

## Hexapotassium (cyclo-Octahydroxotetracosaoxohexadecaborato)dioxouranate(VI) Dodecahydrate, $K_6[UO_2\{B_{16}O_{24}(OH)_8\}].12H_2O$

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(Received 6 July 1984; accepted 8 January 1985)

**Abstract.**  $M_r = 1413.8$ , monoclinic,  $P2_1/n$ ,  $a = 12.024$  (6),  $b = 26.45$  (1),  $c = 12.543$  (4) Å,  $\beta = 94.74$  (3)°,  $V = 3975$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.36$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 4.6$  mm<sup>-1</sup>,  $F(000) = 2744$ ,  $T = 190$  K,  $R = 0.061$  for 6518 independent observed reflections. The structure contains isolated mononuclear  $[UO_2\{B_{16}O_{24}(OH)_8\}]$  complexes. The borate ions, with 16 B atoms, are ring-like and enclose one U atom as the nucleus, thereby forming chelate complexes. The U atom is coordinated to six O atoms of one borate molecule and additionally to two O atoms, forming a 'uranyl dumb-bell'. The uranyl–borate complexes are held together by water molecules and K<sup>+</sup> ions. The present structure is related to the copper borates reported earlier [Behm (1982). *Z. Kristallogr.* **22**, 16; Behm (1983). *Acta Cryst.* **C39**, 20–22]; it is the first uranium borate compound and the first mononuclear ring-like borate complex whose structure has been determined.

**Introduction.** In a systematic study of complex borates several copper chelate complexes have been synthesized (Behm, 1982, 1983). They are all polynuclear. This is a consequence of the relatively small Cu–O distances in connection with the rather rigid quadratic coordination sphere. As a further step in studying complex borates the synthesis of mononuclear complexes was envisaged. Larger cations with higher coordination numbers like  $UO_2^{2+}$  seem to be suitable. This paper reports the synthesis and structure determination of a uranyl–borate chelate and, in contrast to the copper borates, the structure appeared to be mononuclear with a uranyl dumb-bell as the nucleus. Since the borate chelates represent a novel type of borate they were not yet considered in former systematic classifications given by Christ & Clark (1977), Waugh (1968) and Tennyson (1963).

**Experimental.**  $K_6[UO_2\{B_{16}O_{24}(OH)_8\}].12H_2O$  was synthesized from an aqueous solution of potassium tetraborate, to which a solution of  $UO_2$  acetate had

been added. In the resulting amorphous precipitate small lemon-colored crystals appeared after several weeks. The crystals are stable in air and show fluorescence especially in ultraviolet light. Their composition was established by X-ray structure determination.

X-ray investigations: crystal of about  $0.43 \times 0.17 \times 0.05$  mm (fixed with 'apiezon' grease on a capillary glass tube). Space group and crystal data from precession photographs, lattice parameters refined from 25 Bragg reflections measured on a Syntex R3 diffractometer at low temperature of 190 (10) K.

Data collection: 14721 reflections,  $3 < 2\theta < 40^\circ$   $\bar{h}k\bar{l}$ ,  $40 < 2\theta < 56^\circ$   $\bar{h}kl-hkl$ , graphite monochromator, Mo  $K\alpha$  radiation,  $\theta/2\theta$  scan, variable scan speed: min.  $5^\circ$  min<sup>-1</sup>, max.  $12^\circ$  min<sup>-1</sup>, scan range from  $0.9^\circ$  below  $K\alpha_1$  to  $0.9^\circ$  above  $K\alpha_2$ , background/scan ratio 0.5, three standard reflections every 100 reflections, variation  $\pm 3\%$ , Lorentz and polarization corrections with XTape (Sheldrick, 1981), absorption correction with the Gaussian quadrature method, 120 sampling points and optically measured crystal dimensions: min. transmission 0.22, max. 0.79. Averaging gave 6158 symmetrically independent reflections with  $|F| > 5\sigma_F$ ,  $\sigma_F$  from counting statistics,  $R(\text{merge}) = 0.09$  (unit weights) and  $R(\sigma) = 0.05$ . Atomic scattering factors and anomalous-dispersion coefficients for U, K, O and B from *International Tables for X-ray Crystallography* (1974). All further calculations with SHELXTL (Sheldrick, 1981) on a NOVA-3 computer.

Structure determination: structure solved with Patterson methods. After the U atom had been correctly located, all remaining atoms of the complex ions could be found on the Fourier map. Further refinements gave the positions of the K and water O atoms. Two K atoms and several coordinating water molecules were found to be disordered; their positions were split. All atoms were refined anisotropically with the exception of the split water O atoms. For these O atoms a variable site-occupancy factor, with the restriction that the total sum is one, and for the disordered (K, O) positions with the restriction that the total sum is one K and one O, was refined. Each pair of O atoms was refined isotropically with a common temperature factor for

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both positions. Since only few H-atom positions could be obtained from the Fourier map, these atoms were not considered in the final refinements (on  $F$ ). The

Table 1. Atomic coordinates and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

	$x$	$y$	$z$	$U_{eq}/U_{iso}$	S.o.f.
U	0.8991 (1)	0.1364 (1)	0.7916 (1)	6 (1)*	
O A	0.9156 (5)	0.2038 (3)	0.7906 (5)	12 (2)*	
O B	0.8821 (5)	0.0692 (3)	0.7906 (5)	14 (2)*	
K(1)	0.9227 (2)	0.2204 (1)	0.2953 (2)	18 (1)*	
K(2)	0.9284 (2)	0.2659 (1)	0.9757 (2)	22 (1)*	
K(3)	0.8229 (2)	-0.0298 (1)	0.8036 (2)	24 (1)*	
K(4)	0.9184 (2)	0.2648 (1)	0.6060 (2)	19 (1)*	
K(5a)	1.0787 (5)	0.0129 (2)	0.6601 (4)	59 (2)*	0.594 (4)
K(5b)	1.3503 (5)	-0.0184 (2)	0.7152 (5)	41 (2)*	0.406 (4)
K(6a)	0.4822 (4)	0.0877 (2)	0.3897 (4)	56 (2)*	0.586 (4)
K(6b)	0.2749 (4)	0.0669 (2)	0.4780 (4)	26 (1)*	0.414 (4)
B(1)	0.6498 (9)	0.1554 (5)	0.7866 (9)	13 (3)*	
B(2)	0.6703 (8)	0.1312 (4)	0.5892 (8)	13 (3)*	
B(3)	0.8443 (7)	0.1428 (4)	0.5081 (8)	8 (3)*	
B(4)	1.0470 (8)	0.1404 (5)	0.6043 (8)	10 (3)*	
B(5)	1.1534 (7)	0.1280 (4)	0.7991 (8)	8 (3)*	
B(6)	1.1177 (8)	0.1131 (5)	0.9943 (8)	10 (3)*	
B(7)	0.9565 (8)	0.1445 (5)	1.0763 (8)	13 (3)*	
B(8)	0.7577 (8)	0.1583 (4)	0.9787 (7)	5 (2)*	
B(9)	0.5075 (9)	0.1033 (4)	0.6832 (8)	11 (3)*	
B(10)	0.6885 (8)	0.2034 (4)	0.4770 (8)	10 (3)*	
B(11)	1.0104 (8)	0.1093 (4)	0.4219 (8)	8 (3)*	
B(12)	1.1862 (9)	0.2033 (5)	0.6855 (8)	12 (3)*	
B(13)	1.2533 (9)	0.0617 (5)	0.9057 (9)	15 (3)*	
B(14)	1.138 (1)	0.1902 (5)	1.1002 (9)	18 (3)*	
B(15)	0.7826 (8)	0.1253 (5)	1.1617 (8)	13 (3)*	
B(16)	0.6565 (8)	0.2328 (4)	0.8982 (8)	11 (3)*	
O(1)	0.7207 (5)	0.1350 (3)	0.8761 (5)	9 (2)*	
O(2)	0.7187 (5)	0.1483 (3)	0.6949 (5)	10 (2)*	
O(3)	0.7556 (5)	0.1098 (3)	0.5311 (6)	15 (2)*	
O(4)	0.9255 (5)	0.1485 (3)	0.6027 (5)	11 (2)*	
O(5)	1.0744 (5)	0.1144 (3)	0.7070 (5)	10 (2)*	
O(6)	1.0807 (5)	0.1303 (3)	0.8864 (5)	12 (2)*	
O(7)	1.0259 (5)	0.1027 (3)	1.0560 (5)	10 (2)*	
O(8)	0.8793 (5)	0.1560 (3)	0.9817 (5)	10 (2)*	
O(9)	0.5422 (5)	0.1306 (3)	0.7710 (5)	9 (2)*	
O(10)	0.5783 (5)	0.0949 (3)	0.6020 (5)	12 (2)*	
O(11)	0.6195 (5)	0.1745 (3)	0.5291 (5)	11 (2)*	
O(12)	0.8000 (5)	0.1936 (3)	0.4765 (5)	13 (2)*	
O(13)	0.9010 (6)	0.1237 (3)	0.4161 (5)	18 (2)*	
O(14)	1.0781 (5)	0.1115 (3)	0.5129 (5)	11 (2)*	
O(15)	1.1078 (5)	0.1890 (3)	0.6069 (5)	11 (2)*	
O(16)	1.2058 (5)	0.1779 (3)	0.7787 (5)	12 (2)*	
O(17)	1.2425 (5)	0.0908 (3)	0.8161 (6)	16 (2)*	
O(18)	1.1877 (5)	0.0668 (3)	0.9884 (5)	10 (2)*	
O(19)	1.1908 (5)	0.1528 (3)	1.0479 (5)	10 (2)*	
O(20)	1.0244 (5)	0.1906 (3)	1.1064 (5)	12 (2)*	
O(21)	0.8930 (5)	0.1332 (3)	1.1693 (5)	12 (2)*	
O(22)	0.7164 (5)	0.1307 (3)	1.0687 (5)	11 (2)*	
O(23)	0.7162 (5)	0.2111 (3)	0.9821 (5)	13 (2)*	
O(24)	0.6293 (5)	0.2100 (3)	0.8020 (5)	11 (2)*	
OH(1)	0.4042 (5)	0.0831 (3)	0.6713 (6)	18 (2)*	
OH(2)	0.6378 (5)	0.2439 (3)	0.4194 (5)	12 (2)*	
OH(3)	1.0525 (6)	0.0919 (4)	0.3273 (5)	19 (2)*	
OH(4)	1.2472 (7)	0.2465 (3)	0.6732 (5)	23 (2)*	
OH(5)	1.3342 (6)	0.0257 (3)	0.9141 (6)	24 (2)*	
OH(6)	1.2064 (6)	0.2261 (3)	1.1503 (6)	16 (2)*	
OH(7)	0.7312 (5)	0.1121 (3)	1.2517 (5)	18 (2)*	
OH(8)	0.6200 (6)	0.2820 (3)	0.9069 (5)	17 (2)*	
OW(1)	0.9130 (6)	0.3145 (4)	0.4109 (7)	25 (3)*	
OW(2a)	0.808 (1)	0.3422 (6)	0.878 (1)	19 (2)	0.54 (1)
OW(2b)	0.811 (1)	0.3619 (7)	1.000 (1)	19 (2)	0.46 (1)
OW(3)	0.6547 (7)	0.0307 (3)	0.9007 (7)	29 (3)*	
OW(4)	0.0524 (8)	-0.0159 (4)	0.8743 (7)	32 (3)*	
OW(5)	0.8338 (9)	0.3922 (4)	0.694 (1)	51 (4)*	
OW(6)	1.0342 (9)	0.3223 (4)	0.7609 (8)	42 (3)*	
OW(7a)	0.635 (1)	-0.0034 (8)	0.684 (2)	42 (3)	0.58 (2)
OW(7b)	0.654 (2)	-0.007 (1)	0.598 (2)	42 (3)	0.42 (2)
OW(8a)	0.291 (2)	-0.0198 (9)	0.598 (2)	35 (3)	0.47 (1)
OW(8b)	0.473 (1)	-0.0225 (8)	0.781 (2)	35 (3)	0.53 (1)
OW(9)	1.1249 (8)	-0.0157 (4)	0.445 (1)	48 (4)*	
OW(10a)	0.521 (1)	0.0752 (8)	0.089 (2)	53 (4)	0.68 (2)
OW(10b)	0.500 (3)	0.110 (2)	0.072 (3)	53 (4)	0.32 (2)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. For the split atoms the refined site-occupancy factor s.o.f. is also given.

results are:  $R = 0.061$ ,  $wR = 0.063$  with  $w = 1/(\sigma^2 + 0.0035 F^2)$ ,  $S = 1.0$  and a normal-probability-slope value of 0.88; max. final shift-to-error 0.12, mean 0.03; max. height in final difference Fourier map  $4.6 \text{ e \AA}^{-3}$  immediately adjacent to U atom, min.  $-3 \text{ e \AA}^{-3}$ .

**Discussion.** The final atomic parameters are given in Table 1.\* Fig. 1 shows the  $[\text{UO}_2\{\text{B}_{16}\text{O}_{24}(\text{OH})_8\}]$  complex ion, Fig. 2 a schematic packing of the complexes and cations in the unit cell. Bond lengths and angles of the complex ion are given in Tables 2 and 3. The  $\text{UO}_2$ -borate ion is the first-found mononuclear borate chelate complex. Each  $\text{UO}_2$  dumb-bell is surrounded by a ring-like  $[\text{B}_{16}\text{O}_{24}(\text{OH})_8]$  molecule. This borate molecule can be regarded as being built up by a cyclic  $\text{B}_8\text{O}_8$  unit with tetrahedrally coordinated B atoms. Six of the eight O atoms in the ring coordinate

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42013 (62 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

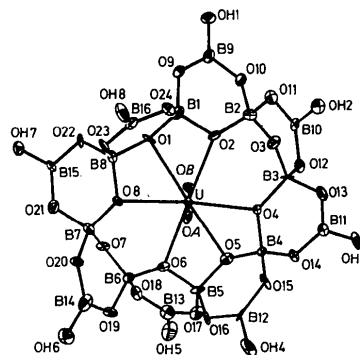


Fig. 1. The complex uranyl-borate anion with numbering of the atoms (50% probability thermal-vibration ellipsoids).

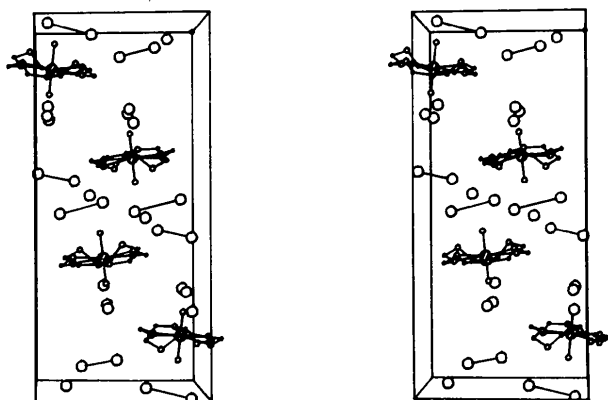


Fig. 2. Stereoscopic view of the packing in the unit cell ( $a$  axis to the left,  $b$  axis down). For clarity only the inner parts of the complexes, the  $\text{UO}_2\text{B}_8\text{O}_8$  rings, are plotted together with the  $\text{K}^+$  ions; split K positions are connected.

as ligands to the UO<sub>2</sub> dumb-bell, while two opposite O atoms are only bonded by B atoms. Additionally eight BO<sub>3</sub> groups connect neighboring tetrahedrally coordinated B atoms, thus forming B<sub>3</sub>O<sub>3</sub> loops which are alternately folded up and down. The structural principle

is very similar to that found for the dodecaborate ion (Menchetti & Sabelli, 1979) except that this molecule, synthesized hydrothermally, has only six tetrahedrally coordinated B atoms in the inner ring. This molecule, however, does not show any complex-like behavior in the structure.

The U atoms have a 2+6 coordination to O. Two U—O bonds, nearly linear and almost perpendicular to the plane of the six other U—O bonds are short with 1.794 (8) and 1.788 (8) Å, forming the uranyl dumb-bell. The U—O bonds to six O atoms of the B<sub>8</sub>O<sub>8</sub> ring are from 2.404 (6) to 2.506 (6) Å. All these O atoms are bonded between two tetrahedrally coordinated B atoms.

Table 2. Bond lengths (Å)

U—O <sub>A</sub>	1.794 (8)	B(1)—O(1)	1.46 (1)
—O <sub>B</sub>	1.788 (8)	—O(2)	1.48 (1)
—O(1)	2.471 (6)	—O(9)	1.45 (1)
—O(2)	2.417 (6)	—O(24)	1.48 (2)
—O(4)	2.438 (6)		
—O(5)	2.506 (6)	B(2)—O(2)	1.47 (1)
—O(6)	2.404 (6)	—O(3)	1.42 (1)
—O(8)	2.472 (6)	—O(10)	1.48 (1)
		—O(11)	1.48 (1)
K(1)—O(12)	2.898 (7)		
—O(13)	2.994 (9)	B(3)—O(3)	1.43 (1)
—O <sub>w</sub> (1)	2.89 (1)	—O(4)	1.48 (1)
—O(20 <sup>a</sup> )	2.865 (7)	—O(12)	1.49 (1)
—O(21 <sup>b</sup> )	2.802 (8)	—O(13)	1.48 (1)
—OH(4 <sup>h</sup> )	2.652 (8)		
—OH(8 <sup>h</sup> )	2.654 (7)	B(4)—O(4)	1.48 (1)
		—O(5)	1.47 (1)
K(2)—O <sub>A</sub>	2.837 (7)	—O(14)	1.45 (1)
—O(8)	2.967 (8)	—O(15)	1.48 (1)
—O(20)	2.770 (7)		
—O(23)	2.941 (7)	B(5)—O(5)	1.48 (1)
—O <sub>w</sub> (2a)	2.72 (2)	—O(6)	1.46 (1)
—O <sub>w</sub> (2b)	2.93 (2)	—O(16)	1.49 (1)
—O(1 <sup>h</sup> )	2.822 (7)	—O(17)	1.46 (1)
—OH(2 <sup>h</sup> )	2.683 (7)		
		B(6)—O(6)	1.46 (1)
K(3)—O <sub>B</sub>	2.723 (8)	—O(7)	1.43 (1)
—O <sub>w</sub> (3)	2.922 (9)	—O(18)	1.49 (1)
—O <sub>w</sub> (7a)	2.70 (2)	—O(19)	1.49 (1)
—O(18 <sup>III</sup> )	2.799 (7)		
—OH(3 <sup>iv</sup> )	2.836 (8)	B(7)—O(7)	1.42 (1)
—O <sub>w</sub> (4 <sup>v</sup> )	2.852 (9)	—O(8)	1.48 (1)
—O <sub>w</sub> (5 <sup>v</sup> )	2.80 (1)	—O(20)	1.50 (1)
		—O(21)	1.48 (1)
K(4)—O <sub>A</sub>	2.825 (7)		
—O(12)	2.798 (7)	B(8)—O(1)	1.46 (1)
—O(15)	3.034 (7)	—O(8)	1.46 (1)
—O <sub>w</sub> (1)	2.774 (9)	—O(22)	1.47 (1)
—O <sub>w</sub> (6)	2.75 (1)	—O(23)	1.49 (1)
—OH(6 <sup>h</sup> )	2.664 (8)		
K(5a)—O(5)	2.748 (9)	B(9)—O(9)	1.35 (1)
—O <sub>w</sub> (9)	2.90 (1)	—O(10)	1.40 (1)
—O <sub>w</sub> (4 <sup>vi</sup> )	2.84 (1)	—OH(1)	1.35 (1)
—O <sub>w</sub> (8a <sup>vii</sup> )	2.87 (2)		
—O <sub>w</sub> (9 <sup>vi</sup> )	2.68 (1)	B(10)—O(11)	1.34 (1)
		—O(12)	1.37 (1)
		—OH(2)	1.40 (1)
K(5b)—OH(5)	2.78 (1)		
—K(6a <sup>iv</sup> )	3.095 (8)	B(11)—O(13)	1.36 (1)
—OH(1 <sup>viii</sup> )	2.83 (1)	—O(14)	1.35 (1)
—OH(7 <sup>III</sup> )	2.71 (1)	—OH(3)	1.41 (1)
K(6a)—K(6b)	2.863 (7)		
—O(10)	2.821 (8)	B(12)—O(15)	1.36 (1)
—K(5b <sup>iv</sup> )	3.095 (8)	—O(16)	1.35 (1)
—O <sub>w</sub> (2a <sup>iv</sup> )	2.79 (2)	—OH(4)	1.37 (1)
—O <sub>w</sub> (2b <sup>iv</sup> )	2.89 (2)		
—O <sub>w</sub> (5 <sup>iv</sup> )	2.96 (1)	B(13)—O(17)	1.36 (1)
—O <sub>w</sub> (6 <sup>iv</sup> )	2.97 (1)	—O(18)	1.36 (1)
—O <sub>w</sub> (7a <sup>III</sup> )	2.75 (2)	—OH(5)	1.36 (1)
—O <sub>w</sub> (7b <sup>III</sup> )	2.70 (3)		
—O <sub>w</sub> (8b <sup>III</sup> )	2.83 (2)	B(14)—O(19)	1.37 (2)
		—O(20)	1.38 (1)
		—OH(6)	1.37 (2)
K(6b)—K(6a)	2.863 (7)		
—OH(1)	2.803 (8)	B(15)—O(21)	1.34 (1)
—O <sub>w</sub> (8a)	2.74 (2)	—O(22)	1.36 (1)
—O(14 <sup>v</sup> )	2.712 (8)	—OH(7)	1.38 (1)
—O <sub>w</sub> (2a)	2.76 (2)		
—O <sub>w</sub> (7a)	2.92 (2)	B(16)—O(23)	1.35 (1)
—O <sub>w</sub> (9 <sup>v</sup> )	2.84 (1)	—O(24)	1.36 (1)
		—OH(8)	1.38 (1)

Symmetry code: (i)  $x, y, 1+z$ ; (ii)  $-0.5+x, 0.5-y, -0.5+z$ ; (iii)  $2-x, -y, 2-z$ ; (iv)  $2-x, -y, 1-z$ ; (v)  $-1+x, y, z$ ; (vi)  $1.5-x, -0.5+y, 1.5-z$ ; (vii)  $1+x, y, z$ ; (viii)  $1-x, -y, 1-z$ .

Table 3. Bond angles (°)

O <sub>A</sub> —U—O <sub>B</sub>	179.2 (3)	O(5)—B(5)—O(6)	102.2 (6)
O <sub>A</sub> —U—O(1)	96.8 (3)	O(5)—B(5)—O(16)	109.5 (7)
O <sub>A</sub> —U—O(2)	87.8 (3)	O(5)—B(5)—O(17)	111.5 (8)
O <sub>A</sub> —U—O(4)	80.7 (3)	O(6)—B(5)—O(16)	112.4 (8)
O <sub>A</sub> —U—O(5)	97.5 (3)	O(6)—B(5)—O(17)	113.4 (8)
O <sub>A</sub> —U—O(6)	88.5 (3)	O(16)—B(5)—O(17)	107.8 (7)
O <sub>A</sub> —U—O(8)	79.5 (3)		
O <sub>B</sub> —U—O(1)	83.4 (3)	O(6)—B(6)—O(7)	111.9 (7)
O <sub>B</sub> —U—O(2)	91.6 (3)	O(6)—B(6)—O(18)	109.8 (8)
O <sub>B</sub> —U—O(4)	98.5 (3)	O(6)—B(6)—O(19)	108.7 (8)
O <sub>B</sub> —U—O(5)	82.3 (3)	O(7)—B(6)—O(18)	109.5 (8)
O <sub>B</sub> —U—O(6)	92.0 (3)	O(7)—B(6)—O(19)	110.1 (8)
O <sub>B</sub> —U—O(8)	101.3 (3)	O(18)—B(6)—O(19)	106.6 (7)
O(1)—U—O(2)	56.1 (2)		
O(1)—U—O(4)	127.3 (2)	O(7)—B(7)—O(8)	110.8 (8)
O(1)—U—O(5)	165.7 (2)	O(7)—B(7)—O(20)	111.2 (7)
O(1)—U—O(6)	124.9 (2)	O(7)—B(7)—O(21)	109.4 (9)
O(1)—U—O(8)	55.5 (2)	O(8)—B(7)—O(20)	109.2 (8)
O(2)—U—O(4)	71.3 (2)	O(8)—B(7)—O(21)	110.2 (7)
O(2)—U—O(5)	124.7 (2)	O(20)—B(7)—O(21)	105.8 (8)
O(2)—U—O(6)	176.3 (2)		
O(2)—U—O(8)	107.6 (2)	O(1)—B(8)—O(8)	103.7 (7)
O(4)—U—O(5)	55.8 (2)	O(1)—B(8)—O(22)	111.8 (7)
O(4)—U—O(6)	107.7 (2)	O(1)—B(8)—O(23)	110.1 (7)
O(4)—U—O(8)	160.2 (2)	O(8)—B(8)—O(22)	111.2 (7)
O(5)—U—O(6)	55.4 (2)	O(8)—B(8)—O(23)	112.1 (8)
O(5)—U—O(8)	127.5 (2)	O(22)—B(8)—O(23)	108.0 (7)
O(6)—U—O(8)	72.1 (2)		
U—O <sub>A</sub> —K(2)	124.6 (3)	O(9)—B(9)—O(10)	120.8 (9)
U—O <sub>A</sub> —K(4)	125.6 (3)	O(9)—B(9)—OH(1)	121.3 (9)
K(2)—O <sub>A</sub> —K(4)	109.7 (3)	O(10)—B(9)—OH(1)	117.9 (9)
U—O <sub>B</sub> —K(3)	170.3 (3)		
		O(11)—B(10)—O(12)	122.9 (9)
O(1)—B(1)—O(2)	102.9 (8)	O(11)—B(10)—OH(2)	115.3 (8)
O(1)—B(1)—O(9)	113.3 (9)	O(12)—B(10)—OH(2)	121.8 (9)
O(1)—B(1)—O(24)	110.8 (8)		
O(2)—B(1)—O(9)	112.8 (8)	O(13)—B(11)—O(14)	123.0 (9)
O(2)—B(1)—O(24)	109.5 (9)	O(13)—B(11)—OH(3)	117.4 (8)
O(9)—B(1)—O(24)	107.5 (8)	O(14)—B(11)—OH(3)	119.6 (8)
O(2)—B(2)—O(3)	109.5 (7)	O(15)—B(12)—O(16)	123 (1)
O(2)—B(2)—O(10)	110.1 (8)	O(15)—B(12)—OH(4)	119.6 (9)
O(2)—B(2)—O(11)	109.7 (8)	O(16)—B(12)—OH(4)	117.0 (8)
O(3)—B(2)—O(10)	112.0 (9)		
O(3)—B(2)—O(11)	109.4 (8)	O(17)—B(13)—O(18)	124 (1)
O(10)—B(2)—O(11)	106.0 (7)	O(17)—B(13)—OH(5)	119 (1)
		O(18)—B(13)—OH(5)	118 (1)
O(3)—B(3)—O(4)	110.9 (8)		
O(3)—B(3)—O(12)	110.5 (7)	O(19)—B(14)—O(20)	122 (1)
O(3)—B(3)—O(13)	110.4 (8)	O(19)—B(14)—OH(6)	116.0 (9)
O(4)—B(3)—O(12)	108.6 (8)	O(20)—B(14)—OH(6)	122 (1)
O(4)—B(3)—O(13)	110.1 (7)		
O(12)—B(3)—O(13)	106.2 (8)	O(21)—B(15)—O(22)	123.4 (9)
		O(21)—B(15)—OH(7)	119.3 (8)
O(4)—B(4)—O(5)	103.3 (7)	O(22)—B(15)—OH(7)	117.3 (8)
O(4)—B(4)—O(14)	112.6 (7)		
O(4)—B(4)—O(15)	111.1 (9)	O(23)—B(16)—O(24)	125 (1)
O(5)—B(4)—O(14)	113.0 (9)	O(23)—B(16)—OH(8)	119.3 (9)
O(5)—B(4)—O(15)	108.2 (7)	O(24)—B(16)—OH(8)	115.5 (8)
O(14)—B(4)—O(15)	108.4 (8)		

The observed B—O bond lengths and angles are comparable with values found in other borate structures. For tetrahedral B atoms the B—O distances are 1.42 (1) to 1.50 (1) Å and the O—B—O angles are 102.2 (6) to 113.4 (8)°. Trigonal B atoms have B—O distances from 1.34 (1) to 1.41 (1) Å and O—B—O angles from 115.3 (8) to 125.1 (10)°.

The surrounding K atoms are differently coordinated, partly to O atoms of the  $\text{UO}_2$  dumb-bell, to O atoms of the borate molecule, to OH groups formed by the terminal O atoms of the  $\text{BO}_3$  groups or to water molecules. K(1)—K(4) and their coordination spheres are well defined. These cations show six- or sevenfold coordination to O atoms with K—O distances from 2.652 (8) to 3.034 (7) Å. The coordinations of K(5*a*,5*b*) and K(6*a*,6*b*) which occupy, together with a water molecule, two positions are less well determined by this disordering. K(5*a*,5*b*) is only coordinated to four or five O atoms, not considering multi-coordinations to split O atoms, with K—O distances of 2.683 (11) to 3.095 (8) Å. The K(6*a*,6*b*) positions have a seven- or eightfold coordination to O atoms with K—O distances of 2.70 (3) to 3.095 (8) Å. The disordering of the two cations found here may be induced by

the similarity of each of these two positions, which can be occupied by a  $\text{K}^+$  ion or by a water molecule. The probable hydrogen-bond system built up by the water molecules and OH groups was not investigated since H-atom positions could not be found beyond doubt on the Fourier map and several water molecules are disordered.

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## Structure du Tétrathiophosphate(V) de Zinc et d'Argent, $\text{ZnAgPS}_4$

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(Reçu le 26 juin 1984, accepté le 14 janvier 1985)

**Abstract.**  $M_r = 332.5$ , orthorhombic,  $Pna2_1$ ,  $a = 12.502$  (2),  $b = 7.599$  (1),  $c = 6.0696$  (7) Å,  $V = 576.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.829$  Mg m<sup>-3</sup>,  $\text{Mo K}\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 9.16$  mm<sup>-1</sup>,  $F(000) = 624$ ,  $T = 294$  (1) K,  $R = 0.030$  for 856 independent reflections [ $I > 3\sigma(I)$ ]. The S atoms adopt an approximately hexagonal close-packed arrangement in which P, Zn and Ag atoms occupy tetrahedral sites. The  $\text{PS}_4$ ,  $\text{ZnS}_4$  and  $\text{AgS}_4$  polyhedra are almost regular [mean distances: P—S 2.052 (3), Zn—S 2.353 (2), Ag—S 2.578 (2) Å]. This structure is closely related to that of the high-temperature form of  $\text{ZnAl}_2\text{S}_4$ .

**Introduction.** La détermination de la structure de  $\text{ZnAgPS}_4$  a été réalisée dans le cadre de l'étude des thio- et des sélénophosphates poursuivie par l'un d'entre nous. Alors que de nombreuses études structurales ont été consacrées aux tétraoxophosphates à deux cations, à notre connaissance, on n'a jamais décrit jusqu'ici de

composés de formule  $M^I M^{II} \text{PS}_4$ . Le produit utilisé a été obtenu en chauffant pendant une semaine, à 700 K, le mélange des éléments pris en proportions stoechiométriques, dans une ampoule de silice vidée d'air et scellée. La composition des cristaux présents dans la préparation a été établie à l'aide d'une sonde électronique CAMECA.

**Partie expérimentale.** Pas de mesure de la masse volumique (très peu de produit, mélange). Cristal parallélépipédique: 0,050 × 0,050 × 0,250 mm. Dimensions de la maille déterminées lors de la mesure des intensités avec 25 réflexions telles que  $3,25 \leq \theta \leq 18,17^\circ$ . Diffractomètre Enraf-Nonius CAD-4.  $0,032 \leq (\sin\theta)/\lambda \leq 0,766$  Å<sup>-1</sup>.  $0 \leq h \leq 19$ ;  $0 \leq k \leq 11$ ;  $0 \leq l \leq 9$ . Réflexions de contrôle des intensités  $\bar{2}21$ ,  $4\bar{1}0$  et  $400$ ;  $\sigma(I)/I$  moyen  $< 4 \times 10^{-3}$ . 1169 réflexions indépendantes mesurées, 313 réflexions inobservées [ $I < 3\sigma(I)$ ]. Corrections d'absorption