

Table 4. *Structural parameters*

	$V(\text{\AA}^3)$	S	$\theta(^{\circ})$
Nd	511.1	763	57.42 (4.22)
Sm	503.8	783	57.38 (4.18)
Eu	499.4	794	57.44 (4.28)
Gd	498.4	800	57.41 (4.28)
Y	484.9	836	57.38 (4.18)
Lu	479.3	855	57.47 (3.95)

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Structure of Silver(I) Barium Phosphoenolpyruvate Trihydrate

BY A. WEICHSEL AND T. LIS

Institute of Chemistry, The University, 50-383 Wrocław, Poland

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Abstract. Barium silver 2-(phosphonoxy)propionate trihydrate, $\text{Ag}^+ \cdot \text{Ba}^{2+} \cdot \text{C}_3\text{H}_2\text{O}_6\text{P}^{3-} \cdot 3\text{H}_2\text{O}$, $M_r = 464.3$, monoclinic, $P2_1/a$, $a = 6.578$ (3), $b = 23.811$ (9), $c = 6.610$ (3) Å, $\beta = 90.57$ (3)°, $V = 1035.3$ (8) Å³, $Z = 4$, $D_m = 2.96$, $D_x = 2.978$ Mg m⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 59.1$ cm⁻¹, $F(000) = 864$, $T = 299$ (1) K, final $R = 0.0274$ for 2144 non-zero reflections. The phosphate ester bond, 1.662 (4) Å, is comparable to the longest bonds of this type. The phosphate group is *trans* to the carboxylate group. The enolpyruvate system deviates slightly from planarity. Two Ag⁺ ions are bridged by two carboxylate groups [Ag...Ag 2.913 (2) Å]. Each phosphoenolpyruvate trianion chelates through phosphate O and methylene C atoms to one Ag⁺ ion and bridges two further Ag⁺ ions through the carboxylate group, thereby forming polymeric chains along the a axis. One water molecule completes the Ag coordination sphere. The Ba²⁺ ions display nine-fold coordination and are bridged by a water molecule and by two kinds of phosphate bridges along the a axis. The Ba²⁺ chains are connected to the Ag chains by phosphate, carboxylate and water oxygens. Only one O atom from the phosphate group does not coordinate to the metal ions but participates in four

hydrogen bonds instead. All water H atoms are involved in hydrogen bonds.

Introduction. This work is a continuation of our investigations into organic phosphates and follows our earlier structural papers on the phosphoenolpyruvate (PEP) moiety (Weichsel & Lis 1990). The free energy of hydrolysis of PEP (-58.5 kJ mol⁻¹) is the highest among naturally occurring phosphates (Lehninger, 1971) and the kinetics of PEP hydrolysis reactions depend strongly on the pH (Benkovic & Schray, 1968). From among four PEP forms the structures of the PEP acid (Weichsel, Lis & Kuczek, 1989), the PEP monoanion [monosodium salt (Katti, Hosur & Viswamitra, 1981), the monopotassium salt (Lis, 1987), the monocyclohexylammonium salts (Weichsel & Lis, 1989)] and the PEP dianion [bis(cyclohexylammonium) methanol solvate 1/0.5 (Weichsel & Lis, 1990)] have been described. Here we present the structure of the PEP trianion as a silver(I) barium trihydrate salt.

The isolation or purification of the PEP trianion by crystallization of a silver barium salt has been described by Baer & Fisher (1949). Quantitative analysis of our sample (Baer, 1952) suggested it was

a dihydrate but X-ray analysis has revealed clearly that the crystal is a trihydrate.

Experimental. The title compound was prepared by combining an equimolar quantity of commercially available cyclohexylammonium PEP, silver nitrate and barium nitrate in water. Needle-shaped crystals were obtained from water solution by slow evaporation in a refrigerator. D_m by flotation in $\text{CH}_2\text{I}_2/\text{C}_2\text{H}_4\text{Br}_2$ mixture. Preliminary Weissenberg photographs uniquely showed the space group $P2_1/a$. A parallelepiped crystal fragment $0.45 \times 0.1 \times 0.2$ mm was cut from a large one. Syntex $P2_1$ diffractometer with graphite monochromator and Mo $K\alpha$ radiation used for lattice parameters (15 reflections in $26 \leq 2\theta \leq 34^\circ$ range) and intensity measurements; $\omega-2\theta$ scan technique. 2948 reflections below $\theta = 28^\circ$ ($0 \leq h \leq 8$, $0 \leq k \leq 31$, $-8 \leq l \leq 8$). After each group of 50 reflections, two standards were measured; variation $\pm 4\%$. 2144 unique reflections; 336 symmetry-related reflections were averaged; 340 unobserved reflections [$I < 3\sigma(I)$]; $R_{\text{merge}} = 0.0195$. Scattering factors for Ba^{2+} , Ag^+ , P, O, C and H were from *International Tables for X-ray Crystallography* (1974). The structure solved by direct methods and refined on F by *SHELX76* (Sheldrick, 1976). The H atoms were found from a difference synthesis and refined with constraints: $\text{O}-\text{H} = 0.97 \text{ \AA}$ and $\text{C}-\text{H} = 1.08 \text{ \AA}$. An absorption correction was made using *DIFABS* (Walker & Stuart, 1983); min. and max. absorption corrections 0.895 and 1.148. Final refinement was performed using anisotropic thermal parameters (isotropic for H atoms) and isotropic extinction correction of the form $1 - xF_c/\sin\theta$; refinement of the parameter x gave the value $1.90(6) \times 10^{-7}$. Final $R = 0.0274$ and $wR = 0.027$, where $w = 1/\sigma^2(I_o)$; max. $\Delta/\sigma = 0.08$. Residual electron density in final difference synthesis within -1.38 and 1.44 e \AA^{-3} .

Discussion. Final atomic parameters are in Table 1 and principal interatomic distances, bond angles and torsion angles in Table 2.* The structure is built up from PEP trianions, Ag^+ and Ba^{2+} cations and water of hydration. The structure of the PEP anion and the atomic numbering scheme are shown in Fig. 1.

The enolpyruvate system is not quite planar. The angle between the carboxylate plane and the plane formed by C(2), C(3) and O(4) atoms is $5.7(8)^\circ$. This value is intermediate between those in the monopotassium salt [$0.7(7)^\circ$] and in the orthorhombic

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}(\text{\AA}^2)$
Ba	0.75284 (4)	0.68488 (1)	0.47973 (4)	0.013 (1)
Ag	1.09055 (6)	0.55547 (2)	0.47839 (7)	0.030 (1)
P	0.28669 (17)	0.67253 (5)	0.75315 (17)	0.012 (1)
O(1)	0.3945 (6)	0.72250 (15)	0.6683 (6)	0.022 (2)
O(2)	0.1106 (6)	0.65109 (17)	0.6315 (7)	0.027 (2)
O(3)	0.2443 (6)	0.67658 (16)	0.9785 (6)	0.021 (2)
O(4)	0.4725 (5)	0.62561 (15)	0.7337 (6)	0.018 (2)
O(5)	0.7683 (6)	0.57050 (16)	0.5807 (7)	0.028 (2)
O(6)	0.6585 (6)	0.48750 (16)	0.6897 (6)	0.024 (2)
O(7)	0.5067 (6)	0.74946 (18)	0.1986 (6)	0.024 (2)
O(8)	0.9396 (8)	0.61638 (22)	0.1663 (8)	0.040 (2)
O(9)	0.5131 (7)	0.61717 (20)	0.2252 (7)	0.036 (2)
C(1)	0.6428 (7)	0.53963 (21)	0.6676 (7)	0.016 (2)
C(2)	0.4567 (7)	0.56833 (20)	0.7528 (7)	0.015 (2)
C(3)	0.3039 (8)	0.54037 (23)	0.8361 (9)	0.023 (2)
H(3)	0.176 (7)	0.559 (3)	0.911 (10)	0.038 (20)
H(31)	0.311 (10)	0.496 (1)	0.860 (10)	0.028 (17)
H(7)	0.632 (8)	0.758 (5)	0.129 (12)	0.091 (35)
H(71)	0.421 (10)	0.725 (3)	0.117 (11)	0.060 (25)
H(8)	1.041 (7)	0.633 (3)	0.079 (8)	0.041 (21)
H(81)	0.816 (6)	0.607 (4)	0.091 (8)	0.051 (23)
H(9)	0.505 (17)	0.577 (1)	0.208 (16)	0.130 (51)
H(91)	0.423 (8)	0.636 (3)	0.131 (8)	0.024 (16)

form of the monocyclohexylammonium PEP salt [$13.9(9)^\circ$].

The torsion angle $\text{P}-\text{O}(4)-\text{C}(2)-\text{C}(3)$, defining the phosphate group orientation with respect to the enolpyruvate system, is $-17.0(7)^\circ$. It confirms our observation of the rotational flexibility of the phosphate group about the enolic bond (related torsion angles are in the $\pm 90^\circ$ range) and also suggests that the conformation about the enolic bond depends upon the cation as well as the solvent used in crystallization. In the present structure the conformation of the PEP trianion is stabilized by the Ag^+ and Ba^{2+} cations, *viz* the two cations are chelated by the same PEP trianion. The rather short enolic bond [$1.374(6) \text{ \AA}$] is in agreement with those found in other PEP structures. A characteristic feature of the doubly ionized phosphate group in phosphate monoesters is the location of one of the terminal phosphate O atoms nearly *trans* to the ester C atom; this O atom is involved in the smallest $\text{O}(\text{ester})-\text{P}-\text{O}(\text{terminal})$ bond angle (Starynowicz, Lis & Weichsel, 1986). This feature also occurs in the present structure. Given $\text{P}-\text{O}(\text{ester})$ bond lengths in PEP structures of $1.578(3)$ and $1.583(3) \text{ \AA}$ in PEP acid, $1.622(2) \text{ \AA}$ in the monopotassium salt, $1.595(5)$ and $1.610(6) \text{ \AA}$ in the monosodium salt, $1.604(2)$ and $1.610(2) \text{ \AA}$ in the monocyclohexylammonium salts, $1.627(3)$ and $1.634(3) \text{ \AA}$ in the bis(cyclohexylammonium) methanol solvate salt and $1.662(4) \text{ \AA}$ in this work, it can be seen that the length of the so called 'high-energy phosphate ester bond' in PEP seems to depend upon the degree of ionization not only of the phosphate ester group but also of the whole PEP moiety. The $\text{P}-\text{O}(\text{ester})$ bond

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52601 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Principal interatomic distances (Å), interatomic angles (°) and torsion angles (°)

P—O(1)	1.497 (4)	O(4)—C(2)	1.374 (6)
P—O(2)	1.493 (4)	O(5)—C(1)	1.250 (6)
P—O(3)	1.521 (4)	O(6)—C(1)	1.254 (6)
P—O(4)	1.662 (4)	C(1)—C(2)	1.515 (7)
C(2)—C(3)	1.329 (7)	Ba—O(1)	2.823 (4)
Ba—O(1 ⁱ)	2.695 (4)	Ba—O(2 ⁱⁱ)	2.673 (4)
Ba—O(4)	2.876 (3)	Ba—O(5)	2.806 (4)
Ba—O(7)	2.895 (4)	Ba—O(7 ⁱ)	2.958 (4)
Ba—O(8)	2.918 (5)	Ba—O(9)	2.804 (5)
Ag—O(2 ⁱⁱ)	2.495 (4)	Ag—O(5)	2.260 (4)
Ag—O(6 ⁱⁱⁱ)	2.245 (4)	Ag—O(8)	2.703 (5)
Ag...Ag ⁱⁱⁱ	2.913 (2)	Ag—C(3 ⁱⁱ)	2.761 (5)
Ag...Ba	3.799 (2)	Ag...Ba ⁱⁱ	5.336 (3)
Ag...Ba ⁱⁱ	5.821 (3)	Ba...Ba ⁱ	4.520 (3)
O(1)—P—O(2)	116.0 (3)	O(5)—C(1)—O(6)	125.6 (5)
O(1)—P—O(3)	114.1 (2)	O(5)—C(1)—C(2)	116.5 (5)
O(1)—P—O(4)	98.8 (2)	O(6)—C(1)—C(2)	118.0 (5)
O(2)—P—O(3)	113.6 (3)	O(4)—C(2)—C(1)	110.6 (4)
O(2)—P—O(4)	107.2 (2)	O(4)—C(2)—C(3)	126.4 (5)
O(3)—P—O(4)	105.1 (2)	C(1)—C(2)—C(3)	123.0 (5)
P—O(4)—C(2)	127.1 (3)	O(1)—Ba—O(1 ⁱ)	79.8 (2)
O(1)—Ba—O(2 ⁱⁱ)	131.7 (2)	O(1)—Ba—O(4)	49.8 (2)
O(1)—Ba—O(5)	103.4 (2)	O(1)—Ba—O(7)	69.6 (2)
O(1)—Ba—O(7 ⁱ)	126.1 (2)	O(1)—Ba—O(8)	148.2 (2)
O(1)—Ba—O(9)	88.9 (2)	O(1 ⁱ)-Ba—O(2 ⁱⁱ)	76.9 (2)
O(1 ⁱ)-Ba—O(4)	110.6 (2)	O(1 ⁱ)-Ba—O(5)	132.3 (2)
O(1 ⁱ)-Ba—O(7)	92.9 (2)	O(1 ⁱ)-Ba—O(7)	70.3 (2)
O(1 ⁱ)-Ba—O(8)	129.8 (2)	O(1 ⁱ)-Ba—O(9)	159.7 (2)
O(2 ⁱⁱ)-Ba—O(4)	101.6 (2)	O(2 ⁱⁱ)-Ba—O(5)	65.7 (2)
O(2 ⁱⁱ)-Ba—O(7)	152.3 (2)	O(2 ⁱⁱ)-Ba—O(7 ⁱ)	83.9 (2)
O(2 ⁱⁱ)-Ba—O(8)	73.9 (2)	O(2 ⁱⁱ)-Ba—O(9)	122.7 (2)
O(4)—Ba—O(5)	53.6 (2)	O(4)—Ba—O(7)	106.1 (2)
O(4)—Ba—O(7 ⁱ)	174.5 (2)	O(4)—Ba—O(8)	114.6 (2)
O(4)—Ba—O(9)	73.0 (2)	O(5)—Ba—O(7)	133.4 (2)
O(5)—Ba—O(7)	130.0 (2)	O(5)—Ba—O(8)	67.1 (2)
O(5)—Ba—O(9)	66.6 (2)	O(7)—Ba—O(7 ⁱ)	68.4 (2)
O(7)—Ba—O(8)	94.5 (2)	O(7)—Ba—O(9)	67.2 (2)
O(7 ⁱ)-Ba—O(8)	66.7 (2)	O(7 ⁱ)-Ba—O(9)	104.2 (2)
O(8)—Ba—O(9)	59.4 (2)	O(2 ⁱⁱ)-Ag—O(5)	77.3 (2)
O(2 ⁱⁱ)-Ag—O(6 ⁱⁱⁱ)	125.5 (2)	O(2 ⁱⁱ)-Ag—O(8)	80.6 (2)
O(5)-Ag—O(6 ⁱⁱⁱ)	156.4 (2)	O(5)-Ag—O(8)	78.7 (2)
O(6 ⁱⁱⁱ)-Ag—O(8)	97.6 (2)	Ag ⁱⁱⁱ ...Ag—O(2 ⁱⁱ)	143.9 (1)
Ag ⁱⁱⁱ ...Ag—O(5)	74.2 (2)	Ag ⁱⁱⁱ ...Ag—O(6 ⁱⁱⁱ)	86.5 (2)
Ag ⁱⁱⁱ ...Ag—O(8)	114.5 (2)	Ag ⁱⁱⁱ ...Ag—C(3 ⁱⁱ)	90.2 (2)
C(3 ⁱⁱ)-Ag—O(2 ⁱⁱ)	75.3 (2)	C(3 ⁱⁱ)-Ag—O(5)	103.6 (2)
C(3 ⁱⁱ)-Ag—O(6 ⁱⁱⁱ)	89.7 (2)	C(3 ⁱⁱ)-Ag—O(8)	154.6 (2)
O(1)—P—O(4)—C(2)	-166.9 (5)	P—O(4)—C(2)—C(1)	163.9 (6)
O(2)—P—O(4)—C(2)	-46.1 (6)	P—O(4)—C(2)—C(3)	-17.0 (7)
O(3)—P—O(4)—C(2)	75.0 (5)	C(3)—C(2)—C(1)—O(5)	175.0 (7)
O(4)—C(2)—C(1)—O(5)	-5.9 (6)	C(3)—C(2)—C(1)—O(6)	-5.0 (7)
O(4)—C(2)—C(1)—O(6)	174.1 (5)		

Symmetry code: (i) 0.5 + x, 1.5 - y, z; (ii) x + 1, y, z; (iii) 2 - x, 1 - y, 1 - z.

in the present work is the longest among all PEP structures and is among the longest such bonds in doubly ionized phosphate monoesters. The only similar P—O(ester) bond lengths occur in phosphate monoesters where the ester O atom is linked to an aromatic ring, e.g. 1.664 (3) Å in bis(cyclohexylammonium) 4-nitrophenyl phosphate (Jones, Sheldrick, Kirby & Abell, 1984), 1.661 (2) Å in flavone-3-monophosphate-magnesium complex (Bergstrom, Satyshur & Sundaralingam, 1981) and 1.646 (3) Å in pentakis(imidazole)copper(II) monophenyl phosphate tetrahydrate (Głowiak & Wnęk, 1985).

Two silver cations related by an inversion centre are held by two bridging carboxylate groups. The very distorted octahedral environment of the Ag⁺ ion is completed by phosphate O and methylene C atoms of the same PEP trianion and by a water molecule. A similar Ag—C interaction was found for example in bis(3-hydroxy-4-phenyl-2,2,3-trimethylcyclohexanecarboxylato)disilver(I) dihydrate (Coggon & McPhail, 1972).

The Ba²⁺ cations display very distorted ninefold coordination, being linked to four phosphate O atoms, the O atom of a carboxylate group and four water molecules. The Ba—O coordination distances vary from 2.673 (4) to 2.958 (4) Å; the shorter contacts involve the terminal phosphate O atoms and the longest, water O atoms. Ba²⁺ ions are bridged to each other by phosphate O atoms and water molecules. The Ba²⁺ and Ag⁺ cations form infinite chains which are bridged by phosphate, carboxylate and water O atoms (Fig. 2).

All water H atoms are involved in hydrogen bonds (Table 3). The O(3) atom which forms the longest of the three P—O(terminal) bonds is involved (as acceptor) in four hydrogen bonds with four water

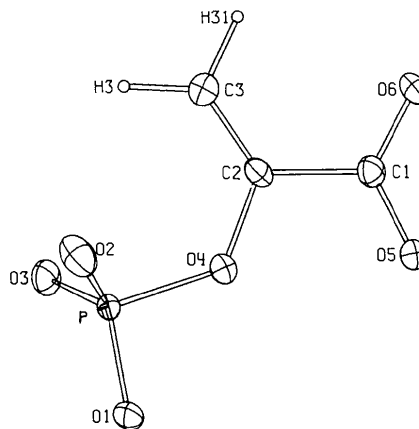


Fig. 1. Molecular geometry and numbering scheme of phosphoenolpyruvate trianion.

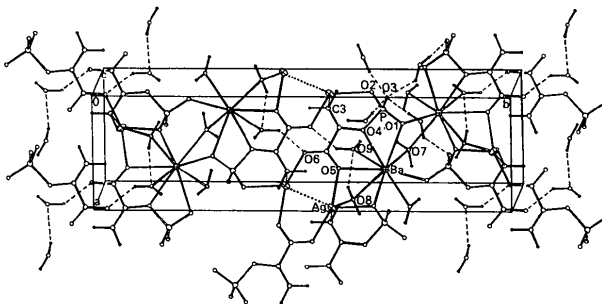


Fig. 2. The packing arrangement. Dashed lines show hydrogen bonds.

Table 3. *Hydrogen-bond geometry* (Å and °)

O—H...O	O...O	O...H	O—H...O
O(7)—H(7)...O(3 ⁱ)	2.776 (5)	1.99 (9)	136 (7)
O(7)—H(71)...O(3 ⁱⁱ)	2.839 (5)	1.87 (7)	175 (6)
O(8)—H(8)...O(3 ⁱⁱⁱ)	2.768 (6)	1.82 (6)	164 (5)
O(8)—H(81)...O(9)	2.836 (6)	2.20 (5)	122 (5)
O(9)—H(9)...O(6 ^{iv})	2.796 (6)	1.99 (7)	139 (8)
O(9)—H(91)...O(3 ^{iv})	2.780 (6)	1.81 (5)	174 (5)

Symmetry code: (i) $x + 0.5, 1.5 - y, z - 1$; (ii) $x, y, z - 1$; (iii) $1 + x, y, z - 1$; (iv) $1 - x, 1 - y, 1 - z$.

molecules and is therefore formally penta-coordinated. A similar type of hydrogen bonding was earlier observed, e.g. in trisodium D-2-phosphoglycerate hexahydrate (Lis, 1985).

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Crystal Chemistry of *cyclo*-Hexaphosphates. IX. Structure of Tetraammonium Dimanganese *cyclo*-Hexaphosphate Oxalate Hexahydrate

BY M. T. AVERBUCH-POUCHOT AND A. DURIF*

Laboratoire de Cristallographie, associé à l'Université J. Fourier, CNRS, 166X, 38042 Grenoble CEDEX, France

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Abstract. $\text{Mn}_2(\text{NH}_4)_4(\text{P}_6\text{O}_{18})(\text{C}_2\text{O}_4)\cdot 6\text{H}_2\text{O}$, $M_r = 851.966$, triclinic, $P\bar{1}$, $a = 9.747$ (3), $b = 9.751$ (3), $c = 7.689$ (3) Å, $\alpha = 99.92$ (5), $\beta = 105.88$ (5), $\gamma = 100.08$ (5)°, $V = 673.1$ Å³, $Z = 1$, $D_x = 2.101$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.465$ mm⁻¹, $F(000) = 432$, $T = 294$ K, final $R = 0.030$ for 2577 reflections. The atomic arrangement is built up by infinite ribbons of P_6O_{18} ring anions and MnO_6 octahedra spreading parallel to the b axis. These ribbons are themselves interconnected by the oxalic groups located between two MnO_6 octahedra belonging to two different ribbons. The hydrogen-bond scheme is described.

Introduction. Phosphates with two different phosphoric anions of different degrees of condensation

are becoming more and more familiar. A review of this type of compound has recently been reported by one of us (Averbuch-Pouchot, 1985). But up to now the coexistence in an atomic arrangement of a condensed phosphoric anion with a non-phosphoric one has not been reported. In this work we describe what we believe is the first example of such a compound: manganese ammonium *cyclo*-hexaphosphate oxalate hexahydrate, $\text{Mn}_2(\text{NH}_4)_4(\text{P}_6\text{O}_{18})(\text{C}_2\text{O}_4)\cdot 6\text{H}_2\text{O}$. In fact, in a good number of compounds (Boudjada, 1985), a condensed phosphoric anion coexists with a $\text{Te}(\text{OH})_6$ group but due to the neutrality of the telluric acid they cannot be considered as mixed-anion salts but as adducts.

Experimental. Crystals of the title compound have been prepared by slow diffusion of an aqueous solution of manganese oxalate into an aqueous solution

* To whom correspondence should be addressed.