Preparation and Crystal Structures of 2-Aminoethyl Phosphate Complexes of Magnesium, Calcium, and Zinc

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Crystalline magnesium, calcium, and zinc 2-aminoethyl phosphate complexes containing the monoanions $PEAH^{\ominus}$ have been prepared as the tetrahydrates (Ca, Zn) and the hexahydrate (Mg), and their structures determined by single-crystal X-ray methods. The structures of monoclinic $Ca(PEAH)_2 \cdot 4\ H_2O$ and $Zn(PEAH)_2 \cdot 4\ H_2O$ (space group $C2/c$) both contain polymeric chains with metal ions connected by bridging phosphate groups. The zinc atoms are in a tetrahedral environment of four oxygen atoms, while the calcium atoms are found to be hexacoordinated with two additional oxygen atoms from water molecules in axial positions. The triclinic $Mg(PEAH)_2 \cdot 6\ H_2O$ (space group $P\bar{1}$) contains discrete complex units with hexacoordinate magnesium atoms octahedrally surrounded by six oxygen atoms, four of which from water molecules in the equatorial plane and two from phosphate groups in axial positions.

Phosphate-containing proteins play an important role in the process of dentin mineralization[1]. They are part of the noncollageneous proteins, the so-called phosphophoryns, of dentin. These are unique proteins which up to this time have only been found in teeth[2]. Their chemical composition varies a lot depending on e.g. the origin of the material, its age, etc., and there appears to be considerable phosphophoryn heterogeneity even within a single tooth depending on both location within the tooth and an in situ degradation[3-6]. However, the most unique feature of the phosphorphoryns as a group is their remarkably high content of aspartic acid on one hand and serine and phosphoserine on the other. Since phosphate and carboxylate groups are known to bind divalent cations[7], it was suggested that a possible biological function of the phosphoprotein was in the initiation of calcification of dentin by acting as a nucleation site for the initial epitactic localization of calcium within the collagen-fibril network. Alternatively, it is also possible that they can inhibit calcification by complexing calcium ions, thereby preventing nucleation[8]. In either case, the elucidation of the interaction of the active sites of the proteins e.g. the phosphate and/or carboxylate functions with the metal center is of interest.

In order to study the complexation ability of the *phosphate* group towards metal ions, 2-aminoethyl phosphate or phosphorylethanolamine, $^{\oplus}NH_3-CH_2-CH_2-O-PO_3H^{\ominus}$ ($PEAH_2$), can serve as an appropriate model compound, since $PEAH_2$ is derived from phosphoserine by removing the β-carboxylate function. The solid-state structure of $PEAH_2$, which also occurs widely in biological systems[9], e.g. as a moiety of the brain lipid phosphatidylethanolamine, exhibits a pronounced gauche conformation of the N–C–C–O unit with respect to the central methylene linkage[10]. This unexpected configuration – if retained during complex formation – could, at least in basic media with deprotonated amino functions predominating, facilitate complexation by N,O chelation.

In order to demonstrate the ligand abilities and evaluate the bonding mode of 2-aminoethyl phosphate towards biologically relevant metals, and also as a part of our study of metal interactions with naturally occurring organophosphorus species[11], we now report the syntheses and crystal structures of calcium, magnesium, and zinc complexes of the $PEAH^{\ominus}$ ion.

Results and Discussion

Aqueous solutions of magnesium bis(2-aminoethyl hydrogen phosphate), $Mg(PEAH)_2$, are obtained by treatment of a suspension of magnesium carbonate in water with two equivalents of 2-aminoethyl phosphate ($PEAH_2$). Reaction (1) leads to a clear solution of pH = 6.5. The product crystallizes as the hexahydrate upon concentration of the solution. The crystals are only very slowly soluble in water. The same product is isolated with magnesium oxide as a starting material instead of magnesium carbonate.

$$2\ PEAH_2 + MgCO_3 \xrightarrow[-CO_2]{+H_2O} Mg(PEAH)_2 \cdot 6\ H_2O \qquad (1)$$

Aqueous solutions of calcium bis(2-aminoethyl hydrogen phosphate), $Ca(PEAH)_2$, and zinc bis(2-aminoethyl hydrogen phosphate), $Zn(PEAH)_2$, can be prepared within several minutes by treating slurries of the corresponding metal oxide with 2-aminoethyl phosphate in the molar ratio 1:2 (eq. 2). Slow evaporation of the solvent results in the formation of colorless crystals, which analyze as $Ca(PEAH)_2 \cdot 4\ H_2O$ and $Zn(PEAH)_2 \cdot 4\ H_2O$. Aqueous solutions of these compounds show pH = 6.5.

$$2\ PEAH_2 + MO \xrightarrow{+H_2O} M(PEAH)_2 \cdot 4\ H_2O \qquad (2)$$
$$M = Ca, Zn$$

The ^{13}C- und ^{31}P-NMR spectra of solutions of all three compounds reveal the resonances of the $PEAH^{\ominus}$ ion. There is little influence of the cations on the observed chemical shifts and coupling constants, indicating dissociation of the compounds in aqueous solution.

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Table 1. Crystallographic data for $Mg(PEAH)_2 \cdot 6\ H_2O$, $Ca(PEAH)_2 \cdot 4\ H_2O$, and $Zn(PEAH)_2 \cdot 4\ H_2O$

	$Mg(PEAH)_2 \cdot 6\ H_2O$	$Ca(PEAH)_2 \cdot 4\ H_2O$	$Zn(PEAH)_2 \cdot 4\ H_2O$
Emp. formula	$C_4H_{26}N_2O_{14}P_2Mg$	$C_4H_{22}N_2O_{12}P_2Ca$	$C_4H_{22}N_2O_{12}P_2Zn$
M_r	412.50	392.26	417.54
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a [Å]	6.614(1)	18.384(2)	14.804(3)
b [Å]	6.918(1)	5.597(1)	12.313(2)
c [Å]	9.517(1)	14.720(2)	9.243(2)
α [°]	89.35(1)	90	90
β [°]	72.65(1)	100.77(1)	108.28(1)
γ [°]	81.34(1)	90	90
V [Å^3]	410.65	1514.50	1599.80
$d_{calcd.}$ [gcm^{-3}]	1.668	1.720	1.733
Z	1	4	4
$F(000)$ [e]	218	824	864
$\mu(MoK_\alpha)$ [cm^{-1}]	3.1	6.7	18.2
T [°C]	23	23	23
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Scan	ω	Θ-Θ	ω
Scan width [° in ω]	0.9 + 0.35 tanΘ	1.2 + 0.3 tanΘ	0.9 + 0.3 tanΘ
hkl range	±8, ±8, +12	±22, +7, +18	±17, +14, +10
$[(\sin\Theta)/\lambda]_{max}$ [Å^{-1}]	0.637	0.615	0.594
Measured reflections	1912	3256	2952
Unique reflections	1785	1468	1410
R_{int}	0.0089	0.0095	0.012
Observed reflections	1607 $[F_o \geq 4\sigma(F_o)]$	1396 $[F_o \geq 2\sigma(F_o)]$	1364 $[F_o \geq 1\sigma(F_o)]$
Refined parameters	150	140	124
R [a]	0.027	0.022	0.025
R_w [b]	0.032	0.025	0.028
$(\text{Shift/error})_{max}$	0.001	0.001	0.003
$\Delta\varrho_{fin}$ (max/min) [e/Å^3]	+0.31/−0.37	+0.29/−0.31	+0.30/−0.64

[a] $R = \Sigma(\| F_o \| - \| F_c \|)/\Sigma \| F_o \|$. — [b] $R_w = [\Sigma w(\| F_o \| - \| F_c \|)^2/ \Sigma w F_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

The solid-state structures of *Ca(PEAH)$_2$ · 4 H$_2$O* and *Zn(PEAH)$_2$ · 4 H$_2$O* appear to be closely related at a first glance: Both compounds crystallize in the monoclinic space group $C2/c$ with four formula units in the unit cell of very similar cell dimensions as summarized in Table 1.

The most prominent structural common feature is the arrangement of the $M(PEAH)_2$ units in polymeric chains, where the metal centers are connected by bridging phosphate groups (Figures 1, 2). The bridging position of the phosphate ions between the metal atoms leads to the formation of eight-membered rings in both structures. However, differences arise from the coordination number of the metal centers, which is four for zinc and six for calcium, as well as from the orientation of the "dangling" $O-CH_2-$

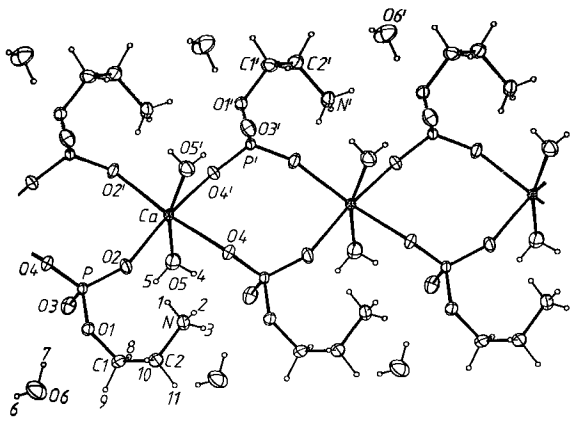

Figure 1. Molecular structure of $Ca(PEAH)_2 \cdot 4\ H_2O$ in the crystal (ORTEP: ellipsoids at the 50% probability level, H atoms with arbitrary radii) with atomic numbering scheme

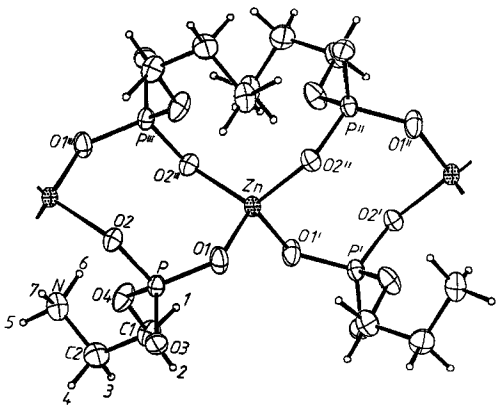

Figure 2. Molecular structure of $Zn(PEAH)_2 \cdot 4\ H_2O$ in the crystal (ORTEP: see Figure 1) with atomic numbering scheme

$CH_2-NH_3^{\oplus}$ units of the ligand. In both structures, the amino functions have – due to their protonation – no metal contacts but are engaged in hydrogen bonding, as are the interstitial water molecules, interconnecting the one-dimensional strings to complicated three-dimensional networks.

The zinc atoms are tetracoordinate in a distorted tetrahedral geometry by four oxygen atoms, which are derived from four different $PEAH^{\ominus}$ ions. The calcium atoms are hexacoordinate in a strongly distorted octahedral array with four equatorial contacts to phosphate oxygen atoms of four different anions and two axial water molecules. In both compounds the structure of the coordinated $PEAH^{\ominus}$ ions is closly related to that of the free $PEAH_2$, with a gauche arrangement of the phosphate and (protonated) amino functions with respect to the C–C axis as indicated by the dihedral angles O–C–C–N of 50.9 and 69.4° for $Zn(PEAH)_2 \cdot 4\ H_2O$ and $Ca(PEAH)_2 \cdot 4\ H_2O$. The corresponding angle for $PEAH_2$ is 59.9° [10].

The relative orientation of the "dangling" $O-CH_2-CH_2-NH_3^{\oplus}$ groups of the coordinated anions is different in the two structures. In the case of the zinc compound, units on the same side of the strings alternatingly point in opposite directions. This orientation with pairs of ligands in close proximity results in a distortion of the regular tetrahedral geometry around the zinc atoms, and is – probably for sterical reasons – not realized in the structure of the hexacoordinate, octahedral calcium compound. In $Ca(PEAH)_2 \cdot 4\ H_2O$, all ligands on either side of the strings point in the same direction, thereby minimizing sterical crowding. This arrangement also leads to a distortion of the regular geometry of the calcium atoms as demonstrated e.g. by the angle O5–Ca–O5′ of 163.4(1)°.

Table 2. Bond distances [Å] and angles [°] for $Ca(PEAH)_2 \cdot 4\ H_2O$ (esd's in units of the last significant figure in parentheses)

P	-- O1	1.627(1)		P	-- O2	1.510(1)	
P	-- O3	1.513(1)		P	-- O4	1.514(1)	
CA	-- O2	2.293(1)		CA	-- O4	2.351(1)	
CA	-- O5	2.419(1)		O1	-- C1	1.442(1)	
N	-- C2	1.520(1)		C1	-- C2	1.502(1)	
O1	-P -O2	105.5(1)		O1	-P -O3	106.8(1)	
O2	-P -O3	114.6(1)		O1	-P -O4	101.7(1)	
O2	-P -O4	114.3(1)		O3	-P -O4	112.6(1)	
O2	-CA -O4	87.6(1)		O2	-CA -O5	89.3(1)	
O4	-CA -O5	87.7(1)		P	-O1 -C1	119.6(1)	
P	-O2 -CA	145.3(1)		O2	-CA -O2'	95.4(1)	
P	-O4 -CA	131.4(1)		O4	-CA -O4'	91.1(1)	
O1	-C1 -C2	110.2(1)		N	-C2 -C1	112.9(1)	
O5	-CA -O5'	163.4(1)		P	-O4 -CA	131.4(1)	

Table 3. Bond distances [Å] and angles [°] for $Zn(PEAH)_2 \cdot 4\ H_2O$ (esd's in units of the last significant figure in parentheses)

ZN	-- O1	1.940(2)		P	-- O1	1.510(2)	
P	-- O2	1.532(2)		P	-- O3	1.501(2)	
P	-- O4	1.597(2)		O4	-- C1	1.433(3)	
C1	-- C2	1.508(4)		C2	-- N	1.480(4)	
ZN	-- O2''	1.972(2)					
O1	-P -O2	113.3(1)		O1	-P -O3	112.2(1)	
O2	-P -O3	111.2(1)		O1	-P -O4	109.5(1)	
O2	-P -O4	101.3(1)		O3	-P -O4	108.7(1)	
ZN	-O1 -P	133.2(1)		O1	-ZN -O1'	108.0(1)	
P	-O4 -C1	122.8(2)		O4	-C1 -C2	106.1(2)	
O1	-ZN -O2'''	112.2(1)		ZN	-O2 -P	123.4(1)	
N	-C2 -C1	110.2(2)		O2''	-ZN -O2'''	117.8(1)	
O1	-ZN -O2''	103.3(1)					

Bond distances, bond angles, and selected hydrogen bonds for both complexes are summarized in Tables 2–5.

$Mg(PEAH)_2 \cdot 6\ H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell. Cell dimensions and crystal data are included in Table 1, and structural details are listed in Tables 6, 7.

Table 4. Hydrogen bonds (X–H···Y) [Å] for $Ca(PEAH)_2 \cdot 4\ H_2O$

X - H ··· Y	X-H	H···Y	X···Y	X-H···Y
N -H1 ··· O2(a)	0.880	2.022	2.882	165.5
N -H2 ··· O4(b)	0.988	1.768	2.751	172.4
N -H3 ··· O1(c)	0.864	2.209	2.977	148.0
O5-H4 ··· O3(d)	0.763	1.965	2.719	170.2
O5-H5 ··· O6(e)	0.822	2.012	2.833	176.3
O6-H6 ··· O3(f)	0.855	1.830	2.677	169.8
O6-H7 ··· O3(a)	0.834	2.047	2.866	167.3

Symmetry positions of atom Y: (a) x, y, z; (b) $-x, -y, -z$; (c) $x, y-1, z$; (d) $-x, y-1, -z+0.5$; (e) $x-0.5, y-0.5, z$; (e) $-x+0.5, y+0.5, -z+0.5$.

Table 5. Hydrogen bonds (X–H···Y) [Å] for $Zn(PEAH)_2 \cdot 4\ H_2O$

X - H ··· Y	X-H	H···Y	X···Y	X-H···Y
N -H5 ··· O3(a)	1.009	1.690	2.693	172.9
N -H6 ··· O6(b)	0.947	1.841	2.767	165.4
N -H7 ··· O2(c)	0.808	2.221	3.022	171.5
O6-H8 ··· O2(d)	0.981	1.918	2.854	158.9
O6-H9 ··· O5(d)	0.851	1.997	2.824	164.2
O5-H10··· O5(e)	1.070	1.818	2.806	170.6
O5-H11··· O3(c)	0.957	1.759	2.709	171.5

Symmetry positions of atom Y: (a) x, y, z; (b) $-x, y, 0.5-z$; (c) $0.5-x, 1.5-y, -z$; (d) $x-0.5, y+0.5, z$; (e) $-x+1, -y+1, -z$.

Table 6. Bond distances [Å] and angles [°] for $Mg(PEAH)_2 \cdot 6\ H_2O$ (esd's in units of the last significant figure in parentheses)

MG	-- O1	2.062(1)		MG	-- O5	2.049(1)	
MG	-- O6	2.124(1)		P	-- O1	1.530(1)	
P	-- O2	1.511(1)		P	-- O3	1.508(1)	
P	-- O4	1.622(1)		O4	-- C1	1.443(2)	
C1	-- C2	1.511(3)		C2	-- N	1.477(2)	
O1	-MG -O5	88.0(1)		O1	-MG -O6	88.0(1)	
O5	-MG -O6	88.9(1)		O1	-P -O2	112.9(1)	
O1	-P -O3	111.1(1)		O2	-P -O3	115.1(1)	
O1	-P -O4	106.4(1)		O2	-P -O4	102.9(1)	
O3	-P -O4	107.7(1)		MG	-O1 -P	137.2(1)	
O1	-MG -O1'	180.0(1)		P	-O4 -C1	122.0(1)	
O5	-MG -O5'	180.0(1)		O4	-C1 -C2	111.6(2)	
C1	-C2 -N	112.2(2)		O6	-MG -O6'	180.0(1)	

Table 7. Hydrogen bonds (X–H···Y) [Å] for $Mg(PEAH)_2 \cdot 6\ H_2O$

X - H ··· Y	X-H	H···Y	X···Y	X-H···Y
N -H1 ··· O1(a)	0.875	2.152	2.953	151.8
N -H2 ··· O3(b)	0.847	1.904	2.716	160.3
N -H3 ··· O1(c)	1.021	1.862	2.838	159.0
O5-H4 ··· O2(c)	0.936	1.820	2.707	157.3
O5-H5 ··· O3(d)	0.969	1.703	2.644	163.1
O6-H6 ··· O2(e)	0.803	1.942	2.735	169.4
O6-H7 ··· O7(f)	0.822	1.970	2.778	167.9
O7-H8 ··· O2(c)	0.885	1.936	2.799	164.6
O7-H9 ··· O4(g)	0.780	2.174	2.873	149.3

Symmetry positions of atom Y: (a) $-x+1, -y, -z+2$; (b) $x+1, y, z$; (c) x, y, z; (d) $x, y+1, z$; (e) $-x, -y+1, -z+2$; (f) $x, y, z+1$; (g) $-x+1, -y+1, -z+1$.

The crystals are built from discrete complex molecules having a crystallographic center of inversion occupied by the magnesium ions (Figure 3), which are in an octahedral environment of six oxygen atoms, four of which are derived from water molecules. These water molecules occupy the positions of an equatorial plane, while two oxygen atoms of two different phosphate groups related by symmetry are coordinated in the axial positions thus defined. The (protonated) amino functions show no metal contacts but are engaged in inter/intramolecular hydrogen bonding. This is also true for the remaining two interstitial water molecules, the coordinated water molecules, and the oxygen atoms of the phosphate groups. Again, the structure of the coordinated $PEAH^{\ominus}$ ions closely resembles that of the free ligand. The gauche conformation with respect to the central C–C axis is obvious from the dihedral angle O–C–C–N of 71.9°. The deviation from the ideal synclinical value of 60° found for $PEAH_2$ is certainly due to packing effects, which in this class of compounds with relatively weak ligands are determined predominantly by the hydrogen bonding within the fixed network.

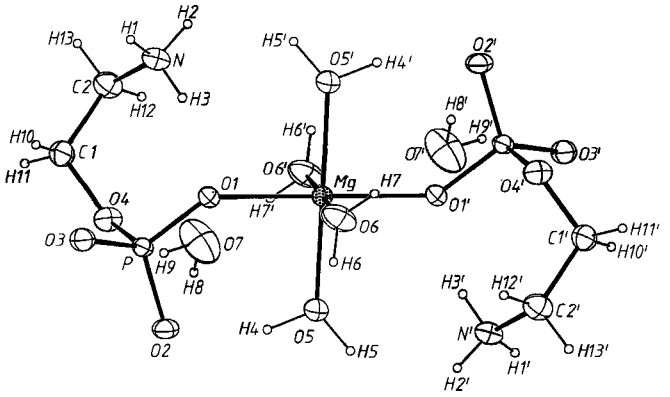

Figure 3. Molecular structure of $Mg(PEAH)_2 \cdot 6\ H_2O$ in the crystal (ORTEP: see Figure 1) with atomic numbering scheme

The results of the structure determination demonstrate that 2-aminoethyl *phosphate* is a more powerful ligand for magnesium than the corresponding 2-aminoethyl *phosphonate*, $^{\oplus}NH_3-CH_2-CH_2-PO_3^{2\ominus}$ ($AEPH^{\ominus}$), for which even in the solid state the anions cannot compete with water molecules for coordination sites in the inner coordination sphere of the metal. This "complex" is thus to be formulated as $\{[Mg(H_2O)_6]^{2\oplus}[AEPH]_2^{\ominus}\} \cdot 2\ H_2O$[11], whereas the phosphate is represented by the stoichiometry $[Mg(H_2O)_4(PEAH)_2] \cdot 2\ H_2O$. Work with multidentate phosphate ligands is in progress.

We thank *J. Riede* for careful work with the X-ray data collection and Professor *H. Schmidbaur* for helpful discussions.

Experimental

All experiments were carried out in pure, fully desalinated water; reagents were of p.a. quality. – pH values were measured using a Knick apparatus and Ingold reference cells. – Elemental analyses were carried out by the Microanalytical Laboratory of this Institute following standard procedures. – NMR spectra: Jeol FX 60 (^{13}C), Jeol CX 270 (^{31}P).

Magnesium Bis(2-aminoethyl hydrogen phosphate) Hexahydrate [$Mg(PEAH)_2 \cdot 6\ H_2O$]: A suspension of 0.30 g (3.5 mmol) of magnesium carbonate in 10 ml of water was treated at room temp. with 1.00 g (7.0 mmol) of 2-aminoethyl dihydrogen phosphate, which was added in small portions. Stirring of the reaction mixture at room temp. for 20 min resulted in a clear solution with pH = 6.5 Slow evaporation of the solvent in a waterbath at 45°C led to the formation of small colorless crystals, which analyzed as the hexahydrae (1.2 g, 82% yield). The crystals are only very slowly soluble in water and lose hydrate water at 225°C without melting. The same product is obtained by using magnesium oxide instead of the carbonate. – ^{13}C NMR [20°C, D_2O, internal CH_3OH (δ = 49.9)]: δ = 64.55 [d, J(PC) = 4.89 Hz, OCH_2], 41.91 [d, J(PC) = 7.82 Hz, NCH]. – ^{31}P NMR (D_2O, external H_3PO_4): δ = 3.8 (s).

$C_4H_{26}MgN_2O_{14}P_2$ (412.5)
Calcd. C 11.65 H 6.35 N 6.79 Mg 5.89
Found C 11.81 H 6.32 N 6.79 Mg 6.00

Calcium Bis(2-aminoethyl hydrogen phosphate) Tetrahydrate [$Ca(PEAH)_2 \cdot 4\ H_2O$]: A suspension of calcium oxide (0.20 g, 3.5 mmol) in 10 ml of water was treated with 1.00 g (7.0 mmol) of 2-aminoethyl dihydrogen phosphate. Stirring of the mixture at room temp. for 10 min led to an almost clear solution with pH = 6.5, which was filtered and slowly evaporated in a waterbath at 45°C. The product was obtained as colorless crystals, which analyzed as the tetrahydrate (1.0 g, 72% yield). The crystals are only very slowly soluble in water. They are stable up to 265°C without melting or loss of hydrate water. – ^{13}C NMR [20°C, D_2O, internal CH_3OH (δ = 49.9)]: δ = 63.27 [d, J(PC) = 4.73 Hz, OCH_2], 42.21 [d, J(PC) = 7.96 Hz, NCH]. – ^{31}P NMR (D_2O, external H_3PO_4): δ = 5.1 (s).

$C_4H_{22}CaN_2O_{12}P_2$ (392.3) Calcd. C 12.24 H 5.66 N 7.14
Found C 12.34 H 5.66 N 7.14

Table 8. Fractional atomic coordinates and equivalent isotropic thermal parameters for $Mg(PEAH)_2 \cdot 6\ H_2O$ [$U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, U_3 are the eigenvalues of the U_{ij} matrix; esd's in parentheses]

ATOM	X/A	Y/B	Z/C	U(eq.)
MG	0.50000	0.50000	1.00000	0.020
P	0.31559(7)	0.20973(6)	0.80291(5)	0.018
O1	0.4161(2)	0.2569(2)	0.9214(1)	0.022
O2	0.1903(2)	0.3880(2)	0.7579(1)	0.028
O3	0.1969(2)	0.0376(2)	0.8437(2)	0.028
O4	0.5128(2)	0.1474(2)	0.6543(1)	0.027
O5	0.2954(2)	0.6689(2)	0.9068(2)	0.038
O6	0.2389(2)	0.4924(3)	1.1938(2)	0.035
O7	0.2522(3)	0.5471(3)	0.4794(2)	0.038
C1	0.6449(3)	-0.0422(3)	0.6341(2)	0.032
C2	0.8457(3)	-0.0371(3)	0.6777(2)	0.028
N	0.8007(3)	-0.0162(3)	0.8389(2)	0.025

Table 9. Fractional atomic coordinates and equivalent thermal parameters for $Ca(PEAH)_2 \cdot 4\ H_2O$ (U_{eq} see Table 8)

ATOM	X/A	Y/B	Z/C	U(eq.)
P	0.41909(2)	0.68050(6)	0.34114(3)	0.012
CA	0.50000	0.16972(7)	0.25000	0.013
O1	0.38791(6)	0.6914(2)	0.43749(7)	0.018
O2	0.45357(6)	0.4404(2)	0.33933(7)	0.025
O3	0.35374(6)	0.7250(2)	0.26394(7)	0.019
O4	0.47420(6)	0.8807(2)	0.35350(7)	0.020
O5	0.37635(7)	0.1084(3)	0.16267(9)	0.024
O6	0.26014(8)	0.4384(3)	0.1551(1)	0.022
N	0.41603(8)	0.1808(3)	0.4943(1)	0.021
C1	0.33152(9)	0.5281(3)	0.4529(1)	0.023
C2	0.3632(1)	0.3539(3)	0.5263(1)	0.024

Table 10. Fractional atomic coordinates and equivalent thermal parameters for $Zn(PEAH)_2 \cdot 4\ H_2O$ (U_{eq} see Table 8)

ATOM	X/A	Y/B	Z/C	U(eq.)
ZN	0.00000	0.51950(3)	0.25000	0.016
P	0.06826(4)	0.65038(5)	0.00763(7)	0.013
O1	0.0776(1)	0.6121(2)	0.1669(2)	0.019
O2	0.0948(1)	0.5632(1)	-0.0903(2)	0.018
O3	0.1218(1)	0.7539(1)	0.0076(2)	0.016
O4	-0.0414(1)	0.6698(2)	-0.0845(2)	0.025
O5	0.4493(2)	0.5477(2)	0.0938(2)	0.035
O6	-0.2306(1)	0.9568(2)	0.0658(3)	0.039
N	0.2770(2)	0.8170(2)	0.2341(3)	0.020
C1	-0.1013(2)	0.7399(3)	-0.0308(3)	0.024
C2	-0.1791(2)	0.7773(2)	-0.1704(3)	0.030

Zinc Bis(2-aminoethyl hydrogen phosphate) Tetrahydrate [$Zn(PEAH)_2 \cdot 4\ H_2O$]: Crystals of the zinc compound were obtained following the same procedure as described for the calcium compound by treating zinc oxide (0.28 g, 3.5 mmol) with 2-aminoethyl dihydrogen phosphate (1.00 g, 7.0 mmol) in 10 ml of water. The crystals formed upon slow evaporation of the solvent analyzed as the tetrahydrate (1.2 g, 81%). They are very soluble in water and lose hydrate water at 114°C without melting. – ^{13}C NMR [20°C, D_2O, internal CH_3OH (δ = 49.9)]: δ = 64.76 [d, J(PC) = 4.57 Hz, OCH_2], 41.41 [d, J(PC) = 7.62 Hz, NCH]. – ^{31}P NMR (D_2O, external H_3PO_4): δ = 3.5 (s).

$C_4H_{22}N_2O_{12}P_2Zn$ (417.5)

Calcd. C 11.51 H 5.31 N 6.71 P 14.84

Found C 11.52 H 5.30 N 6.68 P 14.83

X-ray Structure Determinations[12]: Crystal data and data-collection parameters for $Mg(PEAH)_2 \cdot 6\ H_2O$ (a), $Ca(PEAH)_2 \cdot 4\ H_2O$ (b), and $Zn(PEAH)_2 \cdot 4\ H_2O$ (c) are listed in Table 1. During data collection three standard reflections were periodically measured [(a): 0 4 −1, 4 0 1, 0 2 7; (b): −1 −3 1, 0 0 −12, −12 0 0; (c): −4 −2 0, 0 −2 −2, 0 2 6; Mo-K_α radiation, λ = 0.71069 Å, graphite monochromator], and no appreciable decomposition was observed for all structures. Intensity data were not corrected for absorption effects for (a) and (b), absorption correction was carried out for (c). All structures were solved by direct methods (SHELXS-86) and refined by full-matrix methods (SHELX-76). All hydrogen atoms were located and isotropically refined for (b); all hydrogen atoms were located for (c), seven of which were isotropically refined, whereas four hydrogen atoms of crystal water molecules (O5 and O6) were introduced in the refinement with fixed atomic contributions (U_{iso} = 0.05 Å^2). All but one hydrogen atom (at O5) were located for (a). The hydrogen atom at O5 was calculated at the ideal geometrical position (XANADU). 11 hydrogen atoms were isotropically refined, the hydrogen atoms at O5 were included into the structure-factor calculation with fixed atomic displacement parameters (U_{iso} = 0.05 Å^2). Atomic coordinates for all structures are listed in Tables 8–10.

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[12] Further information on the X-ray structure determinations can be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the dispository number CSD-54882, the names of the authors, and the journal citation.

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