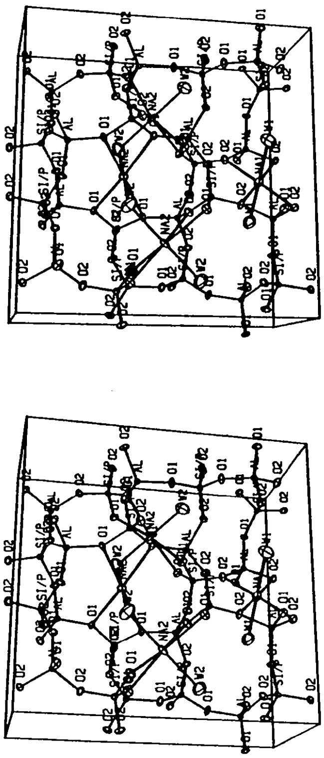

Fig. 2. Stereoplot of atomic positions and ellipsoidal approximation to the displacements in one half of unit cell (30% probability level).

perpendicular to the tetrahedral atoms. Because only half of the Na sites are occupied, the Na—O and Na—*W* distances in Table 2 are probably longer than the actual bonding distances. Some of the displacement of the water O atoms probably results from unbalance of electrostatic forces from Na atoms. In principle, such Na vacancies and H_2O displacements might become ordered, but no evidence was found. Data collection at low temperature could help clarify this point. Protons were not located from the X-ray refinement.

In conclusion, the present study demonstrates that P is substituted in the zeolites synthesized by Flanigen & Grose (1971), and implies that the relative substitutions of P, Al and Si in tetrahedral frameworks are limited by a strong tendency for Al to be ordered with respect to P and Si. This is consistent with the two limiting models in their Table XI.

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Rubidium Pentaborate Tetrahydrate, $Rb[B_5O_6(OH)_4].2H_2O$

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Abstract. $M_r = 339{\cdot}6$, orthorhombic, space group $Aba2$, $a = 11{\cdot}302\,(2)$, $b = 10{\cdot}962\,(2)$, $c = 9{\cdot}335\,(1)$ Å, $V = 1156{\cdot}6\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}95$, $D_m = 1{\cdot}91$ g cm^{-3} (flotation method), $\mu(\text{Mo } K\alpha) = 42{\cdot}15$ cm^{-1}, $F(000) = 663{\cdot}85$, room temperature, $R = 0{\cdot}033$ for 1623 reflections. The absolute configuration has been determined. The structure belongs to the class of soroborates and contains isolated pentaborate

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groups $[B_5O_6(OH)_4]$. $Rb[B_5O_6(OH)_4].2H_2O$ is isotypic with the corresponding potassium and ammonium pentaborates. The significant variations found in the lattice parameters among the three compounds Rb, α-NH_4 and K pentaborate are clearly shown to be induced by both an enlargement of the cation size and a preservation of the hydrogen-bond lengths.

Introduction. A series of pentaborates $M[B_5O_6(OH)_4].xH_2O$ (M = Li, Na, K, Rb, Cs, NH_4, Tl) have been reported (*Gmelins Handbuch der Anorganischen Chemie*, 1975). The crystal structures of two Na compounds have been determined, that of the mineral sborgite, $Na[B_5O_6(OH)_4].3H_2O$, by Merlino & Sartori (1972), and that of synthetic $Na[B_5O_6(OH)_4]$ by Menchetti & Sabelli (1978). The structure of synthetic $K[B_5O_6(OH)_4].2H_2O$ has been determined by Zachariasen & Plettinger (1963) and was redetermined with neutron diffraction by Ashmore & Petch (1970). Merlino & Sartori (1970) found the potassium pentaborate tetrahydrate to be identical with the mineral santite. The structure of α-$NH_4[B_5O_6(OH)_4].2H_2O$ has been reported by Cook & Jaffe (1957) to be isotypic with the corresponding potassium pentaborate; the structure was determined explicitly by Domenech, Solans & Solans (1981). Another phase of ammonium pentaborate, β-$NH_4[B_5O_6(OH)_4].2H_2O$, has been worked out by Merlino (1969). The structure of $Tl[B_5O_6(OH)_4].2H_2O$ has been determined by Woller & Heller (1981). Of all these reported pentaborate structures only the K pentaborate crystallizes in the space group *Aba*2, all other pentaborates are monoclinic.

The crystal structure of rubidium pentaborate tetrahydrate has been assumed to be isotypic with the K and α-NH_4 pentaborate tetrahydrate structures of the santite type (Rosenheim & Leyser, 1921; Cook & Jaffe, 1957; König, 1978), but no complete structure determination has been carried out. In this homologous series the cations control the arrangement of the pentaborate groups in the structure. Since Rb, K and α-NH_4 pentaborates differ significantly in their lattice parameters it seems of interest to study systematically the influence of the cation on the whole structure.

Experimental. $Rb[B_5O_6(OH)_4].2H_2O$ was prepared from an aqueous sodium pentaborate solution to which RbI had been added. The crystals were recrystallized twice at room temperature by evaporation. The resulting crystals (up to a few mm in lengths) showed a column-like habit; most of them were twinned.

Data collection: crystal with natural faces [distances from the centre: (100) 47 µm, $(\bar{1}00)$ 47 µm, $(01\bar{1})$ 173 µm, $(0\bar{1}1)$ 173 µm, (011) 105 µm, $(0\bar{1}\bar{1})$ 105 µm], precession photographs, lattice parameters from 25 Bragg reflections measured on a Syntex *R*3 diffractometer; 6078 reflections, full reciprocal sphere $3 < 2\theta < 50°$, $50 < 2\theta < 65°$ half sphere of reciprocal space, Picker four-circle diffractometer, graphite monochromator, Mo $K\alpha$ radiation, $\theta/2\theta$ scan, scan speed 2° per min, scan range from 0·92° below $K\alpha_1$ to 0·88° above $K\alpha_2$, background 2 × 20 s, three standard reflections every 100 reflections with maximum variation of ± 2%. Data reduction: Lorentz and polarization corrections with a program written by Holub (1982). All further calculations with *SHELXTL* (Sheldrick, 1981), NOVA-3 computer; after averaging $R(\text{merge}) = 0{\cdot}058$, absorption correction using Gaussian quadrature method (minimum and maximum transmission 0·403 and 0·661). 1623 symmetrically independent reflections with $F > 3\sigma_F$, σ_F taken from counting statistics, new $R(\text{merge}) = 0{\cdot}016$ (unit weight), $R(\text{sigma}) = 0{\cdot}025$ where $R(\text{merge}) = \{\sum[N\sum(\bar{F}-F_o)^2]/\sum[(N-1)\sum F_o^2]\}^{1/2}$ and $R(\text{sigma}) = \sum\sigma_{Fo}/\sum F_o$; atomic scattering factors and dispersion coefficients for Rb, O, B and H from *International Tables for X-ray Crystallography* (1974). Structure refinement: Atomic coordinates for Rb, O, B atoms were taken from the structure of potassium pentaborate tetrahydrate and were refined with anisotropic temperature factors to $R = 0{\cdot}034$. From the last difference Fourier map the H-atom positions were perceived and refined with isotropic temperature factors together with all other parameters. Although the heavy atoms themselves form a centrosymmetric substructure, the deviations from Friedel's law were strong enough to allow the determination of the absolute configuration according to a method given by Rogers (1981) which is implemented in the refinement program. Differences of up to 10% were observed for certain Bijvoet pairs of the F_o values. The R values for the inverse structure are $R = 0{\cdot}075$ and $R_w = 0{\cdot}058$; the refinement results for the correct absolute configuration are $R = 0{\cdot}033$, $R_w = 0{\cdot}018$ with a weighting scheme $w = 1/\sigma_F^2$. An extinction correction factor E was refined to $6{\cdot}7 \times 10^{-4}$, with $F_c = F[1 + 2 \times 10^{-3} \times EF^2/\sin(2\theta)]^{1/4}$. $S = 1{\cdot}79$ and the normal probability slope value = 1·38; $(\Delta/\sigma)_{\max} = 0{\cdot}019$, $(\Delta/\sigma)\text{mean} = 0{\cdot}003$; final $\Delta\rho$ excursions −0·8 to (in the neighbourhood of the Rb atom) 1·5 e Å^{-3}.

Discussion. The final atomic parameters are in Table 1.*

$Rb[B_5O_6(OH)_4].2H_2O$ is a soroborate. The supposed isotypism of the Rb, K and α-NH_4 pentaborate structures is confirmed. Interatomic distances are given

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* Lists of structure factors, anisotropic thermal parameters, bond angles and interatomic distances compared for Rb, α-NH_4 and K pentaborate have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38948 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in Table 2. {A comparision with the values found in the K pentaborate by X-ray and neutron diffraction and the values found in the α-$NH_4[B_5O_6(OH)_4].2H_2O$ by X-ray diffraction has been deposited.} The atomic numbering adopted is that of the K pentaborate structure. For the lower symmetry of the α-NH_4 pentaborate (space group *Pn*) the symmetrically independent values are combined to corresponding mean values, since the differences from orthorhombic symmetry are minimal.

The interatomic distances within the pentaborate groups agree well with the values of the X-ray structure determination by Zachariasen & Plettinger (1963); they show similar deviations from the neutron data given by Ashmore & Petch (1970) as have been observed for the K pentaborate with both methods. This may be due to the greater uncertainties in the location of the B atoms by neutron diffraction, as is manifested in the higher standard deviations for these parameters. The agreement with the mean values calculated from the α-$NH_4[B_5O_6(OH)_4].2H_2O$ structure is good.

In the Rb pentaborate the mean B—O distance for the trigonally coordinated B atom is 1·357 (3) Å; for the tetrahedrally coordinated B it is 1·474 (2) Å. All calculated O—H distances for the Rb pentaborate are smaller than the values obtained from neutron diffraction. The angle in the water molecule is similar to that found by the neutron diffraction study. Large O—H distances in the hydroxyl groups as reported by Zachariasen & Plettinger (1963) are not observed.

Rb is likewise coordinated to eight O atoms, with Rb—O distances between 2·942 (1)–3·153 (1) Å, values which are approximately 0·12 Å larger than the K—O distances found in the K pentaborate and 0·014 Å larger than the N—O distances found in the α-NH_4 pentaborate, in accordance with the greater ionic radius of the Rb^+ ion [Rb(CN8) = 1·61, K(CN8) = 1·51 Å (Shannon & Prewitt, 1969)]. Fig. 1 shows the packing of the Rb atoms and of the pentaborate units in the structure. Rb by itself builds up a face-centred lattice. The centres of gravity of the pentaborate units form a similar face-centred lattice, which is displaced along **c** by 0·401*z*. The complete anionic lattice is not centred, since the pentaborate units are alternately tilted about 90° around their long axes by a glide mirror plane and these axes form an angle of about 4° with the *ac* plane.

Since the Rb—O bonds to O atoms of the borate groups lie in a layer parallel to the *ac* plane, the lattice constants *a* and *c* must be increased to accommodate the longer Rb—O bonds [Rb: $a = 11·302$ (2), $c = 9·335$ (1); K: $a = 11·062$, $c = 9·041$ Å]. This expansion would lead to an elongation of the hydrogen bonds which is, however, compensated by a significant shortening of the third lattice constant *b* from 11·175 Å found in K pentaborate to 10·962 (2) Å in Rb pentaborate.

In α-NH_4 pentaborate the lattice constants show a similar behaviour relative to K pentaborate. Although the observed hydrogen bonds are not particularly strong (see Ichikawa, 1978) the structures rearrange themselves to preserve the interatomic distances within the pentaborate groups and also within the O—H···O hydrogen-bond system.

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*
Rb	0	0	0	37 (1)*
B(1)	0	0	4051 (3)	22 (1)*
B(2)	1850 (2)	941 (2)	3153 (2)	23 (1)*
B(3)	1994 (2)	9420 (2)	4940 (4)	27 (1)*
O(1)	659 (1)	852 (1)	3126 (1)	25 (1)*
O(2)	806 (1)	9293 (1)	4973 (2)	27 (1)*
O(3)	2530 (1)	250 (1)	4047 (2)	31 (1)*
O(4)	2389 (1)	1748 (1)	2260 (2)	40 (1)*
O(5)	2751 (1)	8795 (2)	5775 (2)	50 (1)*
O(6)	230 (1)	1732 (1)	7488 (2)	36 (1)*
H(1)	10088 (18)	2592 (34)	7488 (43)	47 (6)
H(2)	9904 (17)	1405 (21)	6812 (29)	41 (7)
H(3)	2009 (18)	1687 (18)	7308 (33)	47 (8)
H(4)	2529 (23)	3322 (18)	1108 (26)	46 (8)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Interatomic distances* (Å) *for rubidium pentaborate tetrahydrate*

Rb—O(1)	3·153 (1)	O(4)—O(6^{vi})	2·700 (2)
—O(3^{i})	2·942 (1)	O(4)—H(3^{vi})	0·69 (2)
—O(5^{ii})	2·954 (1)	O(6)—H(3)	2·02 (2)
—O(6^{iii})	3·029 (2)		
		O(5)—O(4^{vii})	2·670 (2)
B(1)—O(1)	1·474 (2)	O(5)—H(4^{viii})	0·65 (2)
—O(2^{iv})	1·473 (2)	O(4)—H(4)	2·04 (2)
B(2)—O(1)	1·350 (2)	O(6)—O(1^{ix})	2·894 (2)
—O(3)	1·365 (2)	O(6)—O(2^{x})	2·854 (2)
—O(4)	1·359 (3)	O(6)—H(1^{viii})	0·95 (4)
		O(6)—H(2^{viii})	0·81 (3)
B(3)—O(2)	1·351 (2)	O(1)—H(1^{xi})	2·00 (4)
—O(3^{v})	1·375 (3)	O(2)—H(2^{xii})	2·04 (3)
—O(5)	1·344 (3)		

Symmetry code: (i) $0·5-x, -y, -0·5+z$; (ii) $0·5-x, 1-y, -0·5+z$; (iii) $x, y, -1+z$; (iv) $x, -1+y, z$; (v) $x, 1+y, z$; (vi) $0·5-x, y, -0·5+z$, (vii) $x, 0·5+y, 0·5+z$; (viii) $-1+x, y, z$; (ix) $-x, 0·5-y, 0·5+z$; (x) $-x, 1-y, z$; (xi) $1-x, 0·5-y, -0·5+z$; (xii) $1-x, 1-y, z$.

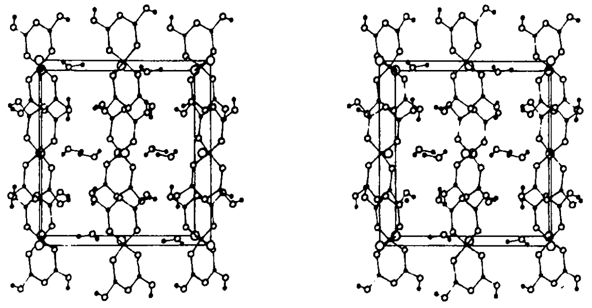

Fig. 1. Stereoscopic view along the twofold axis of the structure of $Rb[B_5O_6(OH)_4].2H_2O$; *a* axis down, *b* axis to the right; circles in decreasing size Rb, O, B; black dots H.

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Bis(dichromate) de Bismuth et de Rubidium, $RbBi(Cr_2O_7)_2$

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Abstract. $M_r = 726{\cdot}4$, monoclinic, $P2_1/a$, $a = 8{\cdot}340\,(4)$, $b = 17{\cdot}069\,(4)$, $c = 8{\cdot}813\,(9)$ Å, $\beta = 91{\cdot}47\,(2)°$, $V = 1254{\cdot}1$ Å^3, $D_m = 3{\cdot}87\,(1)$, $D_x = 3{\cdot}847$ Mg m^{-3}, $Z = 4$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, room temperature, $\mu = 20{\cdot}926$ mm^{-1}, $F(000) = 1312$, $R = 0{\cdot}034$ for 2367 reflections. The new phase $RbBi(Cr_2O_7)_2$ has been studied by single-crystal X-ray structure analysis with an automatic diffractometer. The structure contains $[BiO_8]$ polyhedra linked together by $[Cr_2O_7]$ groups to build complex layers in the *ab* plane. All these layers are linked by Rb^+ ions.

Introduction. L'étude systématique du système quaternaire M_2O–Bi_2O_3–CrO_3–H_2O où $M = K^+$, Rb^+, Tl^+, NH_4^+, Ag^+ a permis de mettre en évidence des composés qui à notre connaissance n'ont jamais été signalés dans la littérature chimique. Ces composés peuvent être classés en trois familles distinctes:

–Des chromates doubles de formule MBi$(CrO_4)_2$ parmi lesquels $AgBi(CrO_4)_2$ a fait l'objet de deux mémoires récents (Gerault & Lecerf, 1979; Riou & Roult, 1979).

–Des chromate–dichromates de formule MBi$(Cr_2O_4)(Cr_2O_7).H_2O$ qui existent seulement pour $M = K^+$ et NH_4^+. Une étude chimique de ces chromate–dichromates ainsi que la structure de $KBi(CrO_4)(Cr_2O_7).H_2O$ sont actuellement publiés (Cudennec, Lecerf, Riou & Gerault, 1981; Riou, Gerault & Cudennec, 1982).

–Des dichromates doubles de formule MBi$(Cr_2O_7)_2$ qui existent dans le cas de $M = Ag^+$, K^+, NH_4^+, Rb^+ et Tl^+. Seule avait été determinée jusqu'à ce jour la structure de $AgBi(Cr_2O_7)_2$ (Riou & Roult, 1980). Le présent mémoire est consacré à la détermination structurale de $RbBi(Cr_2O_7)_2$.

Partie expérimentale. Le mode de préparation des composés MBi$(Cr_2O_7)_2$ avec $M = Ag^+$, Rb^+, Tl^+, NH_4^+, K^+ a été publié antérieurement (Lecerf, Cudennec, Riou & Gerault, 1981). Certains de ces composés présentent au moins deux variétés allotropiques.

Cristaux de $RbBi(Cr_2O_7)_2$ obtenus par une très lente évaporation à 323 K d'une solution aqueuse contenant 1 mol de $RbBi(Cr_2O_7)_2$ et 6 mol de CrO_3; ces cristaux précipitent sous forme de prismes allongés à section carrée. Etudes préliminaires radiocristallographiques menées sur chambres photographiques de Weissenberg et de précession. Paramètres de la maille cristalline

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