

# A Series of Cesium Triphosphates with a Layer Structure: $\text{Cs}_2\text{MP}_3\text{O}_{10}$ ( $M=\text{Ga}, \text{Al}, \text{Cr}$ )

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A series of non-hydrated triphosphates containing cesium,  $\text{Cs}_2\text{MP}_3\text{O}_{10}$  ( $M=\text{Ga}, \text{Al}, \text{Cr}$ ), has been synthesized for the first time. Their original structure crystallizes in the space group  $P2_1/c$ , with  $a \approx 12.3 \text{ \AA}$ ,  $b \approx 9.0 \text{ \AA}$ ,  $c \approx 9.5 \text{ \AA}$  and  $\beta \approx 95^\circ$ . The  $[\text{MP}_3\text{O}_{10}]_\infty$  layers built up of corner-sharing  $\text{MO}_6$  octahedra and tritetrahedral  $\text{P}_3\text{O}_{10}$  groups can be described from  $\text{MP}_3\text{O}_{13}$  units in which one  $\text{MO}_6$  octahedra shares the three corners of one face with one  $\text{P}_3\text{O}_{10}$  group. The open character of the layers makes that  $\text{Cs}^+$  cations are not only interleaved between the layers, but also located in the pseudo-tunnels they present. © 2002 Elsevier Science (USA)

## INTRODUCTION

Ternary phosphates, where  $\text{PO}_4$  tetrahedra are associated to  $\text{MO}_6$  octahedra, belong to a large family of mixed frameworks with various structures, forming large cavities where large univalent or divalent cations can be intercalated. The study of such compounds is of high interest for the generation of new matrices susceptible to accommodate radiative cations like cesium, in view of the storage of nuclear wastes. To date, numerous monophosphates and diphosphates, containing alkaline and alkaline earth cations, are known. In contrast, the number of triphosphates which exhibit a mixed framework built up of “ $\text{P}_3\text{O}_{10}$ ” groups and  $\text{MO}_6$  octahedra is rather limited. Most of the actually known triphosphates are either hydrated or contain OH groups forming hydrogenophosphates, and are thus usually regarded as more soluble than anhydrous ceramic compounds. Consequently, they cannot constitute as good crystalline matrices for the storage of nuclear wastes as for instance monazite- or apatite-type compounds (see for example references (1,2)). Beside the beryllium triphosphates  $\text{Be}_2(\text{NH}_4)\text{P}_3\text{O}_{10}$  and  $\text{Be}_2\text{RbP}_3\text{O}_{10}$  (3,4), where  $\text{BeO}_4$  tetrahedra are associated to the  $\text{P}_3\text{O}_{10}$  groups, the cobalt and nickel triphosphates  $\text{Co}_2\text{LiP}_3\text{O}_{10}$  and  $\text{Ni}_2\text{LiP}_3\text{O}_{10}$  (5,6) seem the only non-hydrated

triphosphates containing  $\text{MO}_6$  octahedra which have been synthesized up to now. Bearing in mind these results, we have investigated Cs–M–P–O systems, where  $M$  is a trivalent cation susceptible to be octahedrally coordinated. We describe here the first non-hydrated cesium triphosphates,  $\text{Cs}_2\text{MP}_3\text{O}_{10}$ , with  $M=\text{Ga}, \text{Al}, \text{Cr}$ , whose original structure is bidimensional.

## EXPERIMENTAL SECTION

### Chemical Preparation

The single crystal used for the structure determination of the gallium phosphate was extracted from a mixture of nominal composition “ $\text{CsGaP}_2\text{O}_7$ ” synthesized in two steps. First,  $\text{CsNO}_3$  (ChemPur, 99.9%),  $(\text{NH}_4)_2\text{HPO}_4$  (Prolabo Normapur, 99.5%) and  $\text{Ga}_2\text{O}_3$  (ChemPur, 99.99%) were mixed in an agate mortar, placed in a platinum crucible and heated in air at 773 K for a few hours. Once the correct weight loss was reached (i.e., when the cesium nitrate and the diammonium hydrogenophosphate were decomposed), the mixture was finely ground and placed in a silica tube which was then evacuated and sealed. It was heated at 1073 K for 30 h. The result was a powder containing colorless crystals.

Crystals of  $\text{Cs}_2\text{AlP}_3\text{O}_{10}$  and  $\text{Cs}_2\text{CrP}_3\text{O}_{10}$  were obtained in a similar way, but starting from the correct chemical composition and using  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Prolabo, 98%), and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (ChemPur, 97%), respectively. The evacuated silica ampoules were heated for 25 h, at 1148 K for the aluminum phosphate and at 1273 K for the chromium one.

The synthesis of  $\text{Cs}_2\text{MP}_3\text{O}_{10}$  compounds in the form of single-phase powder samples were performed in air for  $M=\text{Ga}, \text{Al}$  and  $\text{Cr}$ . The precursors were mixed and placed in a platinum crucible heated in air at 673 K for 5 h; the resulting mixture was then finely ground and heated in air at 923 K for 12 h. Results were white powders for the gallium and aluminum phases and a green powder for the chromium one.

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Note that many attempts were made in order to prepare the iron isotopic compound Cs<sub>2</sub>FeP<sub>3</sub>O<sub>10</sub> reported in literature (7), but all of them led to CsFeP<sub>2</sub>O<sub>7</sub> (8,9). Similarly, all the attempts performed to obtain A<sub>2</sub>GaP<sub>3</sub>O<sub>10</sub> and A<sub>2</sub>AlP<sub>3</sub>O<sub>10</sub> compounds for A = Li, Na, K, Rb failed since only AMP<sub>2</sub>O<sub>7</sub> phases were obtained (10–13).

### Crystal Studies, Structural Determination, and Refinements

The EDS analysis of the colorless crystals obtained for M = Ga and Al and of the green crystals extracted from the chromium preparation were first performed with an OXFORD 6650 microprobe mounted on a PHILIPS XL 30 FEG scanning electron microscope. The presence of Cs, M (M = Ga, Al, Cr) and P in the approximate ratio 2:1:3 was thus evidenced. These results were confirmed for the chromium and gallium phases by the analysis performed with an EDS analyzer mounted on a JEOL 2010 CX transmission electron microscope, which led to the following Cs:M:P ratio:2.2(3):0.9(1):3.0(3) for M = Ga and 2.1(2):0.9(1):3.0(2) for M = Cr.

The green crystals of the chromium phase were too small to allow further studies, so that single-crystal studies could only be performed for the gallium and aluminum phosphates. For each phase, several colorless plate-like crystals were optically selected to be tested by the oscillation and Weissenberg methods using the CuK $\alpha$  radiation. The dimension of the single crystals chosen for the structure determination and refinements are reported in Table 1.

The cell parameters given in Table 1 were determined and refined by diffractometric techniques at 293 K using a least-squares method based upon 25 reflections in the range 18° <  $\theta$  < 22°.

The data were then collected on a CAD4 Enraf-Nonius diffractometer using MoK $\alpha$  radiation for  $-24 \leq h \leq 24$ ,  $-17 \leq k \leq 17$  and  $0 \leq l \leq 18$  with the parameters listed in Table 1.

The reflections were corrected for Lorentz and polarization effects, and for absorption and secondary extinction. Both structures were solved in the P2<sub>1</sub>/c space group (no. 14), deduced from the systematic absences  $l = 2n + 1$  for  $h0l$  and  $k = 2n + 1$  for  $0k0$ , using the heavy atom method and successive difference synthesis and Fourier synthesis. The refinement of the atomic coordinates and of the anisotropic thermal factors of all atoms for Cs<sub>2</sub>AlP<sub>3</sub>O<sub>10</sub>, of Cs, Ga and P in Cs<sub>2</sub>GaP<sub>3</sub>O<sub>10</sub> and of the isotropic thermal parameters of the oxygen atoms in Cs<sub>2</sub>GaP<sub>3</sub>O<sub>10</sub> led to the atomic parameters listed in Table 2 and to the reliability factors given in Table 1. Note that the refinement of the anisotropic thermal factors of the oxygen atoms of Cs<sub>2</sub>GaP<sub>3</sub>O<sub>10</sub> was performed, but it led for O(5) to a not positive definite  $u_{ij}$  matrix, i.e., without any physical

**TABLE 1**  
Summary of Crystal Data, Intensity Measurements and Structure Refinement Parameters for Cs<sub>2</sub>GaP<sub>3</sub>O<sub>10</sub> and Cs<sub>2</sub>AlP<sub>3</sub>O<sub>10</sub>

	Cs <sub>2</sub> GaP <sub>3</sub> O <sub>10</sub>	Cs <sub>2</sub> AlP <sub>3</sub> O <sub>10</sub>
<i>Crystal data</i>		
Crystal dimensions (mm <sup>3</sup> )	0.206 × 0.05 × 0.013	0.29 × 0.039 × 0.019
Space group	P2 <sub>1</sub> /c (no. 14)	P2 <sub>1</sub> /c (no. 14)
Cell dimensions	$a = 12.278(2)$ $b = 8.994(1)$ $c = 9.537(1)$ $\beta = 95.34(1)$	$a = 12.261(2)$ $b = 9.010(1)$ $c = 9.421(1)$ $\beta = 94.91(1)$
Volume (Å <sup>3</sup> )	$V = 1048.6(2)$	$V = 1036.9(2)$
Z	4	4
$\rho_{\text{calc}}$ (g · cm <sup>-3</sup> )	3.727	3.495
<i>Intensity measurements</i>		
$\lambda$ (MoK $\alpha$ )	0.71073	0.71073
Scan mode	$\omega - \frac{2}{3}\theta$	$\omega - \theta$
Scan width (°)	1.50 + 0.35tn $\theta$	1.10 + 0.35tn $\theta$
Slit aperture (mm)	1.80 + tn $\theta$	1.20 + tn $\theta$
Max $\theta$ (°)	45	45
Standard reflections	3 measured every 3600 s	3 measured every 3600 s
Measured reflections	17521	17960
Reflections with $I > 3\sigma$	2458	2306
Independent reflections with $I > 3\sigma$	1464	1400
$\mu$ (mm <sup>-1</sup> )	9.962	7.616
<i>Structure solution and refinement</i>		
Parameters refined	96	146
Agreement factors	$R = 0.044$ $R_w = 0.032$	$R = 0.039$ $R_w = 0.030$
Weighting scheme	$w = 1/\sigma^2$	$w = 1/\sigma^2$
$\Delta/\sigma$ max	$< 3 \times 10^{-4}$	$< 2 \times 10^{-4}$

meaning. Since the reliability factors were not significantly improved by the refinement of the anisotropic thermal parameters of all oxygen atoms except O(5), we have reported in Table 2 the results of the refinement of the isotropic thermal parameters for the oxygen atoms. The calculations were performed with the Xtal 3.7 program (14).

### X-Ray Powder Diffraction Studies

X-ray powder diffraction data were collected for Cs<sub>2</sub>GaP<sub>3</sub>O<sub>10</sub>, Cs<sub>2</sub>AlP<sub>3</sub>O<sub>10</sub> and Cs<sub>2</sub>CrP<sub>3</sub>O<sub>10</sub> on a Philips PW 1830 diffractometer using the CuK $\alpha$  radiation. Data were collected in the range 5° ≤ 2 $\theta$  ≤ 115° with a step of 0.02° for Cs<sub>2</sub>GaP<sub>3</sub>O<sub>10</sub> and Cs<sub>2</sub>AlP<sub>3</sub>O<sub>10</sub> (time per step : 9 and 8.5 s, respectively). For both phases, the X-ray diffraction patterns were indexed in monoclinic cells, where parameters were refined in pattern matching mode with the Fullprof.2k program (13), leading to the values of Table 3 and to the following agreement factors :  $R_p = 8.06$ ,  $R_{wp} = 10.5$ ,  $\chi^2 = 1.34$  for Cs<sub>2</sub>GaP<sub>3</sub>O<sub>10</sub> and  $R_p = 8.53$ ,  $R_{wp} = 11.5$ ,

**TABLE 2**  
Positional Parameters and Their Estimated  
Standard Deviations

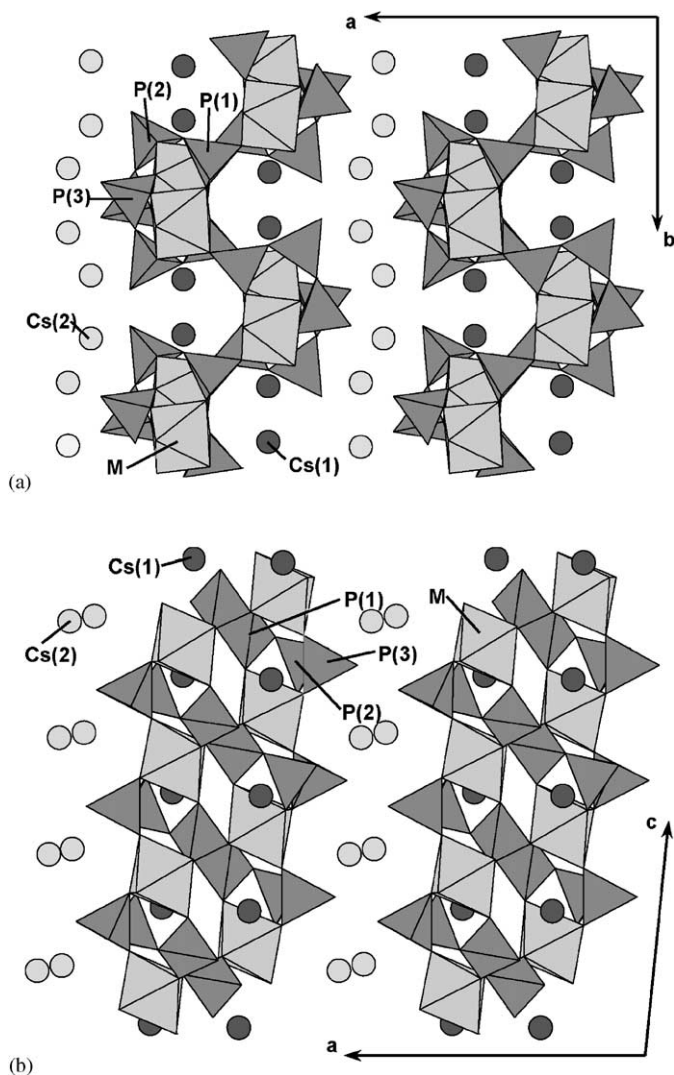
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> * 100(Å <sup>2</sup> )
<b>Cs<sub>2</sub>GaP<sub>3</sub>O<sub>10</sub></b>				
Cs(1)	0.14730(7)	0.1198(1)	0.00773(8)	2.07(5)*
Cs(2)	0.46074(7)	0.1018(1)	0.76127(8)	2.12(5)*
Ga	0.8467(1)	0.1484(1)	0.3549(1)	0.84(6)*
P(1)	-0.0479(2)	0.0821(3)	0.6795(3)	0.9(1)*
P(2)	0.2596(3)	0.0350(3)	0.4177(3)	1.2(2)*
P(3)	0.6876(2)	0.2141(3)	0.0686(3)	1.0(1)*
O(1)	0.7595(6)	0.1277(9)	0.1790(8)	1.6(2)
O(2)	0.9330(6)	0.3143(9)	0.2991(8)	1.3(2)
O(3)	0.7424(7)	0.2801(9)	0.4315(8)	1.4(2)
O(4)	0.9447(6)	0.0032(8)	0.2821(8)	1.3(2)
O(5)	0.9436(6)	0.1559(8)	0.5372(7)	1.0(2)
O(6)	0.7641(7)	-0.0232(9)	0.4298(8)	1.3(2)
O(7)	-0.1444(6)	-0.0417(8)	0.6745(8)	1.3(2)
O(8)	0.3255(6)	0.1626(9)	0.3776(9)	1.8(2)
O(9)	0.3112(6)	-0.1147(9)	0.3729(8)	1.6(2)
O(10)	0.5732(7)	0.1676(9)	0.0541(8)	1.6(2)
<b>Cs<sub>2</sub>AlP<sub>3</sub>O<sub>10</sub></b>				
Cs(1)	0.14600(6)	0.12281(9)	0.00556(7)	2.02(4)*
Cs(2)	0.45843(6)	0.10636(9)	0.75842(7)	2.12(4)*
Al	0.8521(2)	0.1484(3)	0.3539(3)	0.9(2)*
P(1)	-0.0479(2)	0.0840(3)	0.6780(3)	0.8(1)*
P(2)	0.2600(2)	0.0297(3)	0.4229(3)	1.2(1)*
P(3)	0.6945(2)	0.2113(3)	0.0659(3)	1.0(1)*
O(1)	0.7668(5)	0.1344(8)	0.1827(7)	1.4(4)*
O(2)	0.9363(6)	0.3089(7)	0.2974(7)	1.1(4)*
O(3)	0.7525(6)	0.2797(7)	0.4304(7)	1.3(4)*
O(4)	0.9471(6)	0.0078(7)	0.2829(7)	1.0(4)*
O(5)	0.9448(5)	0.1536(8)	0.5325(7)	1.1(4)*
O(6)	0.7712(6)	-0.0157(8)	0.4262(7)	1.5(4)*
O(7)	-0.1484(6)	-0.0338(8)	0.6792(7)	1.4(4)*
O(8)	0.3259(6)	0.1592(8)	0.3877(8)	2.0(4)*
O(9)	0.3185(5)	-0.1164(8)	0.3799(7)	1.8(4)*
O(10)	0.5812(6)	0.1534(8)	0.0480(8)	1.9(4)*

Note. Atoms marked with a star were refined anisotropically and are given in the form of the isotropic equivalent displacement parameter  $U_{\text{eq}}$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

$\chi^2 = 1.29$  for Cs<sub>2</sub>AlP<sub>3</sub>O<sub>10</sub>. For the chromium compound, data were collected in the range  $5^\circ \leq 2\theta \leq 120^\circ$  with a step of 0.02 and 20 s per step. The cell parameters reported in Table 3 result from a Rietveld refinement performed using Fullprof. 2k program (15), which led to the following

**TABLE 3**  
Cell Parameters Obtained from the X-ray Powder Diffraction  
Studies of the Cs<sub>2</sub>MP<sub>3</sub>O<sub>10</sub> Compounds (*M* = Ga, Al, Cr)

Compounds	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>V</i> (Å <sup>3</sup> )
Cs <sub>2</sub> AlP <sub>3</sub> O <sub>10</sub>	12.2586(4)	9.0091(3)	9.4148(3)	94.92(1)	1035.9(1)
Cs <sub>2</sub> CrP <sub>3</sub> O <sub>10</sub>	12.3263(6)	9.0012(4)	9.5863(4)	95.67(2)	1058.4(3)
Cs <sub>2</sub> GaP <sub>3</sub> O <sub>10</sub>	12.2889(3)	9.0003(2)	9.5454(2)	95.36(1)	1051.1(1)



**FIG. 1.** Projection of Cs<sub>2</sub>MP<sub>3</sub>O<sub>10</sub> (*M* = Al, Ga) structure type: (a) along  $c^*$ ; (b) along  $b^*$ .

agreement factors :  $R_p = 8.67$ ,  $R_{wp} = 12.1$ ,  $R_{\text{Bragg}} = 8.86$ ,  $\chi^2 = 4.85$  and confirmed that Cs<sub>2</sub>CrP<sub>3</sub>O<sub>10</sub> crystallizes with the same structure type than Cs<sub>2</sub>GaP<sub>3</sub>O<sub>10</sub> and Cs<sub>2</sub>AlP<sub>3</sub>O<sub>10</sub>.

### Magnetic Measurements

Magnetic susceptibility measurements were performed on a powder sample of Cs<sub>2</sub>CrP<sub>3</sub>O<sub>10</sub> by SQUID magnetometry. After zero cooling and stabilization of the temperature at 4.5 K, a magnetic field of 0.3 T was applied. The magnetic moments were then measured with increasing temperature up to 300 K. The chromium compound shows a paramagnetic behavior and the data were fitted with a Curie-Weiss law:  $\chi_m = C/(T - \theta)$ . The fitting parameter  $C$

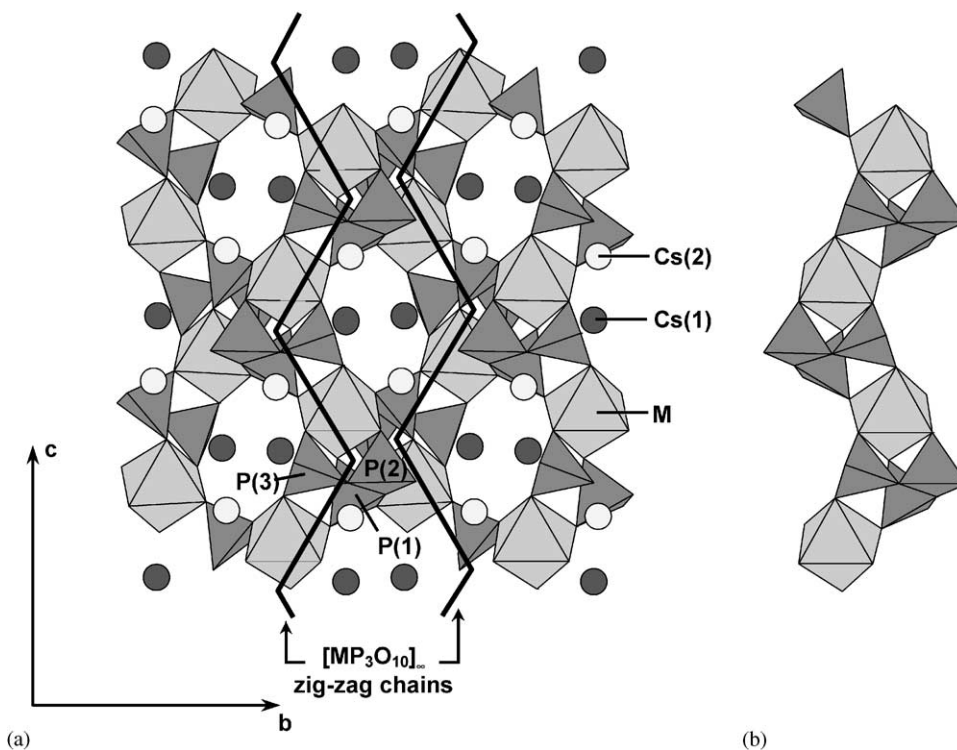


FIG. 2. (a) Projection of  $\text{Cs}_2\text{MP}_3\text{O}_{10}$  structure type ( $M = \text{Al}, \text{Ga}$ ) along  $a'$ , showing one  $[\text{MP}_3\text{O}_{10}]_\infty$  layer resulting from the assemblage of  $[\text{MP}_3\text{O}_{10}]_\infty$  chains; (b) one  $[\text{MP}_3\text{O}_{10}]_\infty$  zig-zag chain running along  $c'$ .

led to a paramagnetic moment of  $3.6 \mu_B$  per  $\text{Cr}^{3+}$  ion, i.e., close to the expected value for an isolated  $\text{Cr}^{3+}$  ion.

#### DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The X-ray diffraction studies performed on the gallium, aluminum and chromium phosphates show that the three compounds crystallize with the same structure. The projections of this structure type along  $c'$  (Fig. 1a) and along  $b'$  (Fig. 1b) show its lamellar character: it is indeed built from  $[\text{MP}_3\text{O}_{10}]_\infty$  layers ( $M = \text{Ga}, \text{Al}, \text{Cr}$ ) parallel to (100) and interleaved with cesium cations. Each  $[\text{MP}_3\text{O}_{10}]_\infty$  layer (Fig. 2a) consists of  $\text{MO}_6$  octahedra and tritetrahedral  $\text{P}_3\text{O}_{10}$  groups sharing corners. It can be described as resulting from an assemblage of  $\text{MP}_3\text{O}_{13}$  units, in which one  $\text{MO}_6$  octahedron shares the three apices of one of its faces with three  $\text{PO}_4$  tetrahedra forming a  $\text{P}_3\text{O}_{10}$  triphosphate group (Fig. 3). Two of the three remaining apices of the  $\text{MO}_6$  octahedron (i.e., O(1) and O(2)) are shared with two tetrahedra of another  $\text{MP}_3\text{O}_{13}$  unit, leading to  $[\text{MP}_3\text{O}_{11}]_\infty$  zig-zag chains running along the [001] direction (Fig. 2b). Finally, the sixth corner (O(14)) of the  $\text{MO}_6$  octahedron is linked to an enantiomorphic  $\text{MP}_3\text{O}_{13}$  unit belonging to an adjacent  $[\text{MP}_3\text{O}_{11}]_\infty$  zig-zag chain (Fig. 2a), and this junction leads to the formation of

$M_2\text{P}_6\text{O}_{24}$  double units presenting an inversion center (Fig. 3). Note the open character of the  $[\text{MP}_3\text{O}_{10}]_\infty$  layers which exhibit very large eight-sided windows delimited by the polyhedra of six different  $\text{MP}_3\text{O}_{13}$  units belonging to four  $M_2\text{P}_6\text{O}_{24}$  double units (Fig. 2a). Moreover, the undulation of the polyhedra of the layers makes that they form pseudo-tunnels running along  $c'$  (Fig. 1a), where  $\text{Cs}^+$  cations are sitting.

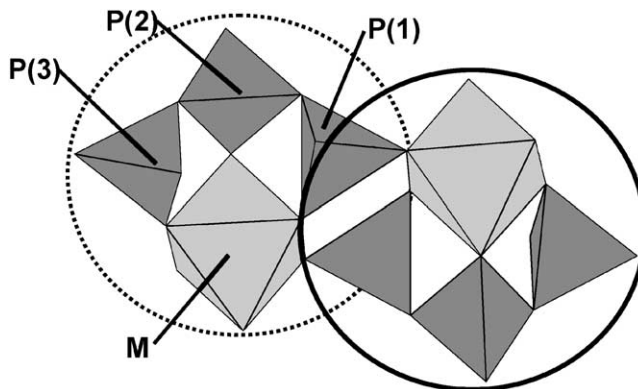


FIG. 3. Assemblage of two  $\text{MP}_3\text{O}_{13}$  units forming one  $M_2\text{P}_6\text{O}_{24}$  double unit.

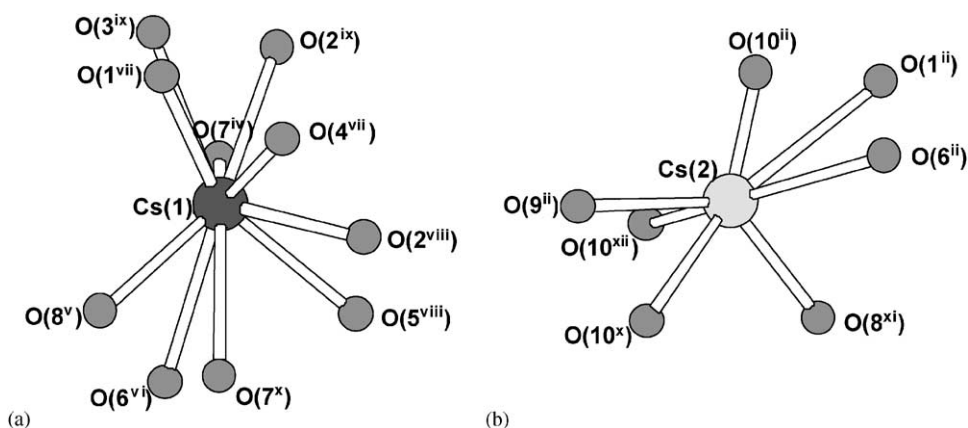


FIG. 4. Cesium environments in  $\text{Cs}_2\text{MP}_3\text{O}_{10}$  structure type ( $M = \text{Al}, \text{Ga}$ ): (a) for Cs(1); (b) for Cs(2).

The cesium cations occupy two independent positions: Cs(1) is located in the cavities of the  $[\text{MP}_3\text{O}_{10}]_\infty$  waved layer, on both sides of the eight-sided windows, whereas Cs(2) sits between two successive  $[\text{MP}_3\text{O}_{10}]_\infty$  layers, ensuring the cohesion of the structure (Fig. 1a).

As a result, Cs(1) and Cs(2) cations present very different environments, as shown in Fig. 4a and 4b. Cs(1) is ten-fold coordinated (Fig. 4a) with Cs(1)–O distances ranging from 3.092(7) to 3.504(7) Å in the gallium phosphate and from 3.074(7) to 3.576(7) Å in  $\text{Cs}_2\text{AlP}_3\text{O}_{10}$  (Table 4). Cs(2) is

surrounded by seven oxygen atoms (Fig. 4b) at distances ranging from 2.970(8) to 3.490(8) Å in  $\text{Cs}_2\text{GaP}_3\text{O}_{10}$  and from 2.987(7) to 3.592(7) Å in  $\text{Cs}_2\text{AlP}_3\text{O}_{10}$ . An analysis of the electrostatic bond strengths was carried out using the Brese and O'Keeffe relation (16): the bond valence sums led to 1.0 for Cs(1) and for Cs(2) in  $\text{Cs}_2\text{GaP}_3\text{O}_{10}$  and to 1.1 for Cs(1) and 1.0 for Cs(2) in  $\text{Cs}_2\text{AlP}_3\text{O}_{10}$ .

Concerning the geometry of the  $\text{P}_3\text{O}_{10}$  triphosphate group, one can notice that the central  $\text{P}(2)\text{O}_4$  tetrahedron, as one of the external tetrahedra,  $\text{P}(3)\text{O}_4$ , present one free

TABLE 4

Distances (Å) and angles (°) in  $\text{Cs}_2\text{GaP}_3\text{O}_{10}$ <sup>a</sup>

Ga	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.914(7)	2.87(1)	2.80(1)	2.64(1)	3.36(1)	2.75(1)
O(2)	96.3(3)	1.933(8)	2.78(1)	2.81(1)	2.67(1)	3.94(1)
O(3)	93.1(3)	91.8(3)	1.937(8)	3.88(1)	2.81(1)	2.74(1)
O(4)	86.3(3)	92.7(3)	175.5(3)	1.947(8)	2.79(1)	2.75(1)
O(5)	175.8(3)	85.2(3)	90.7(3)	89.7(3)	2.014(7)	2.84(1)
O(6)	88.7(3)	175.0(3)	87.8(3)	87.8(3)	89.8(3)	2.014(8)
P(1)	O(2 <sup>i</sup> )	O(4 <sup>ii</sup> )	O(5 <sup>iii</sup> )	O(7)		
O(2 <sup>i</sup> )	1.508(8)	2.44(1)	2.53(1)	2.51(1)		
O(4 <sup>ii</sup> )	108.6(4)	1.498(8)	2.54(1)	2.47(1)		
O(5 <sup>iii</sup> )	114.0(4)	115.6(5)	1.506(8)	2.51(1)		
O(7)	106.4(5)	104.8(4)	106.7(4)	1.623(8)		
P(2)	O(6 <sup>ii</sup> )	O(7 <sup>iv</sup> )	O(8)	O(9)		
O(6 <sup>ii</sup> )	1.513(9)	2.50(1)	2.56(1)	2.50(1)		
O(7 <sup>iv</sup> )	107.0(5)	1.595(8)	2.48(1)	2.49(1)		
O(8)	117.6(5)	107.9(4)	1.475(9)	2.50(1)		
O(9)	108.7(5)	104.1(4)	110.7(5)	1.564(9)		
P(3)	O(1)	O(3 <sup>v</sup> )	O(9 <sup>vi</sup> )	O(10)		
O(1)	1.524(8)	2.49(1)	2.51(1)	2.51(1)		
O(3 <sup>v</sup> )	109.6(5)	1.526(9)	2.52(1)	2.52(1)		
O(9 <sup>vi</sup> )	104.9(4)	105.6(4)	1.637(9)	2.48(1)		
O(10)	114.2(5)	115.2(5)	106.3(5)	1.460(9)		

TABLE 4—Continued

Distances (Å) and angles (°) in Cs<sub>2</sub>AlP<sub>3</sub>O<sub>10</sub><sup>b</sup>

Al	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.850(7)	2.753(9)	2.69(1)	2.593(9)	3.798(9)	2.66(1)
O(2)	95.1(3)	1.880(8)	2.68(1)	2.720(9)	2.614(9)	3.81(1)
O(3)	92.3(3)	90.9(3)	1.887(8)	3.77(1)	2.718(9)	2.67(1)
O(4)	88.0(3)	92.6(3)	176.5(4)	1.882(7)	2.696(9)	2.65(1)
O(5)	177.2(4)	86.1(3)	90.2(3)	89.4(3)	1.949(7)	2.738(9)
O(6)	89.2(3)	175.7(3)	88.7(3)	87.8(3)	89.6(3)	1.936(8)
P(1)	O(2 <sup>i</sup> )	O(4 <sup>ii</sup> )	O(5 <sup>iii</sup> )	O(7)		
O(2 <sup>i</sup> )	1.507(7)	2.45(1)	2.529(9)	2.495(9)		
O(4 <sup>ii</sup> )	109.0(4)	1.507(7)	2.550(9)	2.47(1)		
O(5 <sup>iii</sup> )	114.3(4)	115.8(4)	1.503(7)	2.52(1)		
O(7)	105.5(4)	104.2(4)	107.0(4)	1.627(7)		
P(2)	O(6 <sup>ii</sup> )	O(7 <sup>iv</sup> )	O(8)	O(9)		
O(6 <sup>ii</sup> )	1.510(8)	2.506(9)	2.55(1)	2.51(1)		
O(7 <sup>iv</sup> )	107.1(4)	1.605(7)	2.49(1)	2.51(1)		
O(8)	117.8(4)	107.7(4)	1.473(8)	2.49(1)		
O(9)	109.3(4)	104.4(4)	109.6(4)	1.569(8)		
P(3)	O(1)	O(3 <sup>v</sup> )	O(9 <sup>vi</sup> )	O(10)		
O(1)	1.519(7)	2.491(9)	2.52(1)	2.514(9)		
O(3 <sup>v</sup> )	110.4(4)	1.516(8)	2.53(1)	2.53(1)		
O(9 <sup>vi</sup> )	105.8(4)	106.0(4)	1.646(8)	2.48(1)		
O(10)	113.9(4)	115.2(4)	104.7(4)	1.480(7)		

<sup>a</sup> Cs(1)	–O(4 <sup>vii</sup> ) = 3.092(7)	Cs(2)	–O(8 <sup>xi</sup> ) = 2.970(8)	<sup>b</sup> Cs(1)	–O(7 <sup>iv</sup> ) = 3.074(7)	Cs(2)	–O(8 <sup>xi</sup> ) = 2.987(7)
	–O(7 <sup>iv</sup> ) = 3.114(8)		–O(10 <sup>ii</sup> ) = 3.046(8)		–O(4 <sup>vii</sup> ) = 3.089(6)		–O(10 <sup>xiii</sup> ) = 3.031(7)
	–O(1 <sup>viii</sup> ) = 3.133(8)		–O(10 <sup>xiii</sup> ) = 3.056(8)		–O(2 <sup>viii</sup> ) = 3.158(7)		–O(10 <sup>ii</sup> ) = 3.031(8)
	–O(2 <sup>viii</sup> ) = 3.203(8)		–O(9 <sup>ii</sup> ) = 3.188(8)		–O(1 <sup>vii</sup> ) = 3.160(7)		–O(9 <sup>ii</sup> ) = 3.130(7)
	–O(5 <sup>viii</sup> ) = 3.246(7)		–O(6 <sup>ii</sup> ) = 3.241(8)		–O(5 <sup>viii</sup> ) = 3.211(7)		–O(6 <sup>ii</sup> ) = 3.284(7)
	–O(8 <sup>v</sup> ) = 3.266(8)		–O(10 <sup>x</sup> ) = 3.241(8)		–O(8 <sup>v</sup> ) = 3.221(7)		–O(10 <sup>x</sup> ) = 3.375(8)
	–O(3 <sup>ix</sup> ) = 3.371(8)		–O(1 <sup>ii</sup> ) = 3.490(8)		–O(3 <sup>ix</sup> ) = 3.368(7)		–O(1 <sup>ii</sup> ) = 3.592(7)
	–O(6 <sup>vi</sup> ) = 3.425(8)				–O(6 <sup>vi</sup> ) = 3.456(7)		
	–O(2 <sup>ix</sup> ) = 3.500(8)				–O(7 <sup>x</sup> ) = 3.552(7)		
	–O(7 <sup>x</sup> ) = 3.504(7)				–O(2 <sup>ix</sup> ) = 3.576(7)		

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

apex (respectively, O(8) and O(10)), which correspond to the shortest P–O bonds (from 1.460(9) to 1.480(9) Å). On the opposite, the longest P–O distances are observed for the two bridging oxygen atoms (O(7) and O(9)) of the P<sub>3</sub>O<sub>10</sub> group (Table 4) (from 1.569(8) to 1.646(8) Å). Note that such distances, even if they are rather long, have already been observed in other triphosphates as for example in Co<sub>2</sub>LiP<sub>3</sub>O<sub>10</sub> (5) (1.66 Å) or in (NH<sub>4</sub>)<sub>4</sub>NaP<sub>3</sub>O<sub>10</sub>·4H<sub>2</sub>O (17) and can be regarded as normal since they correspond to P–O–P bridges (18).

Finally, the P–O distances corresponding to the oxygen atoms shared with MO<sub>6</sub> octahedra are rather homoge-

neous, since they are ranging from 1.498(8) to 1.526(9) Å (Table 4). Consequently, the P(1)O<sub>4</sub> tetrahedron presents three standard P(1)–O distances of about 1.50 Å and one very long P(1)–O(7) bond of about 1.62 Å. In the central P(2)O<sub>4</sub> tetrahedron of the triphosphate group, there are two long P–O bonds (from 1.564(9) to 1.605(7) Å), a short one (1.47 Å) and an intermediate one (1.51 Å). The third tetrahedron exhibits one very long P(3)–O distance (1.64 Å), one very short P(3)–O bond and two intermediate ones.

Note that the configuration of this P<sub>3</sub>O<sub>10</sub> triphosphate group is quite unusual, especially because of the

P(1)–P(2)–P(3) angles of  $81.1(1)^\circ$  and  $80.0(1)^\circ$  for the Ga and Al compounds, respectively, i.e., much smaller than in other triphosphates. As a matter of fact, if the P–P distances always present similar values (ca. 2.8–3.0 Å) one can observe very different P(1)–P(2)–P(3) angles in other triphosphates, ranging from  $87.6^\circ$  in  $\text{YbH}_2\text{P}_3\text{O}_{10}$  (19) or  $93.6^\circ$  in  $\text{CuNa}_3\text{P}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$  (20) to  $151.5^\circ$  or  $156.70^\circ$  in the two forms of  $\text{Na}_5\text{P}_3\text{O}_{10}$  (21,22).

The geometry of the  $\text{MO}_6$  octahedron is rather regular. In the gallium phosphate, the Ga–O distances range from 1.914(7) to 2.014(8) Å, whereas the Al–O bonds observed in  $\text{Cs}_2\text{AlP}_3\text{O}_{10}$  are ranging from 1.850(7) to 1.936(8) Å. These results are in agreement with those reported for other gallium and aluminum phosphates (10–13, 23–25). Moreover, one can notice that the cell volume of the aluminum phosphate is significantly smaller than those of the gallium and chromium phases (Table 3): this is consistent with the smaller value of the effective ionic radius of  $\text{Al}^{3+}$  compared to those of  $\text{Ga}^{3+}$  and  $\text{Cr}^{3+}$  (26).

In conclusion, a new series of triphosphates  $\text{Cs}_2\text{MP}_3\text{O}_{10}$  ( $M = \text{Ga}, \text{Al}, \text{Cr}$ ) with an original structure has been synthesized. It is the first non-hydrated triphosphate containing cesium that is known to date. Although the number of non-hydrated triphosphates that have been synthesized up to now is very small, this study suggests that there should exist many others, provided the interpolated  $A$  cation be large enough and in sufficient amount to stabilize the structure.

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#### REFERENCES

- G. J. McCarthy, W. B. White, and D. E. Pfoertsch, *Mater. Res. Bull.* **13**, 1239–1245 (1978).
- J. Carpena and J. L. Lacout, *L'Actualité Chim.* **2**, 3–9 (1997).
- M. T. Averbuch-Pouchot, A. Durif, J. Coing-Boyat, and J. C. Guitel, *Acta Crystallogr. B* **33**, 203–205 (1977).
- M. T. Averbuch-Pouchot and A. Durif, *C.R. Acad. Sci.* **316**, 609–614 (1993).
- F. Erragh, A. Boukhari, and E. M. Holt, *Acta Crystallogr. C* **52**, 867–1869 (1996).
- K. Kissouli, K. Benkhouja, A. Sadel, M. Bettach, M. Zahir, M. Giorgi, M. Pierrot, and M. Drillon, *Eur. J. Solid State Inorg. Chem.* **34**, 221–230 (1997).
- V. A. Lyutsko, O. G. Pap, and N. M. Ksenofontova, *Inorg. Mater.* (Engl. Transl.) **22**, 1203 (1986).
- E. Dvoncova and K. H. Lii, *J. Solid State Chem.* **105**, 279 (1993).
- J. M. M. Millet and B. F. Mentzen, *Eur. J. Solid State Inorg. Chem.* **28**, 493 (1991).
- E. A. Genkin and V. A. Timofeeva, *Zh. Strukt. Khim.* **30**, 173–175 (1989).
- N. Chudinova, *et al.*, *Inorg. Mater.* (Engl. Transl.) **15**, 1710 (1979).
- J. Alkemper, H. Paulus, and H. Fuess, *Z. Kristallogr.* **209**, 616 (1994).
- H. N. Ng and C. Calvo, *Can. J. Chem.* **51**, 2613–2620 (1973).
- S. R. Hall, D. J. du Boulay, and R. Olthof-Hazerkamp, Eds., "Xtal 3.7 System," University of Western Australia, 2000.
- J. Rodriguez-Carjaval, in "Satellite Meeting on Powder Diffraction, Abstracts of the XVth Conference of the International Union of Crystallography" (J. Galy, Ed.) p. 127, Toulouse, 1990.
- N. E. Brese and M. O'Keeffe, *Acta Crystallogr. B* **47**, 192 (1991).
- M. T. Averbuch-Pouchot and A. Durif, *Acta Crystallogr. C* **41**, 1553–1555 (1985).
- A. Durif, in "Crystal Chemistry of Condensed Phosphates," p. 375, Plenum Press, New York, 1995.
- K. K. Palkina, S. I. Maksimova, and V. G. Kuznetsov, *Izv. Akad. Nauk. SSSR, Neorg. Mater.* **15**, 2168–2170 (1979).
- O. Jouini, M. Dabbabi, M. T. Averbuch-Pouchot, A. Durif, and J. C. Guitel, *Acta Crystallogr. C* **40**, 728–730 (1984).
- D. R. Davies and D. E. C. Corbridge, *Acta Crystallogr.* **13**, 263 (1960).
- D. E. C. Corbridge, *Acta Crystallogr.* **11**, 315 (1958).
- A. S. Lyakhov, V. A. Lutsko, G. K. Tuchkovskii, and K. K. Palkina, *Zh. Neorg. Khim.* **36**, 1415–1417 (1991).
- R. Hoppe and M. Serafin, *Z. Anorg. Allg. Chem.* **623**, 39–44 (1997).
- M. T. Averbuch-Pouchot, A. Durif, and J. C. Guitel, *Acta Crystallogr. B* **33**, 1436–1438 (1977).
- R. D. Shannon, *Acta Crystallogr. A* **32**, 751 (1976).