

Crystal Chemistry of *cyclo*-Hexaphosphates. XXI. Structure of Ytterbium *cyclo*-Hexaphosphate Hexadecahydrate

BY M. BAGIEU-BEUCHER

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

AND M. RZAIGUI

Ecole Normale Supérieure, 7021 Zarzouna Bizerte, Tunisia

(Received 27 May 1991; accepted 22 August 1991)

Abstract. $\text{Yb}_2\text{P}_6\text{O}_{18}\cdot 16\text{H}_2\text{O}$, $M_r = 1108.16$, orthorhombic, $P2_12_12_1$, $a = 16.019$ (8), $b = 19.993$ (10), $c = 9.699$ (5) Å, $V = 3106$ (5) Å³, $Z = 4$, $D_x = 2.369$ Mg m⁻³, $\lambda(\text{Ag K}\alpha) = 0.5608$ Å, $\mu = 3.57$ mm⁻¹, $F(000) = 2136$, room temperature, final $R = 0.038$ for 7123 independent reflections. The crystal structure can be described as layers of P_6O_{18} rings interconnected by YbO_8 dodecahedra. The phosphoric ring anion has no internal symmetry. The ytterbium polyhedra do not share any edges or corners.

Introduction. The present work continues the systematic study of *cyclo*-hexaphosphates and more particularly that of trivalent cations. In this domain four types of structure have already been determined: two chromium salts $\text{Cr}_2\text{P}_6\text{O}_{18}$ (Bagieu-Beucher & Guitel, 1977) and $\text{Cr}_2\text{P}_6\text{O}_{18}\cdot 21\text{H}_2\text{O}$ (Bagieu-Beucher, Averbuch-Pouchot & Rzaigui, 1991), the neodymium *cyclo*-hexaphosphate dodecahydrate $\text{Nd}_2\text{P}_6\text{O}_{18}\cdot 12\text{H}_2\text{O}$ (Trunov, Chudinova & Borodina, 1988) and the cerium *cyclo*-hexaphosphate decahydrate $\text{Ce}_2\text{P}_6\text{O}_{18}\cdot 10\text{H}_2\text{O}$ (Bagieu-Beucher & Rzaigui, 1991). $\text{Yb}_2\text{P}_6\text{O}_{18}\cdot 16\text{H}_2\text{O}$ is the first *cyclo*-hexaphosphate obtained with the small radius rare earth of the lanthanide series. The structural characterization of this compound is described here.

Experimental. The chemical preparation of $\text{Yb}_2\text{P}_6\text{O}_{18}\cdot 16\text{H}_2\text{O}$ is reported in a general article dealing with the synthesis of rare-earth *cyclo*-hexaphosphates (Rzaigui, 1991). Crystal size: $0.13 \times 0.24 \times 0.28$ mm. Density not measured. Enraf-Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$ and $00l$, $l = 2n + 1$. 19 reflections ($10.5 < \theta < 12.2^\circ$) for refining unit-cell dimensions. ω scan, scan width: 1.20° , variable scan speed: $0.03\text{--}0.11^\circ \text{ s}^{-1}$. Total background measuring time between 5 and 20 s. 10 033 unique reflections collected ($2 < \theta < 30^\circ$), h , k , l , $h_{\text{max}} = 28$, $k_{\text{max}} = 35$, $l_{\text{max}} = 17$. Two

orientation reflections ($11,2,2$ and $\bar{1}\bar{1},\bar{2},\bar{2}$) measured every hour and two intensity-control reflections ($9,10,0$ and $\bar{9},\bar{10},0$); no significant variation. Lorentz and polarization corrections, no absorption correction. Structure solved by using a three-dimensional Patterson function followed by successive Fourier and difference Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F). Unit weights. Final refinements with 7123 reflections corresponding to $I > 3\sigma(I)$ and $|F_o - F_c| < F_o/4$. Final $R = 0.038$ ($wR = 0.041$), $S = 3.737$, maximum $\Delta/\sigma = 0.00$, maximum peak height in the final difference Fourier synthesis = 2.65 e \AA^{-3} [close to $\text{Yb}(2)$ peak]. No extinction correction. 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 performed using *STRUPLO* program (Fischer, 1985). Table 1 reports the final atomic coordinates.*

Discussion. Fig. 1 shows a projection of the atomic arrangement along the c axis. Table 2 gives the main geometrical features, bond distances and angles, in this arrangement.

The crystal structure can be described as wide layers of P_6O_{18} rings, lying around planes at $z = 0.25$ and 0.75 . The rings of successive layers are shifted in the same manner as in a hexagonal compact assemblage. The cohesion of this stacking is maintained partly by the YbO_8 dodecahedra which interconnect the P_6O_{18} rings between the layers and partly by hydrogen bonds coming from water molecules bonded to the rare-earth atom and from non-bonded ones.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54631 (60 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and B_{eq} (\AA^2) values with e.s.d.'s in parentheses
$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Yb(1)	0.10961 (2)	0.01597 (1)	0.42008 (3)	0.912 (3)
Yb(2)	0.44837 (2)	0.72007 (1)	0.35266 (3)	1.094 (3)
P(1)	0.1499 (1)	0.15149 (9)	0.6521 (2)	1.05 (2)
P(2)	0.2818 (1)	0.05384 (9)	0.6351 (2)	0.97 (2)
P(3)	0.4460 (1)	0.10972 (9)	0.6855 (2)	1.15 (2)
P(4)	0.3735 (1)	0.16155 (9)	0.9351 (2)	1.00 (2)
P(5)	0.2750 (1)	0.2832 (1)	0.8798 (2)	1.27 (3)
P(6)	0.2070 (1)	0.2847 (1)	0.5997 (2)	1.27 (3)
O(L12)	0.2252 (4)	0.1083 (3)	0.7101 (6)	1.69 (9)
O(L23)	0.3624 (3)	0.0965 (3)	0.5980 (6)	1.37 (8)
O(L34)	0.4171 (4)	0.1682 (3)	0.7894 (6)	1.63 (9)
O(L45)	0.2932 (3)	0.2061 (3)	0.9169 (7)	1.48 (8)
O(L56)	0.2777 (4)	0.2821 (4)	0.7152 (6)	1.89 (9)
O(L16)	0.1948 (4)	0.2067 (3)	0.5614 (6)	1.68 (9)
O(E11)	0.0969 (4)	0.1095 (3)	0.5605 (6)	1.61 (9)
O(E12)	0.1123 (4)	0.1838 (3)	0.7750 (6)	1.42 (8)
O(E21)	0.2431 (4)	0.0351 (3)	0.5028 (6)	1.37 (8)
O(E22)	0.3018 (3)	0.0005 (3)	0.7356 (6)	1.22 (7)
O(E31)	0.5077 (4)	0.1391 (3)	0.5893 (7)	1.88 (9)
O(E32)	0.4665 (3)	0.0490 (3)	0.7659 (6)	1.52 (8)
O(E41)	0.4306 (4)	0.1891 (3)	0.0412 (6)	1.9 (1)
O(E42)	0.3415 (4)	0.0921 (3)	0.9547 (6)	1.47 (8)
O(E51)	0.1883 (4)	0.2967 (3)	0.9264 (7)	1.64 (8)
O(E52)	0.3444 (4)	0.3252 (3)	0.9283 (9)	2.4 (1)
O(E61)	0.1282 (4)	0.3104 (3)	0.6584 (7)	1.63 (9)
O(E62)	0.2419 (4)	0.3167 (4)	0.4768 (7)	2.2 (1)
O(W1)	0.4680 (4)	0.4591 (4)	0.5567 (9)	2.8 (1)
O(W2)	0.4224 (4)	0.0239 (3)	0.1453 (7)	2.1 (1)
O(W3)	0.1066 (6)	0.1075 (3)	0.2783 (7)	3.3 (1)
O(W4)	0.0688 (5)	0.2388 (4)	0.0762 (8)	3.0 (1)
O(W5)	0.4561 (4)	0.3140 (3)	0.1461 (8)	2.1 (1)
O(W6)	0.0677 (4)	0.3925 (3)	0.8961 (9)	2.6 (1)
O(W7)	0.4630 (4)	0.1899 (4)	0.3266 (7)	2.6 (1)
O(W8)	0.3164 (6)	0.1236 (6)	0.277 (1)	4.2 (2)
O(W9)	0.0200 (6)	0.0496 (5)	0.867 (1)	3.7 (2)
O(W10)	0.5127 (7)	0.2834 (5)	0.647 (1)	5.0 (2)
O(W11)	0.1582 (5)	0.1010 (4)	0.0140 (8)	2.6 (1)
O(W12)	0.1006 (7)	0.4660 (5)	0.523 (1)	4.6 (2)
O(W13)	0.4079 (6)	0.3423 (6)	0.443 (1)	6.5 (2)
O(W14)	0.3672 (8)	0.4474 (6)	0.793 (1)	5.3 (2)
O(W15)	0.1937 (9)	0.474 (1)	0.780 (2)	9.4 (5)
O(W16)	0.216 (1)	0.2575 (9)	0.219 (1)	8.3 (4)

The cyclohexaphosphate anion. This phosphoric group has no internal symmetry and so is built by six independent PO_4 tetrahedra. Examples of P_6O_{18} rings without any symmetry are not common among the previously studied cyclo-hexaphosphates. Up to now two cases have been observed: the first in $\text{Cu}_2\text{-Li}_2\text{P}_6\text{O}_{18}$ (Laügt & Durif, 1974) and the second in $(\text{C}_2\text{H}_5\text{NH}_3)_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1991a); although, in the first case, the ring anion has a strong $2/m$ pseudosymmetry. The conformation of the P_6O_{18} ring in $\text{Yb}_2\text{P}_6\text{O}_{18}\cdot 16\text{H}_2\text{O}$ is rather irregular since the P—P—P angles vary from 85.11 to 113.23° around the average value of 103.5° (111.1 to 134.3° in the copper salt, 99.6 to 113.5° in the organic salt). The examination of the P—P—P angle list given in a general review of cyclo-hexaphosphate crystal chemistry (Averbuch-Pouchot & Durif, 1991b, 1992) reveals distortions much larger in higher symmetry rings: 94.2 to 142.8° in the centrosymmetric ring of $\text{Cd}_2\text{Na}_2\text{P}_6\text{O}_{18}\cdot 14\text{H}_2\text{O}$, for example (Averbuch-Pouchot, 1990). In most cases, the average value departs significantly from the ideal value (120°).

The ytterbium environment. The two independent Yb atoms are located between the anionic layers.

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in the atomic arrangement of $\text{Yb}_2\text{P}_6\text{O}_{18}\cdot 16\text{H}_2\text{O}$ with e.s.d.'s in parentheses

P(1)O ₄ tetrahedron								
P(1)	O(E11)	O(L12)	O(L16)	O(E12)				
O(E11)	1.488 (5)	109.7 (3)	108.7 (3)	119.6 (4)				
O(L12)	2.516 (9)	1.587 (6)	103.4 (3)	105.1 (3)				
O(L16)	2.498 (8)	2.489 (8)	1.585 (6)	109.1 (3)				
O(E12)	2.568 (8)	2.438 (8)	2.500 (8)	1.482 (6)				
P(2)O ₄ tetrahedron								
P(2)	O(E21)	O(L12)	O(L23)	O(E22)				
O(E21)	1.473 (6)	109.4 (3)	106.4 (3)	118.8 (3)				
O(L12)	2.503 (8)	1.593 (6)	101.5 (3)	108.3 (3)				
O(L23)	2.452 (8)	2.463 (8)	1.588 (6)	111.1 (3)				
O(E22)	2.542 (8)	2.492 (8)	2.531 (8)	1.480 (6)				
P(3)O ₄ tetrahedron								
P(3)	O(E31)	O(L23)	O(L34)	O(E32)				
O(E31)	1.481 (7)	106.8 (3)	107.3 (4)	120.6 (4)				
O(L23)	2.480 (8)	1.607 (6)	102.1 (3)	109.2 (3)				
O(L34)	2.492 (9)	2.503 (8)	1.611 (6)	109.2 (3)				
O(E32)	2.572 (9)	2.517 (8)	2.521 (8)	1.480 (6)				
P(4)O ₄ tetrahedron								
P(4)	O(E41)	O(L34)	O(L45)	O(E42)				
O(E41)	1.483 (7)	108.4 (3)	111.8 (4)	120.6 (4)				
O(L34)	2.487 (9)	1.582 (6)	102.3 (3)	110.1 (3)				
O(L45)	2.532 (8)	2.457 (8)	1.574 (6)	105.1 (3)				
O(E42)	2.551 (8)	2.520 (8)	2.435 (8)	1.493 (6)				
P(5)O ₄ tetrahedron								
P(5)	O(E51)	O(L45)	O(L56)	O(E52)				
O(E51)	1.485 (6)	106.1 (3)	109.4 (4)	120.3 (4)				
O(L45)	2.474 (8)	1.609 (6)	101.9 (4)	109.8 (3)				
O(L56)	2.516 (9)	2.490 (9)	1.597 (6)	107.9 (4)				
O(E52)	2.565 (9)	2.521 (8)	2.481 (10)	1.471 (7)				
P(6)O ₄ tetrahedron								
P(6)	O(E61)	O(L56)	O(L16)	O(E62)				
O(E61)	1.476 (6)	110.3 (4)	108.8 (3)	119.2 (4)				
O(L56)	2.521 (8)	1.594 (6)	102.5 (4)	108.3 (4)				
O(L16)	2.514 (8)	2.502 (9)	1.614 (6)	106.3 (4)				
O(E62)	2.537 (9)	2.480 (9)	2.465 (9)	1.464 (7)				
P(1)—P(2)					2.882 (3)	P(4)—P(5)		2.948 (3)
P(2)—P(3)					2.898 (3)	P(5)—P(6)		2.927 (3)
P(3)—P(4)					2.878 (3)	P(6)—P(1)		2.862 (3)
P(1)—O(L12)—P(2)					130.0 (4)	P(1)—P(2)—P(3)		113.23 (8)
P(2)—O(L23)—P(3)					130.2 (4)	P(2)—P(3)—P(4)		85.11 (7)
P(3)—O(L34)—P(4)					128.7 (4)	P(3)—P(4)—P(5)		111.09 (8)
P(4)—O(L45)—P(5)					135.7 (4)	P(4)—P(5)—P(6)		112.14 (8)
P(5)—O(L56)—P(6)					133.1 (4)	P(5)—P(6)—P(1)		86.80 (8)
P(6)—O(L16)—P(1)					126.9 (4)	P(6)—P(1)—P(2)		112.69 (8)
YbO ₈ dodecahedra								
Yb(1)—O(E11)	2.322 (6)	Yb(1)—O(E42)	2.322 (5)					
Yb(1)—O(E21)	2.316 (6)	Yb(1)—O(W1)	2.334 (7)					
Yb(1)—O(E22)	2.308 (5)	Yb(1)—O(W2)	2.381 (7)					
Yb(1)—O(E32)	2.326 (6)	Yb(1)—O(W3)	2.290 (7)					
Yb(2)—O(E12)	2.282 (5)	Yb(2)—O(W4)	2.335 (8)					
Yb(2)—O(E41)	2.281 (6)	Yb(2)—O(W5)	2.422 (6)					
Yb(1)—O(E51)	2.327 (6)	Yb(2)—O(W6)	2.305 (6)					
Yb(1)—O(E61)	2.330 (6)	Yb(2)—O(W7)	2.324 (7)					
Yb—Yb(2)	5.8136 (4)	Yb(1)—Yb(2)	6.6449 (4)					

Both have an eightfold coordination made by five O atoms and three water molecules for Yb(1), four O atoms and four water molecules for Yb(2). The geometry of the cationic polyhedra is that of distorted dodecahedra; it is noteworthy, however, that the distances Yb—O (average values of 2.319 and 2.305\AA) and Yb—O(W) (average values of 2.335 and 2.347\AA) are only slightly different (general average value of 2.326\AA).

Each YbO_8 dodecahedron joins two P_6O_{18} rings of adjacent layers and each anionic ring is connected to

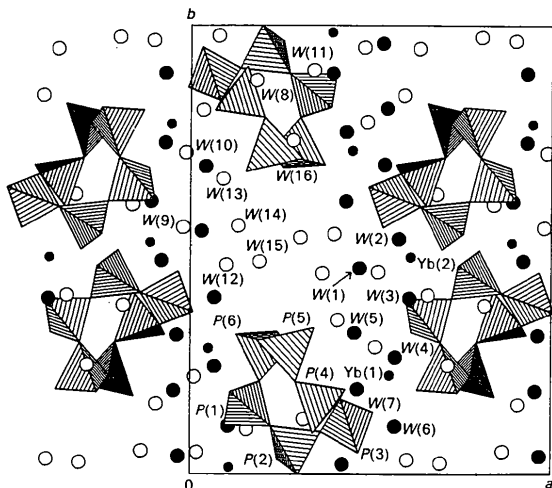


Fig. 1. Projection along the *c* axis of the atomic arrangement of Yb₂P₆O₁₈·16H₂O. The PO₄ tetrahedra of the P₆O₁₈ groups are denoted by the labels of their central P atoms. The water molecules belonging to the Yb coordination are represented by the filled circles [W(1) to W(7)], the non-bonded ones by the empty circles [W(8) to W(16)].

four rare-earth polyhedra. A similar type of connection can be observed in the crystal structure of Nd₂P₆O₁₈·12H₂O (Trunov, Chudinova & Borodina, 1988). Moreover, the YbO₈ dodecahedra are isolated from each other in the sense that they do not share any O atoms. The shortest distance Yb—Yb is 5.8136 (4) Å.

The non-bonded water molecules. In addition to all the internal O atoms, three external ones O(E31), O(E52) and O(E62) as well as nine water molecules are not involved in the coordination of the rare-earth atom. These non-bonded water molecules are charac-

terized by having thermal factors larger than the others (Table 1). They are dispersed in the whole atomic arrangement. In particular, some of them fill channels centred on the 2₁ axes parallel to *c* formed by the special arrangement of the rings (Fig. 1). This type of water molecule acts as an intermediate in the hydrogen-bonding scheme which extends not only between the successive anionic layers but also, probably, inside such layers.

In conclusion, the main features to note in this structure are the absence of symmetry in the P₆O₁₈ anion, the absence of direct bonding between the Yb coordination polyhedra and the absence of bonding between the P₆O₁₈ rings of an anionic layer *via* these cationic polyhedra.

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Phase Transition of Hexaamminecobalt(III) Pentachlorocuprate(II)

BY TOMONORI AOYAMA, SHIGERU OHBA* AND YOSHIHIKO SAITO

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, Kohoku-ku, Yokohama 223, Japan

AND IVAN BERNAL

Department of Chemistry, University of Houston, University Park, 4800 Calhoun Road, Houston, Texas 77204-5641, USA

(Received 14 March 1991; accepted 20 August 1991)

Abstract. The structures above and below the transition temperature of 280.8 K have been investigated

by single-crystal X-ray diffraction. [Co(NH₃)₆][CuCl₅], *M_r* = 401.9, λ(Mo Kα) = 0.71073 Å. A redetermination at *T* = 299 (1) K, (I), cubic, *Fd* $\bar{3}$ *c*, *a* = 22.085 (2) Å, *V* = 10772 (2) Å³, *Z* = 32, *D_x* =

* To whom correspondence should be addressed.