

It is of interest that of the three salts of the form $[M(H_2O)_6](XO_3)_2$ whose structures we have determined, this is the first case in which the halate ion displayed rigid-body motion. In all three cases, the metal–oxygen complex manifested rigid-body motion.

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Crystal Chemistry of *cyclo*-Hexaphosphates. XX. Structure of Cerium *cyclo*-Hexaphosphate Decahydrate

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Abstract. $Ce_2P_6O_{18} \cdot 10H_2O$, $M_r = 934.22$, orthorhombic, $P2_12_12$, $a = 13.522$ (5), $b = 13.105$ (9), $c = 6.938$ (3) Å, $V = 1230$ (2) Å³, $Z = 2$, $D_x = 2.523$ Mg m⁻³, $\lambda(Ag K\alpha) = 0.5608$ Å, $\mu = 2.125$ mm⁻¹, $F(000) = 900$, room temperature, final $R = 0.036$ for 3450 independent reflections. The title compound and the previously described $Ca_2(NH_4)_2P_6O_{18} \cdot 6H_2O$ [Averbuch-Puchot (1990). *Acta Cryst.* **C46**, 2005–2007] have some common features, but they are not isostructural. Of the approximately 55 known *cyclo*-hexaphosphates, these two compounds are unique examples of structures exhibiting a P_6O_{18} ring anion with twofold internal symmetry. The coordination around the Ce atom forms a three-capped trigonal prism. CeO_9 polyhedra interconnect P_6O_{18} rings in a three-dimensional way.

Introduction. This work is part of a systematic investigation of *cyclo*-hexaphosphates of mono-valent, divalent, trivalent and mixed cations. Ce_2 -

$P_6O_{18} \cdot 10H_2O$ is the fourth structural type observed so far in the domain of trivalent cation *cyclo*-hexaphosphates, the previous ones being represented by $Cr_2P_6O_{18}$ (Bagieu-Beucher & Guitel, 1977), $Nd_2P_6O_{18} \cdot 12H_2O$ (Trunov, Chudinova & Borodina, 1988) and $Cr_2P_6O_{18} \cdot 21H_2O$ (Bagieu-Beucher, Averbuch-Pouchot & Rzaigui, 1991). Up to now the existence of isotopic salts has been reported only for the first structure type, namely $Al_2P_6O_{18}$ (Kanene, Konstant & Krasnikov, 1985) and $Ga_2P_6O_{18}$ (Chudinova, Grunze & Guzeva, 1987).

Experimental. The chemical preparation of the title compound has already been described in a general article about the synthesis of rare-earth *cyclo*-hexaphosphates (Rzaigui, 1991). Crystal size: $0.16 \times 0.14 \times 0.13$ mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. 18 reflections ($10.9 < \theta < 13.1^\circ$) for refining unit-cell dimensions. ω scan, scan width: 1.20° , scan speed:

Table 1. Final atomic coordinates and B_{eq} values with *e.s.d.*'s in parentheses
$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
Ce	0.20675 (2)	0.24019 (2)	0.22110 (4)	0.882 (2)
P(1)	0.3710 (1)	0.6576 (1)	0.2716 (2)	1.11 (2)
P(2)	0.0417 (1)	0.8141 (1)	0.9774 (2)	1.30 (2)
P(3)	0.3164 (1)	0.4845 (1)	0.0281 (2)	1.26 (2)
O(L12)	0.0144 (3)	0.1679 (4)	0.7767 (8)	2.33 (7)
O(L13)	0.8467 (4)	0.9572 (3)	0.7776 (9)	2.26 (7)
O(L23)	0.9169 (4)	0.0753 (4)	0.0231 (9)	2.39 (8)
O(E11)	0.1383 (4)	0.1679 (4)	0.5166 (7)	2.39 (8)
O(E12)	0.3135 (3)	0.7264 (4)	0.1442 (6)	1.94 (7)
O(E21)	0.3747 (3)	0.2426 (3)	0.0616 (7)	1.75 (6)
O(E22)	0.4706 (3)	0.7115 (4)	0.8686 (7)	2.14 (8)
O(E31)	0.2982 (5)	0.5590 (3)	0.8693 (7)	2.10 (7)
O(E32)	0.2639 (3)	0.9109 (3)	0.9234 (8)	1.84 (7)
O(W1)	0.4086 (4)	0.8804 (4)	0.6377 (9)	2.7 (1)
O(W2)	0.1533 (5)	0.6363 (6)	0.604 (1)	3.9 (1)
O(W3)	0.2010 (6)	0.8442 (6)	0.506 (1)	4.8 (1)
O(W4)	0.6035 (4)	0.9077 (4)	0.769 (1)	2.79 (9)
O(W5)	0.9142 (7)	0.5655 (7)	0.750 (1)	5.7 (2)

0.02° s⁻¹, total background measuring time: 10 s. 3599 reflections collected ($3 < \theta < 30^\circ$), *h*, *k*, *l*, $h_{\text{max}} = 24$, $k_{\text{max}} = 22$, $l_{\text{max}} = 12$. Two orientation and intensity-control reflections (822 and 0,10,0) measured every 4 h without any significant variation. Lorentz and polarization corrections, no absorption correction. Structure solved by using a three-dimensional Patterson function followed by successive Fourier syntheses. Water molecules located by difference Fourier syntheses. Anisotropic full-matrix least-squares refinement (on *F*). Unit weights. Final refinements with 3450 reflections corresponding to $I > 3\sigma(I)$. Final $R = 0.036$ ($wR = 0.042$), $S = 1.914$, max. $\Delta/\sigma = 0.00$, max. peak height in the final difference Fourier synthesis = 2.96 e \AA^{-3} (near Ce peak). Secondary-extinction correction with $g = 3.51 (14) \times 10^{-7}$ (Stout & Jensen, 1968). Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). *SDP* (Enraf-Nonius, 1977) used for all calculations. Computer used: MicroVAX II. Drawings produced using the program *STRUPLO* (Fischer, 1985).

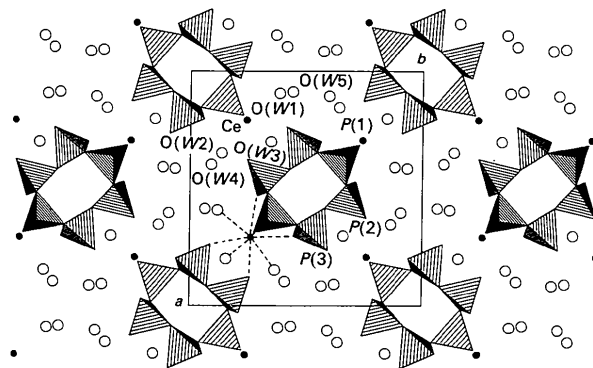
Discussion. Table 1* reports the final atomic coordinates. Fig. 1 is a projection of the atomic arrangement along the *c* axis.

The P₆O₁₈ ring anion is located about the binary axis parallel to the *c* axis. Table 2 gives the main geometrical features of this anion. The variation of the P—P—P angles, from 87.47 to 115.57°, reveals a

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54054 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Main interatomic distances (Å) and bond angles (°) in the atomic arrangement of Ce₂P₆O₁₈·10H₂O with *e.s.d.*'s in parentheses

The P ₆ O ₁₈ ring anion			
The P(1)O ₄ tetrahedron			
P(1)	O(E11)	O(L12)	O(E12)
O(E11)	1.481 (5)	106.5 (3)	106.5 (3)
O(L12)	2.463 (7)	1.592 (4)	103.8 (3)
O(L13)	2.451 (7)	2.493 (7)	1.577 (4)
O(E12)	2.559 (7)	2.511 (6)	2.506 (6)
The P(2)O ₄ tetrahedron			
P(2)	O(E21)	O(L12)	O(L23)
O(E21)	1.493 (4)	107.0 (3)	110.0 (3)
O(L12)	2.490 (6)	1.603 (5)	101.9 (3)
O(L23)	2.523 (7)	2.476 (8)	1.586 (5)
O(E22)	2.556 (6)	2.535 (7)	2.463 (7)
The P(3)O ₄ tetrahedron			
P(3)	O(E31)	O(L13)	O(L23)
O(E31)	1.493 (5)	110.5 (3)	107.2 (3)
O(L13)	2.544 (8)	1.603 (6)	101.7 (3)
O(L23)	2.496 (7)	2.490 (8)	1.608 (5)
O(E32)	2.577 (7)	2.500 (7)	2.547 (7)
P(1)—P(2)	2.907 (2)	P(2)—P(3)	2.944 (2)
P(1)—P(3)	2.923 (2)		
P(1)—O(L12)—P(2)	131.0 (3)	P(1)—O(2)—P(3)	114.38 (6)
P(1)—O(L13)—P(3)	133.7 (4)	P(1)—P(3)—P(2)	115.57 (6)
P(2)—O(L23)—P(3)	134.4 (4)	P(2)—P(1)—P(3)	87.47 (6)
The CeO ₉ polyhedron			
Ce—O(E11)	2.441 (5)	Ce—O(E32)	2.484 (5)
Ce—O(E12)	2.556 (4)	Ce—O(W1)	2.602 (6)
Ce—O(E21)	2.527 (4)	Ce—O(W2)	2.629 (7)
Ce—O(E22)	2.506 (4)	Ce—O(W3)	2.645 (8)
Ce—O(E31)	2.457 (4)		
Ce—Ce	6.9380 (4)		
The water molecules			
O(W1)—O(W3)	2.989 (10)	O(W2)—O(W3)	2.882 (11)
O(W1)—O(W4)	2.811 (8)	O(W2)—O(W4)	2.732 (10)
O(W1)—O(W5)	2.786 (11)	O(W2)—O(W5)	2.976 (12)
O(W5)—O(W5)	2.887 (13)		

Fig. 1. Projection along the *c* axis of the atomic arrangement of Ce₂P₆O₁₈·10H₂O.

quite irregular shape of the P₆O₁₈ ring. The presence of internal twofold symmetry is rather unusual among the 30 already characterized P₆O₁₈ ring anions, the $\bar{1}$ internal symmetry being the most frequent. The only other example has been evidenced

in the *cyclo*-hexaphosphate $\text{Ca}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ (Averbuch-Pouchot, 1990) whose structure is described with reticular parameters and a space group similar to that of $\text{Ce}_2\text{P}_6\text{O}_{18}\cdot 10\text{H}_2\text{O}$. The distribution of the anionic rings in the unit cell is also equivalent, but the geometry of the cationic polyhedra and their arrangement are of course quite different owing to the various valency states of the cations.

The Ce atom is coordinated to the 6 $\text{O}(E)$ atoms of the phosphate tetrahedra and to the three water molecules $\text{O}(W1)$, $\text{O}(W2)$ and $\text{O}(W3)$ with the average distances $\text{Ce}-\text{O}(E) = 2.50$ and $\text{Ce}-\text{O}(W) = 2.63$ Å (Table 2). The CeO_9 polyhedron formed from this environment is a distorted three-capped trigonal prism. Its axis is parallel to a diagonal direction $[110]$ or $[\bar{1}10]$. The three cap atoms are $\text{O}(W1)$, $\text{O}(W2)$ and $\text{O}(E12)$. Such a coordination is commonly observed among the rare-earth compounds, for example it occurs in the neodymium *cyclo*-hexaphosphate (Trunov *et al.*, 1988).

As shown by Fig. 2, the P_6O_{18} rings form layers perpendicular to the c axis. The CeO_9 polyhedra interconnect the P_6O_{18} anions between layers along the c direction and inside a layer along the diagonal directions $[110]$ and $[\bar{1}10]$ to form a three-dimensional network.

Another characteristic feature of this structure is the presence of two free water molecules, $\text{O}(W4)$ and $\text{O}(W5)$, in channels parallel to the binary axis delimited by the $\text{P}_6\text{O}_{18}-\text{CeO}_9$ rows. The $\text{O}(W5)-\text{O}(W5)$ bond of 2.887 Å corresponds to the smallest diameter of a channel. So, among the ten water molecules of the formula unit $\text{Ce}_2\text{P}_6\text{O}_{18}\cdot 10\text{H}_2\text{O}$, four of them do not take part in the coordination of the cation, but probably assure the cohesion between the anionic layers as is the case in the dodecahydrate $\text{Nd}_2\text{P}_6\text{O}_{18}\cdot 12\text{H}_2\text{O}$. The existence of short distances between the water molecules in the channel and

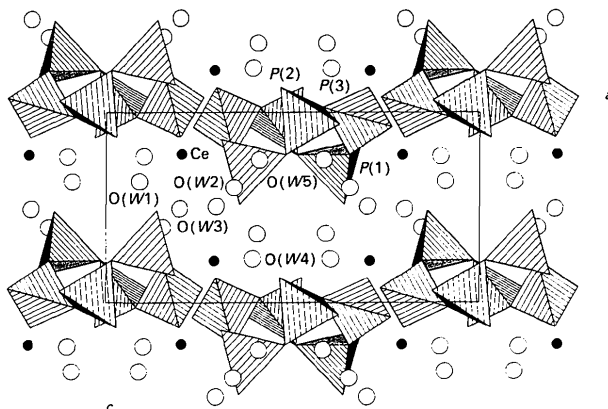


Fig. 2. Projection along the a axis of the atomic arrangement of $\text{Ce}_2\text{P}_6\text{O}_{18}\cdot 10\text{H}_2\text{O}$.

water molecules in the Ce coordination supports this hypothesis: in particular, 2.732 for $\text{O}(W4)-\text{O}(W2)$ and 2.786 Å for $\text{O}(W5)-\text{O}(W1)$.

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Structure of the Metastable Binary $\beta\text{-Mo}_{15}\text{Se}_{19}$

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Abstract. $\text{Mo}_{15}\text{Se}_{19}$, $M_r = 2939.34$, trigonal, $R\bar{3}c$, $a(\text{rh}) = 20.360(1)$ Å, $\alpha(\text{rh}) = 26.981(1)^\circ$, $V(\text{rh}) = 1532.2(1)$ Å³, $Z = 2$, $D_x = 6.371$ g cm⁻³, $\lambda(\text{Mo } K\alpha)$

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$= 0.71073$ Å, $\mu = 281.28$ cm⁻¹, $F(000) = 2552$, $T = 295$ K, $R = 0.029$ for 781 observed reflections. The title compound constitutes the host structure of the

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