given in Table 4.

distilled water before its use in the reactions with barium hydroxide. Cyclohexylamine (cha) was purchased from Aldrich. Bis(cyclohexylammonium) sulfate, $(cha)_2SO_4$, was synthesized from cyclohexylamine and H_2SO_4.[19] Dowex 50-H^+ × 2–100 (Serva) was regenerated after use by washing it with about 100 mL of 3–4 M HCl and then with water until the pH was neutral.

Melting points were recorded on a Boëtius PHMK (VEB Analytik Dresden) melting point apparatus and are uncorrected. NMR spectra were recorded using a Bruker Avance 500 spectrometer. Mass spectra were recorded on a Finnigan MAT TSQ 700 spectrometer.

4.2. Synthesis of compound 5a

$Ba(OH)_2$ solution (400 mL, 0.1 M) was heated up to 96–98 °C. To this vigorously stirred solution, compound **4** (4.0 g, 14.6 mmol), was added. Two layers formed as **4** dissolved, and then disappeared after heating the mixture for 20 min, indicating the completion of the hydrolysis of phenyl ester. The mixture was then cooled to room temperature, and a solution of $(cha)_2SO_4$ (0.32 g, 1.1 mmol, 10% excess) in 7 mL of water was added. The mixture was stirred for 15 min and then the $BaSO_4$ that precipitated was removed by centrifugation (~5000 rpm) and washed several times with small amounts of water. The filtrate and the washings were evaporated under reduced pressure ($T < 40$ °C). The solid residue was dissolved in boiling abs EtOH, and the mixture was filtered on a Büchner funnel in order to remove the excess of $(cha)_2SO_4$ and the inorganic phosphates that possibly formed. If the filtrate was still cloudy, the methods of purification described by Ferroni et al.[12] were applied. Pure compound **5** was dissolved in small amount of water (about 0.5 mL) and the pH of the solution was adjusted to pH 10 with cha. Acetone (1.5 mL) was added, and the mixture was moved to a refrigerator (~7 °C) for 10 h. The crystals of compound **5** so obtained were filtered on a Büchner funnel, washed several times with small amounts of acetone and allowed to air dry (195 mg, 55%). Mp 135–138 °C. ^{1}H NMR (500 MHz; D_2O, Me_4Si; 297 K) δ 4.11 (4H, d, *J* 12.2 Hz), 3.26 (6H, s); ESIMS *m*/*z* 197 (M^-).

4.3. Preparation of the compounds. Crystallization

4.3.1. (cha)[(MeO)$_2$cDHAP]·3H$_2$O (5a) and (cha)[(MeO)$_2$cDHAP]·H$_2$O (5b). Water (100 µL) was added to 100 mg of compound **5**, and the vessel was moved to the temperature of −18 °C. Very small crystals so obtained were used as the crystal nuclei in further recrystallizations from water (for **5a**) and EtOH or 2-PrOH (for **5b**) at 4–7 °C, which gave large, colourless parallelepipeds of **5a** or **5b** (mp 145–150 °C), respectively, with different numbers of water molecules. Fragments of

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

	(cha)[ANION]·3H$_2$O (**5a**)	(cha)[ANION]·H$_2$O (**5b**)	(H_5O_2)[ANION] (**5c**)	Na[ANION]·2H$_2$O (**5d**)
Crystal data				
Empirical formula	$C_{11}H_{30}NO_9P$	$C_{11}H_{26}NO_7P$	$C_5H_{15}O_8P$	$C_5H_{14}NaO_8P$
Formula weight (g mol^{-1})	351.33	315.30	234.14	256.12
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$Pca2_1$	$C2/c$
a (Å)	8.430(2)	14.126(3)	8.497(2)	27.654(4)
b (Å)	25.516(4)	12.449(3)	7.176(2)	6.448(2)
c (Å)	8.269(2)	8.883(2)	17.613(3)	11.988(3)
β (°)	95.14(3)	99.89(3)		96.40(2)
V (Å^3)	1771.5(7)	1538.9(6)	1073.9(4)	2124.3(9)
Z	4	4	4	8
D_{calc} (g cm^{-3})	1.317	1.361	1.448	1.602
μ (mm^{-1})	1.761	0.208	0.274	0.321
F(000)	760	680	496	1072
Crystal size (mm)	0.33 × 0.17 × 0.09	0.38 × 0.13 × 0.09	0.38 × 0.35 × 0.15	0.35 × 0.26 × 0.09
Crystal colour	Colourless	Colourless	Colourless	Colourless
Crystal form	Parallelepiped	Parallelepiped	Thick plate	Plate
Data collection				
Radiation type, λ (Å)	Cu K$_\alpha$, 1.5418	Mo K$_\alpha$, 0.71073	Mo K$_\alpha$, 0.71073	Mo K$_\alpha$, 0.71073
T (K)	100(2)	100(2)	100(2)	100(2)
θ Range (°)	3.46–75.96	3.01–37.07	3.66–37.48	3.25–36.45
h,*k*,*l* range	$-10 \leqslant h \leqslant 10$	$-23 \leqslant h \leqslant 23$	$-14 \leqslant h \leqslant 14$	$-36 \leqslant h \leqslant 45$
	$-31 \leqslant k \leqslant 31$	$-20 \leqslant k \leqslant 20$	$-12 \leqslant k \leqslant 12$	$-5 \leqslant k \leqslant 8$
	$-9 \leqslant l \leqslant 5$	$-11 \leqslant l \leqslant 15$	$-20 \leqslant l \leqslant 28$	$-15 \leqslant l \leqslant 15$
Absorption correction	Analytical	—	—	Analytical
T_{min}/T_{max}	0.635/0.858	—	—	0.904/0.970
Measured reflections	19388	25457	16045	8343
Independent reflections	3539	7390	4097	3099
Observed refl. ($I > 2\sigma(I)$)	3227	4834	3635	2334
R_{int}	0.0337	0.0419	0.0286	0.0475
Refinement				
Refinement on	F^2	F^2	F^2	F^2
Data/restraints/parameters	3539/0/320	7390/0/285	4097/0/186	3099/0/192
$R_1; wR_2 (F_o^2 > 2\sigma(F_o^2))$	0.0382; 0.1050	0.0365; 0.0708	0.0321; 0.0738	0.0483; 0.1175
$R_1; wR_2$ (all data)	0.0409; 0.1079	0.0698; 0.0754	0.0385; 0.0756	0.0653; 0.1234
GooF = *S*	1.047	1.032	1.035	1.043
Weighting parameter *a*/*b*	0.0826/0.2294	0.0300/0.0	0.0458/0.0	0.0769/ 0.0
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.35/−0.40	0.48/−0.32	0.45/−0.21	0.83/−0.35
Flack parameter	—	—	−0.05(6)	—

ANION = (MeO)$_2$cDHAP.

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \sqrt{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]}$; weighting scheme: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 7. Experimental data for **5e**–**h**

	K[ANION]·1.5H_2O (**5e**)	K[ANION]·0.5H_2O (**5e′**)	Ca[ANION]$_2$·2H_2O (**5f**)	CaK[ANION]$_3$·2H_2O (**5g**)	NH_4[ANION] (**5h**)
Crystal data					
Empirical formula	$C_5H_{13}KO_{7.50}P$	$C_5H_{11}KO_{6.50}P$	$C_{10}H_{24}CaO_{14}P_2$	$C_{15}H_{34}CaKO_{20}P_3$	$C_5H_{14}NO_6P$
Formula weight (g mol^{-1})	263.22	245.21	470.31	706.51	215.14
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/c$
a (Å)	14.033(3)	34.593(6)	24.540(3)	17.667(3)	12.258(5)
b (Å)	13.923(4)	6.995(3)	8.360(2)	10.059(2)	6.869(3)
c (Å)	11.396(4)	8.187(3)	9.736(2)	17.734(3)	11.438(5)
β (°)	108.33(3)	102.20(3)	111.54(2)	115.77(3)	97.63(3)
V (Å^3)	2113.6(11)	1936.3(11)	1857.9(6)	2838.1(9)	954.6(7)
Z	8	8	4	4	4
D_{calc} (g cm^{-3})	1.654	1.682	1.681	1.653	1.497
μ (mm^{-1})	0.670	0.717	0.580	0.622	2.655
F(000)	1096	1016	984	1472	456
Crystal size (mm)	0.12 × 0.02 × 0.02	0.28 × 0.24 × 0.02	0.30 × 0.10 × 0.03	0.30 × 0.16 × 0.03	0.19 × 0.03 × 0.02
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colourless
Crystal form	Needle	Plate	Plate	Plate	Plate
Data collection					
Radiation type, λ (Å)	Mo K_α, 0.71073	Mo K_α, 0.71073	Mo K_α, 0.71073	Mo K_α, 0.71073	Cu K_α, 1.5418
T (K)	100(2)	100(2)	100(2)	100(2)	240(2)
θ Range (°)	2.93–26.00	2.97–26.00	3.21–37.41	3.07–28.00	3.64–76.40
h,k,l range	$-17 \leqslant h \leqslant 17$	$-42 \leqslant h \leqslant 42$	$-41 \leqslant h \leqslant 41$	$-23 \leqslant h \leqslant 22$	$-15 \leqslant h \leqslant 13$
	$-17 \leqslant k \leqslant 17$	$-8 \leqslant k \leqslant 7$	$-14 \leqslant k \leqslant 14$	$-13 \leqslant k \leqslant 13$	$-8 \leqslant k \leqslant 5$
	$-10 \leqslant l \leqslant 14$	$-10 \leqslant l \leqslant 9$	$-14 \leqslant l \leqslant 16$	$-23 \leqslant l \leqslant 23$	$-12 \leqslant l \leqslant 14$
Absorption correction	Multi-scan	Analytical	Analytical	Analytical	Analytical
T_{min}/T_{max}	0.909/1.000	0.845/0.977	0.862/0.978	0.868/0.983	0.753/0.945
Measured reflections	22036	6105	15337	25288	7857
Independent reflections	4149	1895	4530	6794	1890
Observed reflections ($I > 2\sigma(I)$)	1814	1330	2877	4568	1188
R_{int}	0.1949	0.0452	0.0629	0.0584	0.0569
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
Data/restraints/parameters	4149/0/288	1895/0/129	4530/0/171	6794/0/497	1890/0/174
R_1; $wR_2(F_o^2 > 2\sigma(F_o^2))$	0.0490; 0.0671	0.0395; 0.0919	0.0417; 0.0548	0.0413; 0.0589	0.0468; 0.1193
R_1;wR_2 (all data)	0.1453; 0.0790	0.0653; 0.0978	0.0855; 0.0590	0.0840; 0.0652	0.0746; 0.1378
GooF = S	1.006	1.056	1.044	1.016	1.007
Weighting parameter a/b	0.0/0.0	0.0515/0.0	0.0100/0.0	0.02/0.0	0.07/0.0
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.50/−0.41	0.75/−0.31	0.49/−0.47	0.35/−0.34	0.25/−0.29

ANION = $(MeO)_2$cDHAP.

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \sqrt{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]}$; weighting scheme: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

the crystals so obtained were used for the X-ray diffraction measurements.

4.3.2. $(H_5O_2)[(MeO)_2cDHAP]$ (5c). A solution of compound **5a** (100 mg, 0.28 mmol) in a minimal quantity of water was passed through an ion-exchange column (Dowex 50-H^+). The acidic solution was evaporated under a nitrogen stream yielding a syrup that was subjected to crystallization at −18 °C in order to prevent the hydrolysis of the acetal group. Water (100 μL) was added to the small crystals of **5c** so obtained, and the crystallization was allowed to continue at 4 °C. Large, colourless parallelepipeds of **5c** were obtained after three days. The crystals were hygroscopic and were measured immediately.

4.3.3. $Na[(MeO)_2cDHAP]\cdot 2H_2O$ (5d), $K[(MeO)_2cDHAP]\cdot 1.5H_2O$ (5e), $[(MeO)_2cDHAP]\cdot 0.5H_2O$ (5e′), $Ca[(MeO)_2cDHAP]_2\cdot 2H_2O$ (5f), $CaK[(MeO)_2cDHAP]_3\cdot 2H_2O$ (5g) and $NH_4[(MeO)_2cDHAP]$ (5h). To the acidic eluant (water solutions of **5c)** freshly prepared from 25 mg (0.07 mmol) of **5a**, the respective bicarbonate: $NaHCO_3$ for **5d**, $KHCO_3$ for **5e** and **5e′**, NH_4HCO_3 for **5h** (in a molar ratio 1:1) or $CaCl_2\cdot 6H_2O$ (in a molar ratio 2:1) for **5f** or $KHCO_3$ and $CaCl_2\cdot 6H_2O$ (in a molar ration 1:1:1) for **5g** were added. A small amount of EtOH was added to **5h**. The solutions were evaporated under a nitrogen stream to syrups, which were allowed to crystallize at 21 °C (for **5d**,**h**,**e′**) or 4 °C (for **5e**,**f**,**g**). Calcium and potassium salts were obtained by the addition of a small amount of water with repeated evaporation of the mixtures. Crystals of **5e′** were grown by recrystallization of the nuclei from a mixture of 1:1:1 MeOH–EtOH–2-PrOH and a small amount of water. Crystals of **5d**–**e′** and **5h** showed a huge tendency to twinning and could not be cut; therefore, these had to be swilled with water to obtain the size required for the X-ray experiment.

4.4. Crystal structures determination

The crystallographic measurements for **5a**–**h** were performed on a Xcalibur PX (for **5a**,**h**) or a Kuma KM4CCD (for **5b**–**g**) automated four-circle diffractometers with the graphite-monochromatized CuK_α (**5a**,**h**) or MoK_α (**5b**–**g**) radiation. The data for the crystals were collected at 100(2) K (for **5a**–**g**) or 240(2) K (for **5h**) using an Oxford Cryosystems cooler. Data collection, cell refinement, and data reduction and analysis were carried out with the Xcalibur PX or KM4CCD software (Oxford Diffraction Poland), CRYSALIS CCD and CRYSALIS RED, respectively.[20] Analytical or multi-scan absorption correction was applied to all the data, except for the **5b** and **5c** crystals, with the use of CRYSALIS RED.[20] All structures were solved by direct methods using SHELXS-97[21] and refined by a full-matrix least-squares technique using SHELXL-97[22] with anisotropic thermal parameters for all non-H atoms. All H atoms were found in difference-Fourier maps and were refined isotropically for **5a**–**d** and **5f**,**g**. In the final refinement cycles for **5e**, **5e′** and **5h**, all the H atoms (except for those from water molecules and NH_4^+ ion) were treated as riding atoms, with C–H distances of 0.97–0.99 Å and with U_{iso} values of $1.2U_{eq}(C)$ for CH_2 groups or $1.5U_{eq}(C)$ for CH_3. In **5e**, H3W and H6W atoms from water molecules were refined with $U_{iso} = 1.5U_{eq}(O)$. The extinction was also refined in **5a**,**h** with the final extinction coefficient amounting to 0.0047(5) in **5a** and 0.0014(6) in **5h**. The Flack parameter in **5c** was −0.05(6). All figures were made using an XP program.[23] Cremer–Pople puckering parameters were calculated using the PLATON program.[24] A summary of the conditions for the data collection and the structure refinement parameters are given in Tables 6 and 7.

The X–ray data for $NH_4[(MeO)_2cDHAP]$ (**5h**) were collected at 240(2) K owing to weak reflections at $b^*/3$ and $2b^*/3$ observed at lower temperatures. (DSC analysis for **5h** confirmed a phase transition about 220 K.) The $[(MeO)_2cDHAP]^-$ ion in **5h** is disordered into two positions corresponding to two different conformations of the 1,3,2-dioxaphosphorinane ring: skew (*S*) with s.o.f = 0.762(9) and chair (*C*) with s.o.f. = 0.238(9). In the final model, the ordered atoms of the anion (O21, O3, O4, O5, C3 and C4) were refined with s.o.f = 1, assuming their positions being common for the two conformations. Remaining atoms were treated as disordered, and their two positions (P/P10, O1/O10, O22/O220, C1/C10, C2/C20 and C5/C50) were refined with s.o.f = 0.762(9) and 0.238(9). The positions of pairs of the atoms P and P10, as well as C2 and C20, were refined with the same fractional coordinates and anisotropic displacement parameters (constrains were applied with EXYZ and EADP instructions).

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Supplementary data

Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 659905 (**5a**), 659906 (**5b**), 659907 (**5c**), 659908 (**5d**), 659909 (**5e**), 659910 (**5e′**), 659911 (**5f**), 659912 (**5g**) and 659913 (**5h**). Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: +44-

1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2007.09.011.

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