forme en réalité. Pour $x = 0{,}20$, on aurait $(Cs_3Nb_{5,8}O_{16})_8$ dans lequel 6,4 atomes de niobium Nb(6) ne seraient plus entourés que de trois atomes d'oxygène.

Les facteurs d'agitation thermique reflètent bien les particularités de cette structure en domaines et traduisent, comme toujours dans ce cas, davantage des déplacements atomiques que des vibrations thermiques. C'est ainsi que les fortes valeurs de B pour les atomes O(10), O(11), O(12) et O(13) (Tableau 1) sont certainement liées à la présence ou à l'absence de Nb(6) dans l'une de ses quatre positions possibles. De même, les valeurs élevées de β_{33} pour Cs(1) et Cs(4) traduisent l'importance de leur cage.

Quoi qu'il en soit, tous ces domaines se groupent en un arrangement structural de symétrie *Amam*, à la fois très proche et très différent de celui de $Cs_2Nb_4O_{11}$ puisque les chaînes d'octaèdres s'y replient en chevrons, isolant ainsi les atomes Nb(6) et O(13) de la charpente octaédrique.

Ce processus, que l'on peut assimiler à un changement de phase lié à la composition, constitue un mécanisme nouveau de non stoechiométrie dans les niobates alcalins.

Sur le plan chimique, la différence entre ces deux niobates de césium est minime puisque la composition passe de $Cs_2O,2Nb_2O_5$ à $Cs_2O,(2-\varepsilon)Nb_2O_5$ avec $\varepsilon = 0{,}0133$, mais elle induit peut-être au niveau des propriétés physiques des variations qu'il serait intéressant d'examiner.

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Tricobalt Hexasodium Hexakis(hexahydroxohexaborate) Hexacosahydrate, $Na_6Co_3[B_6O_7(OH)_6]_6.26H_2O$

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Abstract. $M_r = 2456{\cdot}5$, triclinic, $P\bar{1}$, $a = 9{\cdot}572$ (4), $b = 13{\cdot}560$ (6), $c = 18{\cdot}034$ (6) Å, $\alpha = 109{\cdot}04$ (3), $\beta = 96{\cdot}46$ (3), $\gamma = 102{\cdot}37$ (3)°, $Z = 1$, $V = 2119$ (1) Å^3, $D_x = 1{\cdot}92$, D_m (flotation) = $1{\cdot}88$ Mg m^{-3}, λ(Mo $K\alpha$) = $0{\cdot}71069$ Å, μ(Mo $K\alpha$) = $7{\cdot}63$ cm^{-1}, $F(000) = 1246{\cdot}8$, room temperature, $R = 0{\cdot}042$ for 6670 reflections. The structure belongs to the class of soroborates and consists of hexaborate groups between which the Co atoms are octahedrally coordinated. These Co hexaborate units are surrounded by hydrated Na atoms and water molecules.

Introduction. In their study of polyborates in aqueous solutions, Rosenheim & Leyser (1921) proposed that certain transition-metal ions like Co^{3+} would form anionic borate complexes. Others like Co^{2+} were proposed to exist as hydrated cations.

The crystal structures of two hydrated Co borates have so far been determined: $K_2Co[B_6O_7(OH)_6]_2.4H_2O$ by Silins, Ozols & Ievins (1973), and $Co[B_6O_7(OH)_6].7H_2O$ by Silins, Ozols & Ievins (1974). The bonding of the Co^{2+} ions in the two structures is intermediate between pure ionic bonding and ligand-type bonding. A sodium cobalt(II) borate, $Na_6Co_3[B_6O_7(OH)_6]_6.26H_2O$, largely analogous to the potassium cobalt(II) borate mentioned above, could be synthesized. An attempt to synthesize a Co^{III} borate failed.

Experimental. Crystals of $Na_6Co_3[B_6O_7(OH)_6]_6.26H_2O$ were obtained from a concentrated aqueous Na pentaborate solution to which $Co(OH)_2$ [prepared by the method of Brauer (1962)] had been added. After several days violet crystals appeared while the mother liquor turned from pink to colourless. The shape of the crystals was irregular. Space group and rough crystal data from equi-inclination Weissenberg photographs. Lattice parameters refined from 25 Bragg reflections measured on a Syntex $R3$ diffractometer. 15 570 reflections, $3 \leq 2\theta \leq 50°$, *hkl* range: a whole sphere in reciprocal space, graphite monochromator, Mo $K\alpha$ radiation, $\theta/2\theta$ scan, variable scan speed: max. 15, min.

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

O*e* means O of OH, O*w* means O of H_2O.

	x	*y*	*z*	*U*
Co(1)	5000	5000	5000	17 (1)*
Co(2)	7909 (1)	5198 (1)	8442 (1)	15 (1)*
Na(1)	13910 (1)	10207 (1)	9264 (1)	33 (1)*
Na(2)	417 (1)	9472 (1)	4064 (1)	32 (1)*
Na(3)	1844 (1)	179 (1)	7451 (1)	39 (1)*
B(1)	6451 (3)	7790 (2)	7753 (2)	19 (1)*
B(2)	8235 (3)	7700 (2)	8813 (2)	13 (1)*
B(3)	10376 (3)	6992 (2)	8284 (2)	16 (1)*
B(4)	7868 (3)	6479 (2)	7338 (2)	15 (1)*
B(5)	5503 (3)	3369 (2)	8632 (2)	17 (1)*
B(6)	6322 (3)	7413 (2)	5181 (2)	15 (1)*
B(7)	9535 (3)	2673 (2)	9020 (2)	20 (1)*
B(8)	7628 (3)	2730 (2)	8022 (2)	16 (1)*
B(9)	4063 (3)	8110 (2)	5632 (2)	18 (1)*
B(10)	10804 (3)	8729 (2)	9398 (2)	17 (1)*
B(11)	5804 (3)	3742 (2)	10077 (2)	20 (1)*
B(12)	10148 (3)	6497 (2)	6816 (2)	18 (1)*
B(13)	3773 (3)	6546 (2)	4264 (2)	18 (1)*
B(14)	6017 (3)	6701 (2)	3698 (2)	19 (1)*
B(15)	6600 (3)	9251 (2)	6151 (2)	19 (1)*
B(16)	8009 (3)	3882 (2)	9532 (2)	15 (1)*
B(17)	5058 (3)	1687 (2)	7446 (2)	19 (1)*
B(18)	2037 (3)	7658 (2)	4508 (2)	20 (1)*
O(1)	11311 (2)	7924 (1)	8935 (1)	19 (1)*
O(2)	7006 (2)	8032 (1)	8542 (1)	18 (1)*
O(3)	6897 (2)	7216 (1)	4441 (1)	19 (1)*
O(4)	10998 (2)	6856 (1)	7565 (1)	19 (1)*
O(5)	8672 (2)	6239 (1)	6691 (1)	20 (1)*
O(6)	8911 (2)	7207 (1)	8105 (1)	12 (1)*
O(7)	6510 (2)	1826 (1)	7425 (1)	18 (1)*
O(8)	6823 (2)	7042 (1)	7150 (1)	19 (1)*
O(9)	9236 (2)	3448 (1)	9634 (1)	20 (1)*
O(10)	4547 (2)	6384 (1)	3597 (1)	21 (1)*
O(11)	4563 (2)	2429 (1)	7984 (1)	20 (1)*
O(12)	4755 (2)	7458 (1)	4982 (1)	14 (1)*
O(13)	7169 (2)	8434 (1)	5772 (1)	18 (1)*
O(14)	9356 (2)	8644 (1)	9374 (1)	18 (1)*
O(15)	4942 (2)	3516 (1)	9360 (1)	21 (1)*
O(16)	7270 (2)	3918 (1)	10194 (1)	21 (1)*
O(17)	8862 (2)	2352 (1)	8249 (1)	20 (1)*
O(18)	2462 (2)	6814 (1)	4032 (1)	22 (1)*
O(19)	2775 (2)	8296 (1)	5261 (1)	23 (1)*
O(20)	6990 (2)	3158 (1)	8757 (1)	14 (1)*
O(21)	5144 (2)	9144 (1)	6075 (1)	22 (1)*
O*e*(1)	10116 (2)	6008 (1)	8467 (1)	20 (1)*
O*e*(2)	8437 (2)	4931 (1)	9445 (1)	22 (1)*
O*e*(3)	7190 (2)	5522 (1)	7490 (1)	22 (1)*
O*e*(4)	5108 (2)	3791 (2)	10718 (1)	24 (1)*
O*e*(5)	8059 (2)	3626 (1)	7735 (1)	19 (1)*
O*e*(6)	3739 (2)	7521 (2)	6164 (1)	24 (1)*
O*e*(7)	6659 (2)	6514 (2)	3047 (1)	33 (1)*
O*e*(8)	11833 (2)	9650 (1)	9890 (1)	28 (1)*
O*e*(9)	5502 (2)	8345 (2)	7588 (1)	32 (1)*
O*e*(10)	3475 (2)	5571 (1)	4467 (1)	22 (1)*
O*e*(11)	7831 (2)	6875 (1)	9172 (1)	18 (1)*
O*e*(12)	4035 (2)	781 (1)	6923 (1)	29 (1)*
O*e*(13)	5672 (2)	4339 (1)	8411 (1)	19 (1)*
O*e*(14)	6378 (2)	6537 (1)	5469 (1)	19 (1)*
O*e*(15)	7606 (2)	10205 (1)	6615 (1)	31 (1)*
O*e*(16)	10853 (2)	6417 (2)	6191 (1)	31 (1)*
O*e*(17)	10568 (2)	2191 (2)	9208 (1)	43 (1)*
O*e*(18)	800 (2)	7889 (2)	4228 (1)	31 (1)*
O*w*(1)	3914 (2)	5397 (2)	6013 (1)	30 (1)*
O*w*(2)	7171 (2)	8682 (2)	11164 (1)	34 (1)*
O*w*(3)	14668 (2)	8674 (2)	9442 (1)	39 (1)*
O*w*(4)	9008 (2)	8329 (2)	12769 (1)	36 (1)*
O*w*(5)	10382 (2)	8996 (2)	6159 (1)	42 (1)*
O*w*(6)	8251 (2)	9417 (2)	14597 (1)	38 (1)*
O*w*(7)	12882 (2)	8992 (2)	7873 (1)	34 (1)*
O*w*(8)	9013 (2)	5968 (2)	14710 (1)	43 (1)*
O*w*(9)	13880 (3)	9420 (2)	11215 (2)	63 (1)*
O*w*(10)	9311 (2)	5915 (2)	13047 (2)	53 (1)*
O*w*(11)	13541 (3)	6113 (2)	7837 (1)	49 (1)*
O*w*(12)	9530 (3)	9781 (2)	7886 (2)	66 (1)*
O*w*(13)	2122 (8)	3916 (7)	8597 (5)	70 (3)
H(1)	7862 (32)	3481 (24)	7301 (18)	35 (8)
H(2)	7175 (23)	6791 (17)	9255 (13)	0 (5)
H(3)	6618 (27)	6758 (20)	5907 (15)	16 (6)
H(4)	5033 (36)	8045 (27)	7153 (20)	49 (10)
H(5)	2934 (37)	7341 (28)	6117 (21)	53 (10)
H(6)	5420 (30)	4699 (24)	8705 (17)	31 (8)
H(7)	5607 (27)	3794 (21)	11091 (15)	18 (7)
H(8)	9548 (37)	8064 (28)	12483 (21)	49 (10)
H(9)	6714 (29)	5151 (22)	7196 (16)	25 (7)
H(10)	6083 (37)	6343 (28)	2728 (21)	53 (10)
H(11)	8439 (45)	7823 (33)	12785 (24)	73 (12)
H(12)	6609 (36)	8197 (26)	11191 (19)	42 (9)
H(13)	11549 (30)	10007 (23)	10133 (17)	26 (7)
H(14)	15055 (32)	8480 (24)	9208 (18)	31 (8)
H(15)	11050 (42)	2469 (32)	9640 (24)	73 (12)
H(16)	8941 (29)	5309 (22)	9732 (16)	24 (7)
H(17)	10504 (23)	6065 (17)	8726 (13)	0 (5)
H(18)	13672 (49)	8158 (36)	9261 (26)	88 (14)
H(19)	10355 (35)	6347 (27)	5831 (20)	46 (9)
H(20)	9339 (49)	8502 (35)	5980 (26)	85 (14)
H(21)	4382 (38)	383 (30)	6673 (22)	58 (11)
H(22)	7305 (38)	10604 (30)	6866 (22)	58 (11)
H(23)	10801 (49)	8675 (35)	5930 (26)	84 (14)
H(24)	2865 (29)	5219 (22)	4231 (16)	23 (7)
H(25)	445 (36)	7486 (27)	3858 (20)	48 (10)
H(26)	3533 (56)	−1133 (41)	7755 (29)	102 (16)
H(27)	2094 (53)	1254 (40)	5469 (30)	111 (17)
H(28)	−3913 (46)	4019 (35)	3967 (26)	85 (14)
H(29)	2165 (49)	1529 (36)	8950 (26)	86 (14)
H(30)	7286 (38)	3661 (30)	2300 (22)	59 (11)
H(31)	2357 (50)	−1542 (37)	7848 (27)	87 (14)
H(32)	−1377 (65)	6512 (50)	4815 (37)	155 (21)
H(33)	−576 (42)	5967 (32)	4384 (24)	71 (12)
H(34)	6181 (52)	4221 (40)	2542 (30)	110 (16)
H(35)	−3020 (67)	4984 (51)	4070 (38)	161 (22)
H(36)	10544 (58)	−5955 (41)	7385 (32)	112 (17)
H(37)	5765 (121)	−173 (101)	8143 (73)	347 (38)
H(38)	−2096 (85)	−237 (67)	4579 (49)	230 (28)
H(39)	6628 (66)	1004 (54)	8969 (39)	155 (22)
H(40)	−1286 (99)	−46 (75)	7373 (58)	268 (32)
H(41)	118 (140)	127 (105)	8329 (77)	386 (39)
H(42)	−1681 (58)	−3955 (41)	2892 (31)	113 (17)

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

5° min^{-1}, scan range from 1·0° below $K\alpha_1$ to 1·0° above $K\alpha_2$, background/scan ratio 0·5, three standard reflections every 100 reflections: variation ±5%. Lorentz and polarization corrections with *XTAPE* (Sheldrick, 1981), no absorption correction. Averaging gave 6670 symmetrically independent reflections with $|F| \geq 3\sigma_F$, σ_F from counting statistics. R(merge) was 0·028 (unit weight) and $R(\sigma)$ 0·027 [$R(\sigma) = \sum\sigma_{Fo}/\sum F_o$ and $R(\text{merge}) = (\sum\{N\sum[F(\text{mean}) - F_o]^2\}/\sum[(N-1) \times \sum(F_o^2)])^{1/2}$]. Atomic scattering factors and anomalous-dispersion coefficients for Co, Na, O, B and H from *International Tables for X-ray Crystallography* (1974). All calculations made with the program system *SHELXTL* (Sheldrick, 1981) on a NOVA 3 computer. Structure solved by Patterson methods. Starting with the three Co atoms all other nonhydrogen atoms could be successively found by Fourier maps and refinements. With anisotropic thermal parameters for all atoms except for one obviously disordered water O atom, 42 H atoms of the expected 44 could be located from difference Fourier maps and were isotropically refined. No indication for a noncentrosymmetric space group was found. The results of the refinements are: $R = 0{\cdot}042$, $R_w = 0{\cdot}041$ with $w = (1/\sigma_{Fo}^2 + 0{\cdot}00035F^2)$, $S = 1{\cdot}392$, normal-probability-slope value 1·199; maximum final shift-to-error ratio 0·05, mean 0·013; maximum height in final difference Fourier map 1 e Å^{-3}, minimum −0·5 e Å^{-3}.

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

The crystal structure belongs to the class of soroborates. The Co atoms are situated between hexaborate groups which are separated from one another by hydrated Na atoms and H_2O molecules.

Non-isolated hexaborate groups were first found by Clark (1964) in the mineral tunnelite where they are connected to sheets. Isolated hexaborate groups were found in the minerals macallisterite (Dal Negro, Sabelli & Ungaretti, 1969), aksaite (Dal Negro, Ungaretti & Sabelli, 1971), rivadavite (Dal Negro & Ungaretti, 1973) and in the synthetic compounds $Co[B_6O_7(OH)_6].7H_2O$, $Ni[B_6O_7(OH)_6].7H_2O$ (Silins, Ozols & Ievins, 1974), $Ni[B_6O_7(OH)_6].5H_2O$ (Silins & Ievins, 1976), $K_2Co[B_6O_7(OH)_6]_2.4H_2O$ (Silins, Ozols & Ievins, 1973) and $Mg[B_6O_7(OH)_6].3H_2O$ (Genkina, Rumanova & Belov, 1976).

The molecular arrangement around the two symmetrically independent Co atoms is shown in Fig. 1. Co(1) at a centre of symmetry possesses a slightly elongated octahedral coordination to four OH groups of two hexaborate groups and additionally to two water molecules. Co(2) lies at the centre of a slightly shortened octahedron whose apices are six OH groups belonging to two hexaborate groups. All OH groups in the Co coordination polyhedra are bonded to the tetrahedrally coordinated B atoms of the hexaborate groups.

The coordination of Co(1) is very similar to that found in $K_2Co[B_6O_7(OH)_6]_2.4H_2O$ (Silins, Ozols & Ievins, 1973), while the coordination of Co(2) (exclusively to six OH groups of only two hexaborate groups) is comparable with the octahedral coordination of Mg in $Mg[B_6O_7(OH)_6].3H_2O$ (Genkina, Rumanova & Belov, 1976). Bond distances are given in Table 2.

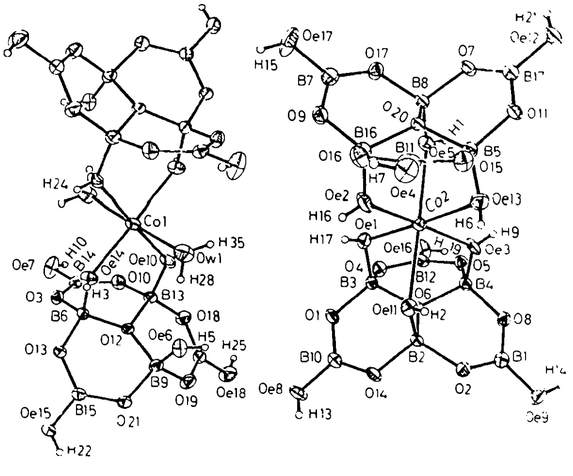

Fig. 1. Molecular arrangements around Co(1) and Co(2).

Table 2. *Bond lengths* (Å) *and* O—H···O *distances* (Å) *less than* 2·9 Å

Co(1)—O*e*(10)	2·075 (2)	Co(1)—O*e*(14)	2·054 (2)
Co(1)—O*w*(1)	2·177 (2)	Co(2)—O*e*(1)	2·150 (2)
Co(2)—O*e*(2)	1·990 (2)	Co(2)—O*e*(3)	1·993 (2)
Co(2)—O*e*(5)	2·142 (2)	Co(2)—O*e*(11)	2·247 (2)
Co(2)—O*e*(13)	2·193 (2)	Na(1)—O*e*(8)	2·493 (2)
Na(1)—O*w*(3)	2·445 (3)	Na(1)—O*w*(7)	2·445 (2)
Na(1)—O*w*(2^{i})	2·277 (3)	Na(1)—O*w*(3^{ii})	2·385 (2)
Na(1)—O*w*(9^{ii})	2·390 (3)	Na(2)—O*e*(18)	2·356 (3)
Na(2)—O*e*(15^{iii})	2·406 (2)	Na(2)—O*w*(4^{iv})	2·390 (2)
Na(2)—O*w*(5^{iii})	2·495 (3)	Na(2)—O*w*(6^{iv})	2·378 (3)
Na(2)—O*w*(6^{v})	2·416 (2)	Na(3)—O*e*(12)	2·489 (2)
Na(3)—O*w*(2^{vi})	2·416 (2)	Na(3)—O*w*(4^{vi})	2·464 (3)
Na(3)—O*w*(5^{vii})	2·414 (2)	Na(3)—O*w*(7^{viii})	2·339 (3)
Na(3)—O*w*(12^{vii})	2·443 (3)	B(1)—O(2)	1·365 (3)
B(1)—O(8)	1·364 (3)	B(1)—O*e*(9)	1·363 (4)
B(2)—O(2)	1·438 (4)	B(2)—O(6)	1·520 (3)
B(2)—O(14)	1·462 (2)	B(2)—O*e*(11)	1·470 (4)
B(3)—O(1)	1·445 (3)	B(3)—O(4)	1·460 (4)
B(3)—O(6)	1·513 (3)	B(3)—O*e*(1)	1·454 (4)
B(4)—O(5)	1·457 (3)	B(4)—O(6)	1·504 (3)
B(4)—O(8)	1·455 (4)	B(4)—O*e*(3)	1·447 (4)
B(5)—O(11)	1·450 (3)	B(5)—O(15)	1·445 (4)
B(5)—O(20)	1·518 (3)	B(5)—O*e*(13)	1·475 (4)
B(6)—O(3)	1·466 (3)	B(6)—O(12)	1·521 (3)
B(6)—O(13)	1·440 (3)	B(6)—O*e*(14)	1·451 (4)
B(7)—O(9)	1·360 (3)	B(7)—O(17)	1·350 (3)
B(7)—O*e*(17)	1·366 (4)	B(8)—O(7)	1·457 (3)
B(8)—O(17)	1·454 (4)	B(8)—O(20)	1·516 (3)
B(8)—O*e*(5)	1·469 (4)	B(9)—O(12)	1·531 (3)
B(9)—O(19)	1·445 (4)	B(9)—O(21)	1·461 (3)
B(9)—O*e*(6)	1·455 (4)	B(10)—O(1)	1·359 (3)
B(10)—O(14)	1·361 (3)	B(10)—O*e*(8)	1·367 (3)
B(11)—O(15)	1·356 (3)	B(11)—O(16)	1·352 (3)
B(11)—O*e*(4)	1·388 (4)	B(12)—O(4)	1·370 (3)
B(12)—O(5)	1·354 (3)	B(12)—O*e*(16)	1·365 (4)
B(13)—O(10)	1·464 (4)	B(13)—O(12)	1·507 (3)
B(13)—O(18)	1·435 (4)	B(13)—O*e*(10)	1·464 (4)
B(14)—O(3)	1·370 (3)	B(14)—O(10)	1·352 (3)
B(14)—O*e*(7)	1·363 (4)	B(15)—O(13)	1·356 (4)
B(15)—O(21)	1·357 (3)	B(15)—O*e*(15)	1·371 (3)
B(16)—O(9)	1·442 (4)	B(16)—O(16)	1·448 (4)
B(16)—O(20)	1·502 (3)	B(16)—O*e*(2)	1·457 (4)
B(17)—O(7)	1·369 (3)	B(17)—O(11)	1·360 (3)
B(17)—O*e*(12)	1·370 (3)	B(18)—O(18)	1·360 (4)
B(18)—O(19)	1·360 (3)	B(18)—O*e*(18)	1·372 (4)
O*e*(6)—O*e*(9)	2·654 (3)	O*e*(2)—O(9^{ix})	2·691 (3)
O*e*(15)—O(7^{x})	2·702 (3)	O*e*(3)—O(10^{xi})	2·721 (3)
O*w*(11)—O*e*(4^{ix})	2·724 (4)	O*w*(2)—O*e*(17^{ix})	2·728 (4)
O*e*(12)—O(21^{xii})	2·749 (3)	O*w*(10)—O*e*(18^{xiii})	2·775 (4)
O*e*(8)—O(14^{i})	2·806 (3)	O*e*(11)—O*e*(4^{vi})	2·815 (3)
O*e*(13)—O*e*(4^{vi})	2·817 (3)	O*w*(10)—O*e*(7^{xiv})	2·826 (4)
O*w*(8)—O*e*(16^{xiv})	2·833 (4)	O*e*(14)—O(8)	2·842 (3)
O*w*(1)—O*e*(6)	2·846 (4)	O*e*(2)—O*e*(13)	2·851 (3)
O*e*(10)—O(5^{xi})	2·853 (3)	O*e*(16)—O*e*(6^{xv})	2·859 (3)
O*e*(10)—O*w*(1)	2·866 (4)	O*e*(17)—O*e*(11^{ix})	2·869 (3)
O*w*(7)—O*e*(9^{v})	2·875 (4)	O*w*(11)—O(4)	2·878 (4)
O*w*(8)—O*w*(1^{vi})	2·891 (5)	O*w*(6)—O(3^{xiv})	2·895 (4)
O*w*(2)—O(11^{vi})	2·897 (3)		

Equivalent positions are generated as follows: (i) $2-x$. $2-y$, $2-z$; (ii) $3-x$, $2-y$, $2-z$; (iii) $1-x$, $2-y$, $1-z$; (iv) $-1+x$, y, $-1+z$; (v) $1-x$, $2-y$, $2-z$; (vi) $1-x$, $1-y$, $2-z$; (vii) $-1+x$, $1-y$, z; (viii) $-1+x$, $-1+y$, z; (ix) $2-x$, $1-y$, $2-z$; (x) x, $1+y$, z; (xi) $1-x$, $1-y$, $1-z$; (xii) x, $-1+y$, z; (xiii) $1+x$, y, $1+z$; (xiv) x, y, $1+z$; (xv) $1+x, y, z$.

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* Lists of structure factors, bond angles and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38604 (49 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In the Co(1) octahedron the Co(1)—O (O of OH) distances are 2·054 (2) and 2·075 (2) Å, while the Co(1)—O (O of H_2O) distance is 2·177 (2) Å. The O—Co(1)—O angles range from 84·7 (1) to 95·3 (1)°. In the Co(2) coordination octahedron the six symmetrically independent Co(2)—O (O of OH) distances are from 1·990 (2) to 2·247 (2) Å and the O—Co(2)—O angles are 83·2 (1) to 97·9 (1)°.

In the hexaborate groups all terminal O atoms (labelled O*e*) are protonated. The B—O distances for the tetravalent B atoms range from 1·435 (4) to 1·531 (3) Å. The distances longer than 1·5 Å are those to the trigonally coordinated O atoms at the centre of the hexaborate groups. These B_3O arrangements form nearly trigonal pyramids with displacements of the central O atom out of the B_3 planes between 0·178 (4) and 0·246 (4) Å. The O—B—O angles in the tetrahedra range from 104·5 (2) to 113·1 (2)°.

In the trigonal BO_3 units the B—O distances are 1·350 (3) to 1·388 (4) Å and the O—B—O angles are 115·2 (2) to 123·9 (3)°. The bond lengths and angles are similar to those found in previously reported hexaborate groups.

The Co dihexaborate complexes together with water molecules form parallel layers to which the planes of the hexaborate groups are themselves parallel. Adjacent layers are connected by hydrated Na^+ cations, as shown in Fig. 2.

The Na atoms are octahedrally coordinated, partly by OH groups of the hexaborate, partly by water molecules (labelled O*w*), as shown in Fig. 3. The Na—O distances range from 2·277 (3) to 2·495 (3) Å. Additionally, four water molecules are found having only O atoms as nearest neighbours. One of these water molecules, O*w*(13), seemed to be disordered and its population factor could be refined to only 39% with an isotropic temperature factor. The protonated O atoms form O—H···O hydrogen bonds of different strengths as can be deduced from the O—O distances which are listed up to values of 2·9 Å in Table 2. The higher values of the temperature factors observed for the Na and protonated O atoms can be attributed to the relatively large amplitude of the thermal vibrations of these atoms. This is a consequence of the rather weak bonds in the cation–water arrangements between the layers.

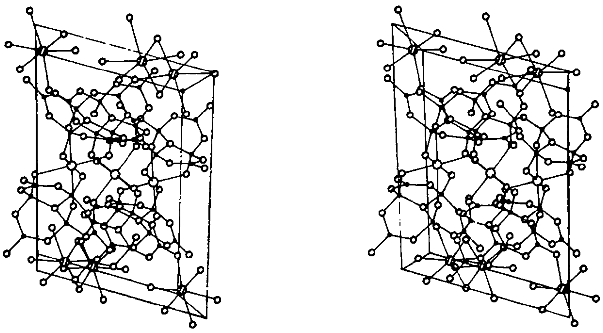

Fig. 2. Stereoscopic view of the structure approximately along **a**. Nonbonded water molecules and all H atoms are omitted for clarity. Shaded circles: Na atoms, open circles with decreasing size: Co, O, B.

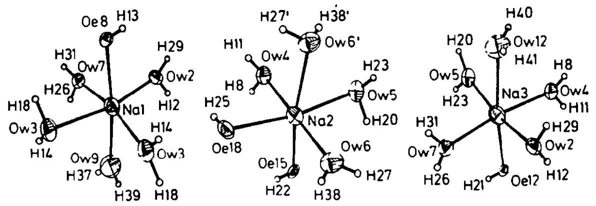

Fig. 3. Coordination octahedra around Na(1), Na(2) and Na(3).

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