

Crystal Chemistry of *cyclo*-Hexaphosphates. XVI. Structures of Potassium *cyclo*-Hexaphosphate Ditetellurate Trihydrate and Rubidium *cyclo*-Hexaphosphate Tritellurate Tetrahydrate

BY M. T. AVERBUCH-POUCHOT AND A. DURIF

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

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Abstract. $K_6P_6O_{18} \cdot 2Te(OH)_6 \cdot 3H_2O$, $M_r = 1224.75$, trigonal (rhombohedral), $R\bar{3}c$, $a = 13.084$ (5), $c = 34.80$ (2) Å, $V = 5159$ (7) Å³, $Z = 6$, $D_x = 2.365$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å, $\mu = 2.856$ mm⁻¹, $F(000) = 3558$, $T = 294$ K, final $R = 0.030$ for 1565 independent reflections. $Rb_6P_6O_{18} \cdot 3Te(OH)_6 \cdot 4H_2O$, $M_r = 1747.632$, triclinic, $P1$, $a = 11.222$ (8), $b = 8.077$ (6), $c = 11.731$ (9) Å, $\alpha = 111.11$ (2), $\beta = 104.66$ (2), $\gamma = 83.25$ (2)°, $V = 959$ (2) Å³, $Z = 1$, $D_x = 3.025$ Mg m⁻³, $\lambda(Ag K\alpha) = 0.5608$ Å, $\mu = 5.742$ mm⁻¹, $F(000) = 814$, $T = 294$ K, final $R = 0.035$ for 5408 independent reflections; the corresponding caesium salt is isotopic. The atomic arrangement of the potassium salt can be described as a stacking of two types of planes perpendicular to the c axis. The first type is made up of $Te(OH)_6$ groups, P_6O_{18} ring anions and one of the K atoms. The second type of plane contains the water molecules and one of the K atoms. These planes are separated by a distance of about $c/12$. The rubidium salt is made up of a very simple stacking of $Te(OH)_6$ and P_6O_{18} groups which are both located around inversion centres of the triclinic cell, and interconnected by RbO_7 and RbO_9 polyhedra and water molecules.

Introduction. Like *cyclo*-tri- and *cyclo*-tetraphosphates, *cyclo*-hexaphosphates have the property to form adducts with telluric acid. During the course of a systematic investigation of *cyclo*-hexaphosphate crystal chemistry, we recently reported the chemical preparation and crystal structure of the first example of such a compound: $(NH_4)_6P_6O_{18} \cdot Te(OH)_6 \cdot 2H_2O$ (Averbuch-Pouchot & Durif, 1990). In the present work we describe chemical preparations and crystal structures for two other members of this family: $K_6P_6O_{18} \cdot 2Te(OH)_6 \cdot 3H_2O$ and $Rb_6P_6O_{18} \cdot 3Te(OH)_6 \cdot 4H_2O$. The caesium salt, $Cs_6P_6O_{18} \cdot 3Te(OH)_6 \cdot 4H_2O$, is an isotype of the rubidium compound and has the following unit-cell dimensions: $a = 11.549$ (8), $b = 8.228$ (4), $c = 11.946$ (6) Å, $\alpha = 111.08$ (5), $\beta = 103.13$ (5), $\gamma = 82.26$ (5)°.

Experimental. Crystals of the title compounds have been prepared by adding an aqueous solution of telluric acid to an aqueous solution of the corresponding alkali *cyclo*-hexaphosphate so as to have the proper stoichiometry in the final mixture. The solutions obtained were then slowly evaporated at room temperature. Crystals of the potassium salt appear as large multifaceted rhombohedra while those of the rubidium salt are thick plates or triclinic prisms.

$K_6P_6O_{18} \cdot 2Te(OH)_6 \cdot 3H_2O$. Crystal size: $0.32 \times 0.30 \times 0.25$ mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. 18 reflections ($11.0 < \theta < 13.0^\circ$) for refining unit-cell dimensions. $\omega/2\theta$ scan, scan width 1.20° , scan speed 0.02° s⁻¹, total background measuring time 6 s. 5795 reflections collected ($3 < \theta < 35^\circ$), $\pm h, k, l$, $h_{max} = 18$, $k_{max} = 18$, $l_{max} = 56$. Two orientation and intensity control reflections (834 and $\bar{8}\bar{3}\bar{4}$) measured every 6 h without any significant variation. 2034 independent reflections ($R_{int} = 0.023$). Lorentz and polarization corrections, no absorption correction.

$Rb_6P_6O_{18} \cdot 3Te(OH)_6 \cdot 4H_2O$. Crystal size: $0.30 \times 0.25 \times 0.20$ mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. 18 reflections ($11.30 < \theta < 17.50^\circ$) for refining unit-cell dimensions. ω scan, scan width 1.20° , scan speed 0.03° s⁻¹, total background measuring time 6 s. 7585 reflections collected ($3 < \theta < 30^\circ$), $\pm h, \pm k, l$, $h_{max} = 19$, $k_{max} = 14$, $l_{max} = 15$. Two orientation and intensity control reflections ($6\bar{2}\bar{4}$ and $\bar{6}24$) measured every 6 h without any significant variation. 7219 independent reflections after averaging Friedel pairs ($R_{int} = 0.035$). Lorentz and polarization corrections, no absorption correction.

The crystal structure of the potassium salt was solved by using direct methods (*MULTAN77*; Main, Lessinger, Woolfson, Germain & Declercq, 1977). H atoms belonging to the $Te(OH)_6$ groups were located by difference Fourier syntheses but due to the high thermal factor of the water molecule its H atoms could not be located. In the case of the rubidium salt

Table 1. Final atomic coordinates and B_{eq}/B_{iso} values for $K_6P_6O_{18} \cdot 2Te(OH)_6 \cdot 3H_2O$

H atoms were refined isotropically. E.s.d.'s are given in parentheses.

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{eq}/B_{iso}(\text{\AA}^2)$
Te	0	0	0.13939 (1)	1.378 (3)
K(1)	0.43031 (9)	0	↓	2.06 (2)
K(2)	↓	0	↓	5.13 (4)
P	0.47833 (6)	0.37028 (6)	0.84847 (2)	1.36 (1)
O(1)	0.1320 (2)	0.0377 (2)	0.32827 (9)	2.64 (5)
O(2)	0.1362 (2)	0.0984 (2)	0.10866 (8)	1.96 (4)
O(E1)	0.2491 (3)	0.3228 (2)	0.16494 (9)	2.74 (6)
O(E2)	0.4656 (2)	0.3470 (2)	0.27905 (7)	2.04 (5)
O(L)	0.4771 (3)	0.1971 (2)	0.31754 (8)	2.97 (5)
O(W)	0.2153 (9)	0	↓	17.7 (6)
H(1)	0.097 (7)	0.189 (6)	0.164 (2)	4 (2)
H(2)	0.762 (6)	0.479 (6)	0.247 (2)	4 (2)

the atomic arrangement was determined by using the Patterson function. Here all H atoms were located by difference Fourier syntheses. For both structures anisotropic full-matrix least-squares refinements (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 (1977) SDP operating on a MicroVAX II used for all calculations. For $K_6P_6O_{18} \cdot 2Te(OH)_6 \cdot 3H_2O$ final $R = 0.030$ ($wR = 0.034$) for 1565 reflections corresponding to $I > 4\sigma(I)$, $S = 1.970$, maximum $\Delta/\sigma = 0.02$, maximum peak height in the final difference Fourier map = $0.475 e \text{\AA}^{-3}$. No secondary-extinction correction. For $Rb_6P_6O_{18} \cdot 3Te(OH)_6 \cdot 4H_2O$ final $R = 0.035$ ($wR = 0.039$) for 5408 reflections corresponding to $I > 4\sigma(I)$, $S = 1.967$, maximum $\Delta/\sigma = 0.12$, maximum peak height in the final difference Fourier map = $1.748 e \text{\AA}^{-3}$. No secondary-extinction correction.

Tables 1 and 3 report the final atomic coordinates for these two structures.* Drawings were made using STRUPLO (Fischer, 1985).

Discussion. $K_6P_6O_{18} \cdot 2Te(OH)_6 \cdot 3H_2O$. The atomic arrangement of the potassium salt can be easily described as made up of two alternating types of planes perpendicular to the threefold axis and separated by a distance of about $c/12$. Planes of the first type contain P_6O_{18} ring anions, TeO_6 octahedra and the K(2) atoms. A projection of part of the structure along the c axis ($-0.075 < z < 0.075$) gives a good representation of such a plane. Planes of the second type contain the water molecules and K(1) atoms. A projection of the arrangement made along the c axis ($0.008 < z < 0.158$) gives the respective locations of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53954 (53 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 $K_6P_6O_{18} \cdot 2Te(OH)_6 \cdot 3H_2O$

E.s.d.'s are given in parentheses.

The P_6O_{18} ring anion

P	O(E1)	O(E2)	O(L)	O(L)
O(E1)	1.475 (3)	2.557 (4)	2.506 (5)	2.444 (4)
O(E2)	↓	1.478 (3)	2.441 (4)	2.549 (4)
O(L)	105.6 (2)	112.2 (2)	1.592 (3)	2.473 (4)
O(L)	109.9 (2)	105.6 (2)	↓	1.585 (3)

P—P—P 107.85 (4) P—O(L)—P 134.8 (2)

P—P 2.934 (1)

$Te(OH)_6$ octahedron

Te—O(1)	Te—O(1)—H	110 (6)
1.908 (3) (×3)	Te—O(2)—H	111 (5)
1.918 (2) (×3)		

K(1) O_8 polyhedron

K(1)—O(2)	K(1)—O(E2)	2.720 (3) (×2)
2.813 (2) (×2)	K(1)—O(W)	2.813 (11) (×2)
2.852 (3) (×2)		

K(2) O_6 polyhedron

K(2)—O(1)	K(2)—O(2)	3.037 (3) (×2)
2.933 (3) (×2)		
2.765 (4) (×2)		

The hydrogen bonds

O(1)—H(1)	0.81 (6)	H(1)···O(E1)	1.88 (6)
O(2)—H(2)	1.05 (8)	H(2)···O(E2)	1.75 (7)
O(1)—H(1)···O(E1)	159 (7)	O(2)—H(2)···O(2)	163 (5)

Table 3. Final atomic coordinates and B_{eq}/B_{iso} values for $Rb_6P_6O_{18} \cdot 3Te(OH)_6 \cdot 4H_2O$

H atoms were refined isotropically. E.s.d.'s are given in parentheses.

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{eq}/B_{iso}(\text{\AA}^2)$
Te(1)	0	0	0	1.000 (6)
Te(2)	0	0	↓	1.277 (7)
Te(3)	↓	0	↓	1.117 (7)
Rb(1)	0.09874 (4)	0.50476 (6)	0.20369 (5)	1.984 (9)
Rb(2)	0.28192 (5)	0.78401 (6)	0.80670 (5)	2.317 (9)
Rb(3)	0.30979 (5)	0.01054 (9)	0.39746 (6)	3.23 (11)
P(1)	0.4291 (1)	0.1608 (1)	0.7742 (1)	1.01 (2)
P(2)	0.2224 (1)	0.3856 (1)	0.8636 (1)	0.99 (2)
P(3)	0.3651 (1)	0.6012 (1)	0.1024 (1)	1.01 (2)
O(1)	0.0845 (3)	0.7741 (4)	0.9694 (3)	1.76 (7)
O(2)	0.0686 (3)	0.0342 (4)	0.8756 (3)	1.75 (6)
O(3)	0.1327 (3)	0.1155 (5)	0.1344 (3)	1.62 (6)
O(4)	0.1051 (3)	0.1872 (5)	0.5280 (3)	2.02 (7)
O(5)	0.1372 (4)	0.8785 (5)	0.5731 (4)	2.25 (8)
O(6)	0.0421 (3)	0.8856 (5)	0.3403 (3)	1.78 (7)
O(7)	0.4494 (4)	0.7423 (5)	0.5216 (4)	2.49 (8)
O(8)	0.3717 (4)	0.4266 (6)	0.3524 (4)	2.52 (8)
O(9)	0.3846 (3)	0.4904 (5)	0.5929 (3)	1.86 (7)
O(E11)	0.4619 (3)	0.9720 (4)	0.7622 (3)	1.64 (6)
O(E12)	0.4173 (3)	0.2101 (5)	0.6611 (3)	1.84 (7)
O(L12)	0.3082 (3)	0.2087 (4)	0.8288 (3)	1.24 (6)
O(L13)	0.4747 (3)	0.7158 (4)	0.1087 (3)	1.48 (6)
O(L23)	0.3193 (3)	0.5362 (4)	0.9513 (3)	1.10 (5)
O(E21)	0.1667 (3)	0.4311 (4)	0.7489 (3)	1.54 (6)
O(E22)	0.1428 (3)	0.3579 (4)	0.9380 (3)	1.62 (6)
O(E31)	0.2692 (3)	0.7215 (5)	0.1599 (3)	1.81 (7)
O(E32)	0.4123 (4)	0.4468 (5)	0.1421 (3)	1.90 (7)
O(W1)	0.3442 (4)	0.0833 (5)	0.0578 (4)	2.26 (8)
O(W2)	0.1329 (4)	0.5120 (6)	0.4702 (5)	3.3 (1)
H(1)	0.144 (8)	0.76 (1)	0.051 (8)	3 (2)
H(2)	0.083 (9)	0.13 (1)	0.895 (9)	3 (2)
H(3)	0.192 (8)	0.11 (1)	0.111 (8)	3 (2)
H(4)	0.128 (9)	0.27 (1)	0.620 (9)	3 (2)
H(5)	0.13 (1)	0.77 (1)	0.52 (1)	5 (3)
H(6)	0.001 (9)	0.09 (1)	0.725 (9)	3 (2)
H(7)	0.455 (8)	0.78 (1)	0.571 (8)	3 (2)
H(8)	0.382 (9)	0.44 (1)	0.276 (9)	4 (3)
H(9)	0.404 (9)	0.37 (1)	0.618 (9)	3 (2)
H(W11)	0.390 (9)	0.08 (1)	0.129 (9)	4 (3)
H(W12)	0.36 (1)	0.20 (2)	0.05 (1)	6 (3)
H(W21)	0.100 (8)	0.42 (1)	0.468 (8)	2 (2)
H(W22)	0.195 (9)	0.50 (1)	0.480 (9)	3 (2)

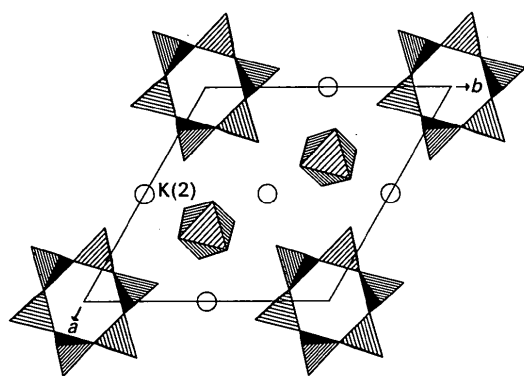


Fig. 1. Projection along the *c* axis of part of the atomic arrangement of K₆P₆O₁₈·2Te(OH)₆·3H₂O ($-0.075 < z < 0.075$).

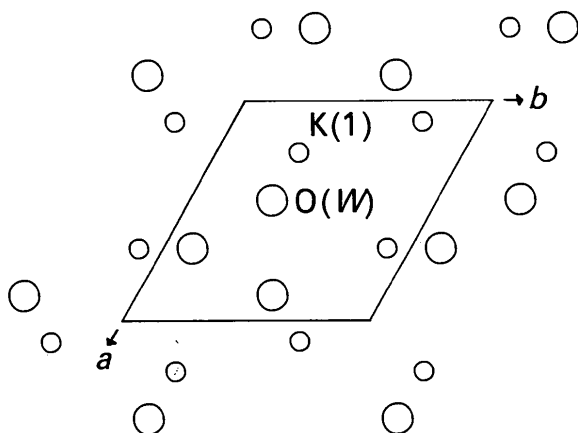


Fig. 2. Projection along the *c* axis of part of the atomic arrangement of K₆P₆O₁₈·2Te(OH)₆·3H₂O ($0.008 < z < 0.158$).

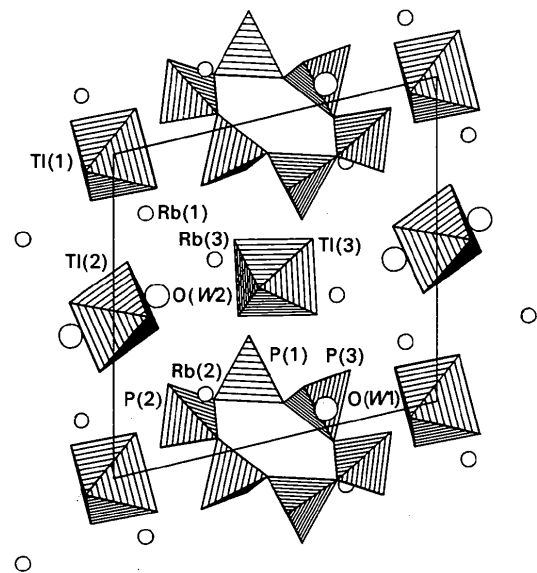


Fig. 3. Projection along the *b* axis of the atomic arrangement of Rb₆P₆O₁₈·3Te(OH)₆·4H₂O.

Table 4. Main interatomic distances (Å) and bond angles (°) in the atomic arrangement of Rb₆P₆O₁₈·3Te(OH)₆·4H₂O

E.s.d.'s are given in parentheses.

The P₆O₁₈ ring anion

P(1)O₄ tetrahedron

P(1)	O(E11)	O(E12)	O(L12)	O(L13)
O(E11)	1.490 (3)	2.543 (6)	2.463 (4)	2.507 (4)
O(E12)	117.3 (2)	1.488 (4)	2.570 (6)	2.543 (5)
O(L12)	106.0 (2)	113.0 (2)	1.593 (4)	2.443 (4)
O(L13)	108.3 (2)	110.8 (2)	99.8 (2)	1.601 (3)

P(2)O₄ tetrahedron

P(2)	O(L12)	O(L23)	O(E21)	O(E22)
O(L12)	1.610 (3)	2.516 (4)	2.533 (5)	2.470 (5)
O(L23)	103.2 (1)	1.601 (3)	2.474 (4)	2.524 (5)
O(E21)	109.7 (2)	106.4 (2)	1.488 (4)	2.574 (6)
O(E22)	106.1 (2)	110.0 (2)	120.3 (2)	1.480 (4)

P(3)O₄ tetrahedron

P(3)	O(L13)	O(L23)	O(E31)	O(E32)
O(L13)	1.596 (4)	2.365 (4)	2.517 (5)	2.544 (6)
O(L23)	94.8 (2)	1.617 (3)	2.531 (5)	2.536 (5)
O(E31)	109.5 (2)	109.2 (2)	1.486 (4)	2.558 (5)
O(E32)	111.6 (2)	109.8 (2)	119.2 (3)	1.480 (4)

P(1)—O(L12)—P(2)	133.3 (2)	P(1)—P(2)—P(3)	96.65 (4)
P(2)—O(L23)—O(P3)	127.3 (3)	P(2)—P(3)—P(1)	144.87 (6)
P(1)—O(L13)—P(3)	131.1 (3)	P(3)—P(1)—P(2)	102.24 (4)

P(1)—P(2)	2.940 (1)
P(1)—P(3)	2.911 (1)
P(2)—P(3)	2.884 (1)

The Te(OH)₆ groups

Te(1)O₆ octahedron

Te(1)—O(1)	1.911 (3)	(× 2)	Te(1)—O(1)—H(1)	114 (4)
Te(1)—O(2)	1.925 (4)	(× 2)	Te(1)—O(2)—H(2)	109 (8)
Te(1)—O(3)	1.911 (3)	(× 2)	Te(1)—O(3)—H(3)	112 (6)

Te(2)O₆ octahedron

Te(2)—O(4)	1.911 (4)	(× 2)	Te(2)—O(4)—H(4)	114 (7)
Te(2)—O(5)	1.911 (4)	(× 2)	Te(2)—O(5)—H(5)	102 (7)
Te(2)—O(6)	1.920 (4)	(× 2)	Te(2)—O(6)—H(6)	119 (6)

Te(3)O₆ octahedron

Te(3)—O(7)	1.916 (4)	(× 2)	Te(3)—O(7)—H(7)	112 (11)
Te(3)—O(8)	1.903 (3)	(× 2)	Te(3)—O(8)—H(8)	119 (5)
Te(3)—O(9)	1.916 (4)	(× 2)	Te(3)—O(9)—H(9)	109 (6)

The RbO_x polyhedra

Rb(1)—O(1)	3.018 (3)	Rb(2)—O(1)	3.293 (4)
Rb(1)—O(3)	2.954 (3)	Rb(2)—O(2)	3.022 (3)
Rb(1)—O(6)	2.990 (3)	Rb(2)—O(5)	3.113 (4)
Rb(1)—O(8)	3.234 (4)	Rb(2)—O(9)	3.127 (3)
Rb(1)—O(E21)	3.118 (4)	Rb(2)—O(E11)	2.912 (4)
Rb(1)—O(E22)	3.057 (4)	Rb(2)—O(L12)	3.388 (3)
Rb(1)—O(E22)	3.112 (3)	Rb(2)—O(L23)	2.991 (4)
Rb(1)—O(E31)	2.987 (2)	Rb(2)—O(E21)	3.048 (4)
Rb(1)—O(W2)	3.032 (6)	Rb(2)—O(W1)	3.040 (3)
Rb(3)—O(4)	3.016 (4)	Rb(3)—O(7)	3.286 (5)
Rb(3)—O(6)	3.115 (4)	Rb(3)—O(E12)	2.932 (3)
Rb(3)—O(7)	3.097 (4)	Rb(3)—O(E12)	3.454 (4)
Rb(3)—O(E31)	2.889 (3)		

The hydrogen bonds

O—H...O	O—H	H...O	O...O	O—H...O
O(1)—H(1)...O(E31)	1.06 (9)	1.72 (9)	2.757 (5)	164 (9)
O(2)—H(2)...O(E22)	0.76 (10)	1.87 (10)	2.624 (5)	171 (11)
O(3)—H(3)...O(W1)	0.77 (10)	1.93 (10)	2.697 (6)	175 (10)
O(4)—H(4)...O(E21)	1.02 (9)	1.60 (8)	2.609 (4)	167 (11)
O(5)—H(5)...O(W2)	0.86 (9)	1.96 (11)	2.766 (6)	157 (11)
O(6)—H(6)...O(2)	0.89 (10)	1.91 (11)	2.789 (6)	170 (10)
O(7)—H(7)...O(E11)	0.54 (9)	2.20 (8)	2.742 (5)	173 (12)
O(8)—H(8)...O(E32)	0.97 (12)	1.72 (12)	2.682 (7)	176 (9)
O(9)—H(9)...O(E12)	1.08 (11)	1.54 (12)	2.620 (6)	172 (9)
O(W1)—H(W1)...O(E11)	0.86 (10)	1.94 (10)	2.742 (5)	154 (10)
O(W1)—H(W12)...O(E32)	0.96 (14)	2.00 (11)	2.870 (5)	150 (10)
O(W2)—H(W21)...O(4)	0.85 (10)	2.23 (11)	3.003 (7)	151 (7)
O(W2)—H(W22)...O(9)	0.69 (10)	2.21 (9)	2.843 (5)	155 (11)
H(W11)—O(W1)—H(W12)	103 (10)	H(W21)—O(W2)—H(W22)	108 (11)	

water molecules and of K(1) atoms in such a plane. Figs. 1 and 2 report these two projections. The cohesion between these planes is established through the potassium polyhedra and the hydrogen bonds. The main interatomic distances and bond angles in this arrangement are given in Table 2.

The phosphoric ring anion observed in this arrangement is very regular with a P—P—P angle of 107.85° . H atoms of the $\text{Te}(\text{OH})_6$ group are only involved in hydrogen bonds interconnecting these groups to external O atoms of the phosphoric rings (Table 2).

$\text{Rb}_6\text{P}_6\text{O}_{18}\cdot 3\text{Te}(\text{OH})_6\cdot 4\text{H}_2\text{O}$. Here the P_6O_{18} ring anion located around the inversion centre at $\frac{1}{2}, 0, 0$ is significantly more distorted, with P—P—P angles ranging from 96.65 to 144.87° . A recent review of the geometry of this kind of ring anion (Averbuch-Pouchot & Durif, 1991) shows that this range of distortion is the common rule for P_6O_{18} rings having $\bar{1}$ internal symmetry. TeO_6 octahedra also located around inversion centres are almost regular as usually observed. The $\text{Te}(1)(\text{OH})_6$ and $\text{Te}(2)(\text{OH})_6$ groups aligned along the c axis are interconnected by one hydrogen bond: $\text{O}(6)\text{—H}(6)\cdots\text{O}(2)$ while the

third one, $\text{Te}(3)(\text{OH})_6$, does not establish such bonds with the other telluric groups. The H atoms of the $\text{Te}(\text{OH})_6$ groups are involved in hydrogen bonds connecting them either to the external O atoms of the P_6O_{18} ring, or to water molecules.

The very simple stacking of $\text{Te}(\text{OH})_6$ and P_6O_{18} groups is shown in Fig. 3, a projection of this atomic arrangement along the b axis. Table 4 gives the main interatomic distances and bond angles in this salt where within a range of 3.5 \AA the three independent Rb atoms have from seven to nine neighbours.

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Crystal Chemistry of *cyclo*-Hexaphosphates. XVIII. Structures of Ethylammonium *cyclo*-Hexaphosphate Tetrahydrate and Hydrazinium(1+) Hydrazinium(2+) *cyclo*-Hexaphosphate

BY M. T. AVERBUCH-POUCHOT AND A. DURIF

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

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Abstract. $(\text{C}_2\text{H}_5\text{N})_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$, $M_r = 822.444$, monoclinic, $P2_1/a$, $a = 16.804(10)$, $b = 23.883(10)$, $c = 10.623(8) \text{ \AA}$, $\beta = 109.66(2)^\circ$, $V = 4015(8) \text{ \AA}^3$, $Z = 4$, $D_x = 1.360 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $\mu = 0.351 \text{ mm}^{-1}$, $F(000) = 1744$, $T = 294 \text{ K}$, final $R = 0.035$ for 6795 independent reflections. $(\text{N}_2\text{H}_5)_2(\text{N}_2\text{H}_6)_2\text{P}_6\text{O}_{18}$, $M_r = 608.058$, triclinic, $P\bar{1}$, $a = 8.175(8)$, $b = 7.926(8)$, $c = 8.457(7) \text{ \AA}$, $\alpha = 105.05(2)$, $\beta = 102.08(2)$, $\gamma = 86.42(2)^\circ$, $V = 517.5(1.5) \text{ \AA}^3$, $Z = 1$, $D_x = 1.951 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $\mu = 0.627 \text{ mm}^{-1}$, $F(000) = 312$, $T = 297 \text{ K}$, final $R = 0.032$ for 4869 independent reflections. The atomic arrangement of the ethylammonium salt is built up of arrays of P_6O_{18} ring anions and ethylammonium groups parallel to the c axis and arranged in an almost hexagonal way. This

hexagonal packing is centred by a centrosymmetric cluster of eight water molecules forming a branched hexagon. The phosphoric ring anion has no internal symmetry. Six crystallographically independent ethylammonium groups coexist in the arrangement. The hydrogen-bond geometry is described. The second structure is a very simple one. The centrosymmetrical P_6O_{18} groups are located around the inversion centres at $0, 0, \frac{1}{2}$. The wide channels parallel to the c axis created by the anion stacking are lined by both hydrazinium(1+) and hydrazinium(2+) groups. The hydrogen-bond network is reported.

Introduction. The present investigation is part of a systematic study of the organic cation derivatives of *cyclo*-hexaphosphates. Some results in this field have