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Crystal Chemistry of *cyclo*-Hexaphosphates. XVII. Structure of Chromium *cyclo*-Hexaphosphate Henicosahydrate

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Abstract. Cr₂[P₆O₁₈].21H₂O, $M_r = 956.13$, cubic, $P\bar{4}3n$, $a = 19.052(10)$ Å, $V = 6915(11)$ Å³, $Z = 8$, $D_x = 1.837$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.062$ mm⁻¹, $F(000) = 3936$, room temperature, final $R = 0.053$ for 1655 independent reflections. The atomic arrangement of Cr₂P₆O₁₈.21H₂O is a stacking of P₆O₁₈ ring anions, Cr(H₂O)₆ octahedra and non-bonded water molecules interconnected by hydrogen bonds only. The phosphoric ring anion has a three-fold internal symmetry. One of the water molecules building the coordination polyhedron of Cr(1) is disordered.

Introduction. Crystal structure of anhydrous chromium *cyclo*-hexaphosphate, Cr₂P₆O₁₈, was determined some years ago (Bagieu-Beucher & Guitel, 1977). Up to now, no mention of the existence of possible hydrates of this salt has been reported in the chemical literature. Recently one of us (Rzaigui, 1990) characterized the first hydrate of this phosphate: Cr₂P₆O₁₈.21H₂O. The present work is devoted to the determination of the crystal structure of this hydrate.

Experimental. The preparation of Cr₂P₆O₁₈.21H₂O and its main chemical properties have been reported elsewhere (Rzaigui, 1990). Crystal size: 0.32 × 0.32 × 0.27 mm (a rhombic dodecahedron). Density not measured. Nicolet diffractometer, graphite monochromator. 25 reflections ($10.75 < \theta < 12.60^\circ$) for refining unit-cell dimensions. ω scan, scan width 1.40°, scan speed 0.01° s⁻¹, total background measuring time 14 s. 7359 measured reflections, h , k , l ,

$h_{\max} = k_{\max} = l_{\max} = 26$. Three intensity and orientation reference reflections (222, $\bar{2}\bar{2}\bar{2}$, 411) measured every 500 reflections with no significant variations. The systematic absences, hhl ($l = 2n$), the symmetry of the intensities and the study of the Patterson function lead to the space group $P\bar{4}3n$. Lorentz and polarization corrections, no absorption correction. 1807 unique reflections ($R_{\text{int}} = 0.02$). The crystal structure has been solved by classical methods: study of the three-dimensional Patterson function followed by successive Fourier syntheses. A problem occurred with the water molecule O(W1); first refined in the special position 12(f), this molecule had a very high thermal factor with an abnormally short Cr(1)—O(W1) distance. A careful examination of Fourier maps showed that this water molecule is in fact disordered and split into three fragments of approximately identical weight. Two of these fragments occupy the general position while the third one is located on the special position 12(f). These three fragments are denoted O(W1), O(W11) and O(W12). Refinements of the occupancy rates of these three fragments led to 0.186, 0.166 and 0.157 respectively, whose sum (0.499) is close to the expected value of 0.500. H atoms were located by difference Fourier syntheses with the exception of those corresponding to the disordered water molecule and to O(W9), a non-bonded water molecule. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf-Nonius SDP (1977) used for all calculations. Com-

Table 1. Final atomic coordinates and B_{eq} values (B_{iso} for H atoms) for $\text{Cr}_2\text{P}_6\text{O}_{18}\cdot 21\text{H}_2\text{O}$, with e.s.d.'s in parentheses

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	$B_{\text{eq}}/B_{\text{iso}}(\text{\AA}^2)$
Cr(1)	0	0	0	1.37 (1)
Cr(2)	0	1/2	1/2	2.21 (3)
Cr(3)	0.19291 (4)	0.19291 (4)	0.19291 (4)	1.370 (5)
P(1)	0.81004 (9)	0.26868 (8)	0.06546 (8)	1.85 (2)
P(2)	0.44922 (8)	0.37318 (8)	0.25257 (8)	1.93 (2)
O(E11)	0.2916 (3)	0.3845 (2)	0.1750 (2)	2.74 (9)
O(E12)	0.2116 (3)	0.3185 (4)	0.5084 (3)	4.5 (1)
O(L1)	0.4263 (3)	0.2925 (3)	0.2539 (3)	3.9 (1)
O(L2)	0.2729 (3)	0.3780 (3)	0.4105 (3)	4.4 (1)
O(E21)	-0.0004 (3)	0.1906 (2)	0.1106 (2)	2.53 (8)
O(E22)	0.6786 (3)	0.1124 (3)	0.0307 (3)	3.0 (1)
O(W1)	0.8976 (9)	0	0	2.7 (3)
O(W11)	-0.916 (1)	0.028 (1)	0.049 (1)	2.0 (5)
O(W12)	-0.946 (1)	0.088 (1)	-0.032 (1)	2.2 (5)
O(W2)	0.3960 (3)	0	0	3.7 (2)
O(W3)	0.3976 (3)	0	1/2	3.5 (1)
O(W4)	0.1045 (4)	1/2	0	3.8 (1)
O(W5)	0.7268 (2)	0.3666 (2)	0.3830 (2)	2.08 (8)
O(W6)	0.2499 (2)	0.1596 (2)	0.2724 (2)	2.39 (8)
O(W7)	0.1925 (3)	0.0815 (3)	0.3745 (3)	3.6 (1)
O(W8)	0.1768 (4)	0.4123 (3)	0.0776 (4)	4.8 (1)
O(W9)	0.8342 (4)	0.1108 (4)	0.4521 (4)	6.5 (2)
H(2)	0.485 (5)	0.457 (4)	0.129 (4)	3 (2)
H(3)	0.959 (5)	0.473 (5)	0.132 (5)	3 (2)
H(4)	0.125 (5)	0.482 (5)	0.051 (5)	4 (3)
H(51)	0.613 (5)	0.286 (5)	0.410 (5)	3 (2)
H(52)	0.234 (5)	0.080 (5)	0.144 (5)	3 (2)
H(61)	0.806 (5)	0.363 (5)	0.271 (5)	3 (2)
H(62)	0.784 (4)	0.224 (4)	0.346 (4)	2 (2)
H(71)	0.664 (5)	0.141 (5)	0.457 (5)	3 (2)
H(72)	0.395 (5)	0.163 (5)	0.108 (5)	3 (2)
H(81)	0.683 (5)	0.475 (5)	0.110 (5)	4 (3)
H(82)	0.721 (5)	0.413 (5)	0.081 (6)	4 (3)

puter used: MicroVAX II. No secondary-extinction correction. Final refinements with 3892 reflections [$I > 1/2\sigma(I)$]. Final $R = 0.053$ ($wR = 0.053$), $S = 3.544$, max. $\Delta/\sigma = 0.05$, max. peak height in the final difference Fourier synthesis = 0.491 e \AA^{-3} .

Table 1* reports the final atomic coordinates for this arrangement. The drawings were prepared using STRUPLO (Fischer, 1985).

Discussion. The present atomic arrangement is essentially that of a stacking of P_6O_{18} ring anions, $\text{Cr}(\text{H}_2\text{O})_6$ octahedra and non-bonded water molecules. So, in such a structure in which there is no common O atom between the phosphoric anion and the associated cation polyhedra, the three-dimensional cohesion is performed only by hydrogen bonds.

The phosphoric ring anion. The unit cell contains eight P_6O_{18} ring anions. Located around the three-fold axes these anions have ternary internal symmetry and so are built by only two independent PO_4 tetrahedra. The P—P—P angles vary from 104.43 to

* Lists of structure factors and anisotropic thermal parameters for non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53952 (16 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 (\AA) and bond angles ($^\circ$) in the atomic arrangement of $\text{Cr}_2\text{P}_6\text{O}_{18}\cdot 21\text{H}_2\text{O}$, with e.s.d.'s in parentheses

P(1)O ₄ tetrahedron				
P(1)	O(E11)		O(E12)	O(L1)
O(E11)	1.478 (5)		2.514 (7)	2.484 (7)
O(E12)	117.3 (3)		1.466 (5)	2.518 (8)
O(L1)	108.0 (3)		110.9 (3)	1.590 (5)
O(L2)	111.7 (3)		108.4 (3)	98.9 (3)
P(2)O ₄ tetrahedron				
P(2)	O(L1)		O(L2)	O(E21)
O(L1)	1.597 (5)		2.455 (8)	2.544 (7)
O(L2)	101.2 (3)		1.580 (6)	2.452 (7)
O(E21)	111.5 (3)		106.5 (3)	1.480 (5)
O(E22)	105.2 (3)		111.7 (3)	119.2 (3)
CrO ₆ octahedra				
Cr(1)—O(W1)	1.952 (16) (× 6)		Cr(2)—O(W2)	1.982 (6) (× 2)
Cr(1)—O(W11)	1.931 (24) (× 12)		Cr(2)—O(W3)	1.952 (6) (× 2)
Cr(1)—O(W12)	2.058 (26) (× 12)		Cr(2)—O(W4)	1.990 (7) (× 2)
Cr(3)—O(W5)	1.949 (4) (× 2)		Cr(3)—O(W6)	1.969 (4) (× 2)
Hydrogen bonds				
O—H—O	O—H	H—O	O—O	O—H—O
O(W2)—H(2)···O(E22)	1.00 (9)	1.65 (8)	2.636 (6)	171 (7)
O(W3)—H(3)···O(W9)	1.10 (9)	1.53 (9)	2.598 (8)	164 (8)
O(W4)—H(4)···O(W8)	1.09 (9)	1.74 (10)	2.622 (8)	134 (8)
O(W5)—H(51)···O(E21)	0.87 (9)	1.78 (9)	2.644 (6)	175 (8)
O(W5)—H(52)···O(E12)	0.74 (9)	1.86 (9)	2.548 (7)	154 (9)
O(W6)—H(61)···O(W7)	0.87 (9)	1.81 (9)	2.681 (7)	173 (9)
O(W6)—H(62)···O(E11)	0.66 (8)	1.98 (8)	2.607 (6)	159 (9)
O(W7)—H(71)···O(E22)	0.96 (9)	1.86 (9)	2.815 (7)	175 (8)
O(W7)—H(72)···O(W8)	0.86 (9)	2.11 (9)	2.933 (9)	161 (9)
O(W8)—H(81)···O(E12)	1.10 (10)	1.97 (10)	2.704 (8)	121 (7)
O(W8)—H(82)···O(E11)	0.88 (9)	2.25 (10)	2.917 (8)	133 (8)
H(2)—O(W2)—H(2)	123 (7)		H(61)—O(W6)—H(62)	107 (9)
H(3)—O(W3)—H(3)	118 (7)		H(71)—O(W7)—H(72)	104 (8)
H(4)—O(W4)—H(4)	138 (7)		H(81)—O(W8)—H(82)	98 (9)
H(51)—O(W5)—H(52)	103 (9)			

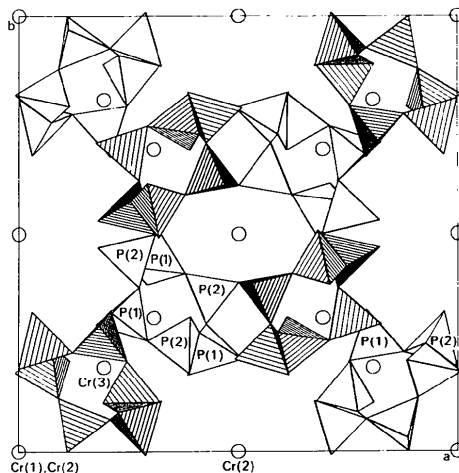


Fig. 1. Projection along the c axis of the arrangement of P_6O_{18} ring anions and Cr atoms in $\text{Cr}_2\text{P}_6\text{O}_{18}\cdot 21\text{H}_2\text{O}$. Water molecules have been removed. Cr(1) and Cr(2) atoms are superimposed in projection.

109.50°. This variation agrees well with the average values observed in P_6O_{18} rings with 3 or $\bar{3}$ internal symmetries which were recently reviewed (Averbuch-Pouchot & Durif, 1991).

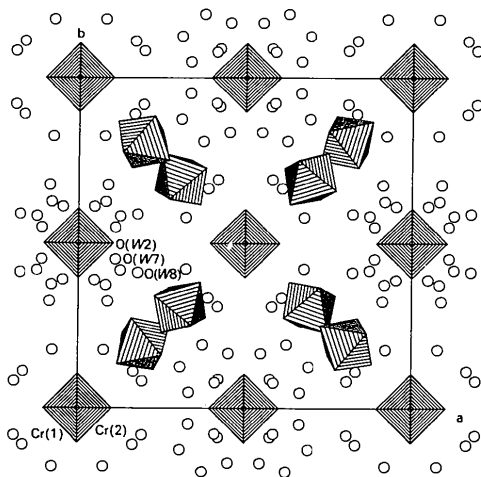


Fig. 2. Projection along the *c* axis of $\text{Cr}(\text{H}_2\text{O})_6$ octahedra and non-bonded water molecules in $\text{Cr}_2\text{P}_6\text{O}_{18}\cdot 21\text{H}_2\text{O}$. The ring anions have been removed. $\text{Cr}(1)(\text{H}_2\text{O})_6$ and $\text{Cr}(2)(\text{H}_2\text{O})_6$ octahedra are superimposed in projection.

The $\text{Cr}(\text{H}_2\text{O})_6$ octahedra. The chromium coordination polyhedra are all built by water molecules and do not share any corner or edge. The $\text{Cr}(1)(\text{H}_2\text{O})_6$ octahedron has a disordered coordination already discussed in *Experimental*. $\text{Cr}(2)$ located on the special position $6(b)$ is surrounded by $\text{O}(W2)$, $\text{O}(W3)$

and $\text{O}(W4)$ water molecules building an almost regular octahedron of symmetry 222 . $\text{Cr}(3)$ is located on the ternary axis; $\text{O}(W5)$ and $\text{O}(W6)$ are built around it in a quasi-regular octahedron with threefold internal symmetry.

In addition, it must be noted that $\text{O}(W7)$, $\text{O}(W8)$ and $\text{O}(W9)$ water molecules are not involved in the associated cation polyhedra. Two of these molecules have thermal factors significantly larger than those belonging to the chromium coordination.

Main interatomic distances and bond angles in this arrangement as well as the hydrogen-bond scheme are reported in Table 2. Fig. 1 reports in projection along the *c* axis the arrangement of P_6O_{18} ring anions and Cr atoms while Fig. 2 gives in projection along the same axis the arrangement of $\text{Cr}(\text{H}_2\text{O})_6$ octahedra and non-bonded water molecules.

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Structure of $\text{Er}_2\text{Ba}_3\text{Cu}_2\text{PtO}_{10}$

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Abstract. $M_r = 1228.7$, monoclinic, $C2/m$, $a = 12.465(3)$, $b = 5.795(1)$, $c = 7.362(1)$ Å, $\beta = 105.54(2)^\circ$, $V = 509.9(2)$ Å³, $Z = 2$, $D_x = 8.01$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 45.8$ mm⁻¹, $F(000) = 960$, room temperature, final $R = 0.043$ for 982 [$|F_o| > 3\sigma(F_o)$] unique reflections. The crystal is one of the compounds of rare-earth–barium–copper–platinum complex-oxides series and isomorphous with other $R_2\text{Ba}_3\text{Cu}_2\text{PtO}_{10}$ ($R = \text{Y}, \text{Ho}$) oxides. In this compound, two distorted square pyramids of Cu^{II} and one distorted octahedron of Pt^{IV} are connected with each other by face sharing of the

polyhedra. The relationship between crystal structure and equilibrium stability of $R_2\text{Ba}_3\text{Cu}_2\text{PtO}_{10}$ and $R_2\text{Ba}_2\text{CuPtO}_8$ is discussed.

Introduction. Recently, a new series of quadruple oxides composed of rare earth, barium, copper, platinum and oxygen (RBCPO; $R = \text{rare-earth elements}$) was found during the single-crystal growth of $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\sigma}$ superconductors by the CuO self-flux method. In this series two types of compounds, $R_2\text{Ba}_2\text{CuPtO}_8$ ($R = \text{Ho}, \text{Er}, \text{Y}$; Saito, Ukei, Shishido & Fukuda, 1990; Ukei, Shishido & Fukuda, 1988; Laligant, Ferey, Hervieu & Raveau, 1987; Swinnea & Steinfink, 1987) and $R_2\text{Ba}_3\text{Cu}_2\text{PtO}_{10}$ ($R = \text{Ho}, \text{Y}$; Geiser, Porter, Wang, Allen & Williams, 1988), have

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