

Thus the atomic arrangement of $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$ may be schematically represented as a stacking of alternate P_4O_{12} and $\text{Li}_8\text{O}_{16}(\text{H}_2\text{O})_6$ rings along the twofold axes.

In addition, the existence of two water molecules should be noted: $\text{O}(W1)$ and $\text{O}(W5)$ not bonded to the associated cations. During the structure determination, they appeared to be affected by large thermal factors. In such cases, it is always difficult to decide if the magnitude of these factors corresponds to the mobility of this type of water or to a partially occupied crystallographic site.

The group of five water molecules builds pentagonal rings around the c axis. In these pentagonal rings the average $\text{O}(W)\text{—O}(W)\text{—O}(W)$ angle is 107.6° showing these rings to be flat within the experimental-error range since this value should be 108° for a flat regular pentagon.

Table 2 reports the main interatomic distances and bond angles in this atomic arrangement.

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Structure of Tetraesium Tetrametaphosphate Tetrahydrate

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Abstract. $\text{Cs}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$, $M_r = 916.56$, tetragonal, $P4_1$, $a = 9.466$ (5), $c = 21.933$ (9) Å, $V = 1965.3$ Å³, $Z = 4$, $D_x = 3.107$ Mg m⁻³, $\lambda(\text{Ag K}\alpha) = 0.5608$ Å, $\mu = 4.05$ mm⁻¹, $F(000) = 1664$, $T = 293$ K, final $R = 0.035$ for 1654 independent observed reflexions. The atomic arrangement may be described as alternating layers of P_4O_{12} ring anions and caesium polyhedra perpendicular to the c axis. The rubidium salt $\text{Rb}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ is isotypic, with $a = 9.163$ (3), $c = 21.356$ (8) Å, $D_x = 2.703$ Mg m⁻³ and $V = 1793.8$ Å³.

Introduction. Various alkali-metal tetrametaphosphates have previously been described: $\text{Li}_4\text{P}_4\text{O}_{12}\cdot 5\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1986), two crystalline forms of $\text{Na}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ (Ondik, 1964; Ondik, Block & MacGillavry, 1961), $\text{Na}_4\text{P}_4\text{O}_{12}\cdot \text{H}_2\text{O}$ and $\text{Na}_4\text{P}_4\text{O}_{12}$ (Wiench & Jansen, 1983), $\text{K}_4\text{P}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1985*b*), $\text{K}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1985*a*) but, up to now, nothing was known concerning the rubidium and caesium tetrametaphosphates. In the present study, we describe the crystal structure of caesium tetrametaphosphate tetrahydrate: $\text{Cs}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$.

Experimental. Rubidium and caesium tetrametaphosphate tetrahydrates have been synthesized by slowly adding the stoichiometric amount of P_4O_{10} to a water

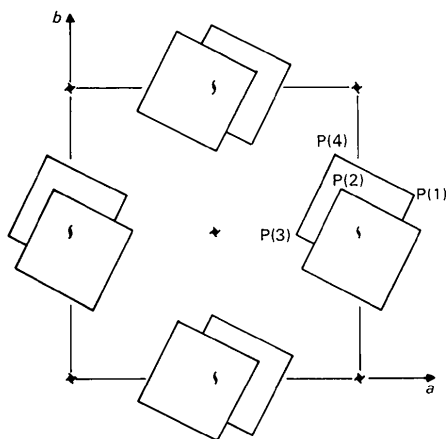
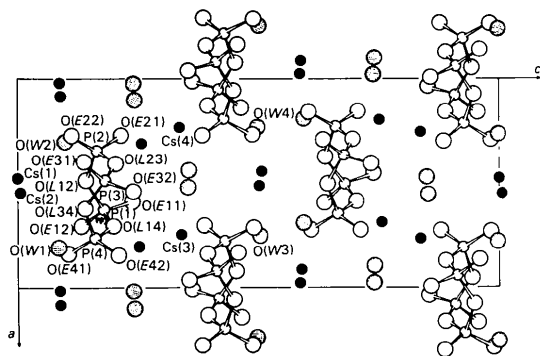
solution of the appropriate carbonate kept at 273 K. The resulting solution is then slowly evaporated at room temperature. Crystals of these two salts are large distorted octahedra.

Density not measured. Cubic fragment $0.25 \times 0.25 \times 0.25$ mm. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: $00l$, $l = 4n$. 18 reflexions ($9 < \theta < 12^\circ$) for refining unit-cell dimensions. ω scan. 2087 reflexions measured ($3 < \theta < 25^\circ$), hkl , $h_{\max} = 14$, $k_{\max} = 14$, $l_{\max} = 33$. Scan width 1.20° , scan speed $0.02^\circ \text{ s}^{-1}$, total background measuring time 20 s. Two orientation and intensity reflexions (008 and $00\bar{8}$) every 2 h, no variation. Lorentz and polarization correction, no absorption correction. Classical methods for structure determination: Patterson and successive Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F). Unit weights. Final refinement with 1654 reflexions corresponding to $I > 6\sigma(I)$. Final $R = 0.035$ ($wR = 0.040$). For the complete set of unique reflexions (2087) $R = 0.043$. Extinction coefficient refined: 0.34×10^{-8} (Stout & Jensen, 1968). $S = 4.12$. Max. $\Delta/\sigma = 0.29$ [β_{11} of $\text{O}(W4)$]. Max. peak height in final difference Fourier synthesis $0.692 \text{ e } \text{Å}^{-3}$. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. H atoms could not be located.

Table 1. Final atomic coordinates and B_{eq}

$$B_{eq} = \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
Cs(1)	0.4821 (1)	0.1962 (1)	0	2.42 (3)
Cs(2)	0.4515 (1)	0.3128 (1)	0.50468 (7)	2.69 (3)
Cs(3)	0.0867 (1)	0.2556 (1)	0.08807 (7)	2.43 (3)
Cs(4)	0.2354 (1)	0.0202 (1)	0.33618 (7)	2.64 (3)
P(1)	0.1983 (5)	0.6275 (5)	0.4270 (2)	1.6 (1)
P(2)	0.3510 (5)	0.9431 (5)	0.1640 (2)	1.8 (1)
P(3)	0.4922 (5)	0.2178 (5)	0.1793 (2)	1.6 (1)
P(4)	0.9207 (5)	0.7679 (5)	0.4100 (2)	1.8 (1)
O(E11)	0.730 (1)	0.412 (1)	0.9845 (7)	2.5 (4)
O(E12)	0.277 (1)	0.709 (1)	0.3806 (7)	2.6 (4)
O(L12)	0.493 (1)	0.865 (1)	0.1414 (6)	2.1 (4)
O(L14)	0.710 (1)	0.943 (1)	0.1971 (6)	1.8 (3)
O(E21)	0.274 (1)	0.858 (1)	0.2107 (7)	2.7 (4)
O(E22)	0.280 (2)	-0.010 (1)	0.1076 (7)	3.0 (4)
O(L23)	0.926 (1)	0.413 (1)	0.4514 (6)	1.8 (3)
O(E31)	0.404 (1)	0.298 (1)	0.1359 (7)	2.7 (4)
O(E32)	0.541 (2)	0.287 (1)	0.2356 (7)	3.1 (5)
O(E41)	0.839 (1)	0.035 (1)	0.1025 (6)	2.3 (4)
O(E42)	0.846 (1)	0.165 (1)	0.2065 (7)	2.6 (4)
O(L43)	0.624 (1)	0.156 (1)	0.1395 (6)	2.0 (4)
O(W1)	0.525 (2)	0.834 (2)	0.3509 (7)	3.8 (5)
O(W2)	0.446 (2)	0.285 (2)	0.3524 (7)	3.9 (5)
O(W3)	0.721 (2)	0.103 (2)	0.4921 (8)	4.4 (6)
O(W4)	0.734 (2)	0.982 (2)	0.9883 (8)	4.2 (6)

Fig. 1. Projection along the *c* axis of the respective locations of the P_4O_{12} ring anions in $Cs_4P_4O_{12} \cdot 4H_2O$.Fig. 2. Projection along the *b* axis of the atomic arrangement of $Cs_4P_4O_{12} \cdot 4H_2O$.

Discussion. Final atomic coordinates and B_{eq} are reported in Table 1. * Fig. 1 gives in projection along the *c* axis the distribution of the P_4O_{12} ring anions inside the unit cell, while Fig. 2 is a projection of the atomic arrangement along the *b* axis. The crystal structure can be easily described as a succession of layers perpendicular to the *c* axis and separated by $c/12$. The P_4O_{12} ring anions spread in layers located at $z \sim (3n + 2)/12$.

* Lists of structure factors and of anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42569 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in $Cs_4P_4O_{12} \cdot 4H_2O$

P(1) O_4 tetrahedron					
P(1)	O(E11)	O(E12)	O(L12)	O(L14)	
O(E11)	<u>1.48 (1)</u>	2.55 (1)	2.57 (1)	2.47 (1)	
O(E12)	119.1 (5)	<u>1.479 (9)</u>	2.46 (1)	2.55 (1)	
O(L12)	112.5 (5)	<u>105.6 (5)</u>	<u>1.613 (9)</u>	2.50 (1)	
O(L14)	105.7 (5)	110.8 (4)	101.8 (3)	<u>1.611 (8)</u>	
P(2) O_4 tetrahedron					
P(2)	O(E21)	O(E22)	O(L12)	O(L23)	
O(E21)	<u>1.491 (9)</u>	2.58 (1)	2.57 (1)	2.44 (1)	
O(E22)	121.0 (5)	<u>1.47 (1)</u>	2.45 (1)	2.54 (1)	
O(L12)	111.7 (5)	<u>105.0 (6)</u>	<u>1.608 (8)</u>	2.49 (1)	
O(L23)	104.0 (6)	111.4 (5)	102.1 (3)	<u>1.599 (8)</u>	
P(3) O_4 tetrahedron					
P(3)	O(E31)	O(E32)	O(L23)	O(L43)	
O(E31)	<u>1.477 (9)</u>	2.55 (1)	2.56 (1)	2.48 (1)	
O(E32)	119.3 (5)	<u>1.47 (1)</u>	2.47 (1)	2.57 (1)	
O(L23)	111.1 (4)	<u>105.6 (5)</u>	<u>1.627 (7)</u>	2.54 (1)	
O(L43)	105.6 (5)	111.5 (5)	102.4 (3)	<u>1.628 (9)</u>	
P(4) O_4 tetrahedron					
P(4)	O(E41)	O(E42)	O(L14)	O(L43)	
O(E41)	<u>1.491 (9)</u>	2.59 (1)	2.56 (1)	2.48 (1)	
O(E42)	120.2 (5)	<u>1.499 (9)</u>	2.47 (1)	2.57 (1)	
O(L14)	110.9 (4)	<u>104.7 (5)</u>	<u>1.619 (8)</u>	2.52 (1)	
O(L43)	104.7 (5)	111.4 (5)	102.3 (3)	<u>1.612 (8)</u>	
P(1)–P(2)		2.953 (4)	P(2)–P(3)		2.943 (4)
P(1)–P(4)		2.968 (4)	P(3)–P(4)		2.951 (4)
P(1)–O(L12)–P(2)		133.0 (7)	P(2)–O(L23)–P(3)		131.6 (7)
P(1)–O(L14)–P(4)		133.4 (6)	P(3)–O(L43)–P(4)		131.2 (6)
P(1)–P(2)–P(3)		89.2 (1)	P(2)–P(3)–P(4)		89.6 (1)
P(3)–P(4)–P(1)		88.8 (1)	P(4)–P(1)–P(2)		89.0 (1)
Cs O_n polyhedra					
Cs(1)–O(E11)		3.130 (8)	Cs(2)–O(E11)		3.150 (9)
O(E31)		3.22 (1)	O(E12)		3.171 (9)
O(E32)		3.110 (9)	O(L12)		3.480 (9)
O(E42)		3.179 (8)	O(E21)		3.108 (9)
O(L43)		3.361 (8)	O(E32)		3.312 (9)
O(W1)		3.28 (1)	O(W2)		3.35 (1)
O(W3)		3.43 (1)	O(W3)		3.24 (1)
O(W4)		3.14 (1)	O(W4)		3.32 (1)
Cs(3)–O(L14)		3.392 (8)	Cs(4)–O(E12)		3.128 (8)
O(E22)		3.141 (8)	O(E21)		3.17 (1)
O(E31)		3.206 (9)	O(E22)		3.288 (9)
O(E41)		3.154 (8)	O(L23)		3.437 (9)
O(E42)		3.130 (9)	O(E41)		3.101 (7)
O(W1)		3.18 (1)	O(W1)		3.28 (1)
O(W2)		3.41 (1)	O(W2)		3.22 (1)
O(W3)		3.39 (1)	O(W3)		3.44 (1)
			O(W4)		3.35 (1)

Details of interatomic distances and bond angles in these groups are reported in Table 2. They have no internal symmetry. Mixed layers containing both Cs atoms and water molecules correspond to $z \sim 3n/12$ and $(3n + 1)/12$. Caesium coordination polyhedra located in layers separated by $c/12$ share O atoms while between two layers separated by $c/6$ only water molecules are shared. Cs—O distances in the various caesium polyhedra are given in Table 2.

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Structure Refinement of Lead Nitrate

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Abstract. $\text{Pb}(\text{NO}_3)_2$, $M_r = 331.20$, cubic, $Pa3$, $a = 7.8586(2) \text{ \AA}$, $V = 485.33 \text{ \AA}^3$, $Z = 4$, $D_x = 4.535 \text{ Mg m}^{-3}$, neutrons, $\lambda = 0.8313(9) \text{ \AA}$, $\mu = 0.0015 \text{ mm}^{-1}$, room temperature. The atomic arrangement was refined with single-crystal neutron diffraction data to $R = 0.019$ for 297 reflections. The structure is built up by a cubic face-centred-type arrangement of Pb^{2+} ions with nitrate groups in between. The N—O bond length (uncorrected for thermal vibration) is $1.2469(6) \text{ \AA}$, the deviation of the N atom from the O_3 plane is $0.0102(7) \text{ \AA}$. The amplitudes of the thermal vibrations have normal values.

Introduction. In connection with recent structural work on $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$ (Nowotny & Heger, 1983) it seemed interesting to refine also the structure of $\text{Pb}(\text{NO}_3)_2$ from carefully measured single-crystal neutron diffraction data. The structure of $\text{Pb}(\text{NO}_3)_2$ was determined by Vegard & Bilberg (1931) from X-ray powder data and by Hamilton (1957) from

neutron powder data assuming space group $Pa3$. Weber & Haussühl (1977) found this space group compatible with careful determinations of physical properties, but Arkhipenko, Bokiy, Fyodorova & Shebanin (1983) recently reported space group $P2_13$ for this compound.

Experimental. A single crystal of $\text{Pb}(\text{NO}_3)_2$ (grown from aqueous solution at about 320 K, size approximately $1.8 \times 2.9 \times 3.0 \text{ mm}$) was mounted on the $P110$ neutron four-circle diffractometer at the 5C2 beam of the ORPHEE reactor at CEN Saclay (France) [wavelength, according to the lattice constant $a = 7.8586(2) \text{ \AA}$ (Swanson, Gilfrich & Ugrinic, 1955), $0.8313(9) \text{ \AA}$]. Before the measurements the crystal was quenched in liquid nitrogen (Heger & Kuhs, 1979). The remaining extinction effects had to be corrected in the structure refinement.

1296 reflections with $\sin\theta/\lambda \leq 0.8 \text{ \AA}^{-1}$ were measured of which 195 were 'forbidden' reflections in space group $Pa3$; range of hkl : $0 \leq h \leq 12$, $-12 \leq k \leq 0$, $0 \leq l \leq 12$. Standard reflection: 006, mean intensity measured 2995.12 counts, σ (calculated from counting statistics) 5.12.

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