Linear Metaborate Anions, BO_2^-, in Apatitic Phosphates

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Summary Crystals, apatite-like in structure, with composition $M_{9+y}Na_x(PO_4)_6B_{x+2y}O_2$ (M = Ca or Sr) have been obtained by the direct reaction of $M_3P_2O_8$ and $Na_2B_4O_7$; these crystals contain O–B–O groupings with the B atom on an inversion centre and with B–O bond lengths of 1·25 ± 0·02 Å.

$M_3(PO_4)_2$(M = Sr or Ca), heated with $Na_2B_4O_7,10H_2O$ up to 1400 °C and slowly cooled yields crystals of $M_{9+y}Na_x(PO_4)_6B_{x+2y}O_2$, with $9+y+x < 10$, $x+2y<1$, $x>0$ and $y>0$, upon extraction with hot water. The compositions determined from crystal-structure refinements and unit-cell parameters for five such preparations are shown in Table 1. The calcium-containing variety are needle-shaped and generally multi-crystals, while those containing Sr occur as truncated octahedra. Sample 1 was subjected to a complete chemical analysis and the Sr:Na ratios of samples 1 and 2 were determined by neutron activation analysis. Neutron magnetic resonance of both ^{23}Na and ^{11}B were detected on an aggregate of crystals in both samples 1 and 3. The i.r. spectra showed 2 absorptions near 2000 cm^{-1} suggestive of isotopic splitting of the B–O stretch in each case. The stronger and weaker peaks are at 1940 ± 10 and 2040 ± 15 cm^{-1} in sample 1 and 1945 ± 5 and 2015 ± 5 cm^{-1} in sample 3 respectively. These lie near the value of 2041 cm^{-1} reported for the BO stretch in B_2O_3 vapour.[1] The analogous values for $^{13}C^{18}O_2$ and $^{13}C^{16}O_2$, which are isoelectronic with the BO_2^- ion, the observed fundamentals, ν_3, are at 2284·5 and 2349·3 cm^{-1} respectively,[2] suggesting that the B–O bond is weaker than the C–O bond. The ratio of the two frequencies in sample 3 is given by equation (1), where $M(x)$ represents the mass

$$[\nu_3(^{11}BO_2)/\nu_3(^{10}BO_2)]^2 = M(^{11}BO_2)/M(^{10}BO_2) \qquad (1)$$

of species x. The right-hand side yields 0·932 ± 0·010 compared with the theoretical value of 0·9307.

The unit-cell parameters were obtained by least-squares methods from single crystals. Complete data sets were taken for crystals from batches 1, 2, 3, and 5 and models based upon a perturbed apatite structure[4] were refined to

TABLE 1. Unit cell parameters for $M_{9+x+y}Na_x(PO_4)_6B_{x+2y}O_2$

No.	Composition	r^a	a/Å	b/Å	c/Å	α/°	β/°	γ/°
1	$Sr_{9\cdot40}Na_{0\cdot21}(PO_4)_6B_{0\cdot99}O_2$[b]	1:6	9·734(4)	9·734	7·279(2)	90	90	120
2	$Sr_{9\cdot21}Na_{0\cdot79}(PO_4)_6B_{0\cdot93}O_2$[c] ..	1:3	9·752(15)	9·752	7·280(3)	90	90	120
3	$Ca_{9\cdot11}Na_{0\cdot89}(PO_4)_6B_{0\cdot96}O_2$	1:7	9·438(8)	9·330(6)	6·930(4)	91·16(3)	89·51(5)	119·44(4)
4	$Ca_9(Ca,Na)(PO_4)_6BO_2$	1:3	9·372(12)	9·380(10)	6·935(10)	89·87(10)	89·64(11)	119·58(9)
5	$Ca_{9\cdot13}Na_{0\cdot87}(PO_4)_6B_{0\cdot92}O_2$	1:10	9·395(14)	9·282(9)	6·928(4)	91·56(6)	88·79(9)	119·27(8)

[a] Mol ratio $M_3P_2O_8:Na_2B_4O_7$, $10H_2O$ in the initial mix. [b] Found (wt. %) SrO, 65·9; Na_2O, 0·46; P_2O_5, 31·1; B_2O_3, 2·44; CaO, 0·12; calc. (wt. %) SrO, 68·9; Na_2O, 0·43; P_2O_5, 30·1; B_2O_3, 2·46. [c] Mol ratio of Sr:Na: 11·3 ± 1:1; calc. 11·6:1.

R values of 0·041, 0·063, 0·062, and 0·056. The X-ray structure analysis shows that these structures are indeed related to that of apatite with the symmetry reduced from $P6_3/m$ to $P\bar{3}$ for the Sr members and to $P\bar{1}$ for the Ca members. This is primarily as a result of substitution of Na in alternate cation sites in the chain of trigonal prisms paralleling the c axis. The phosphate groups, no longer constrained to have a crystallographic mirror plane, rotate so as to increase the number of near-neighbour oxygen atoms for the Ca- or Sr-rich sites and decrease the number for the Na-rich site. The average composition of the cation sites and their co-ordination is indicated in Table 2.

TABLE 2. Sodium ion content and co-ordination numbers for the cation sites

Sample No.	1		2		3	
Site	C.N.	f_{Na^+}	C.N.	f_{Na^+}	C.N.	f_{Na^+}
M(1A)	VI	0·104[a]	VI	0·388	VII	0·143
M(1B)	XI	0	XI	0	VIII	0·034
M(2A)	VII	0	VII	0	VII	0·069
M(2B)					VII	0·102
M(2C)					VII	0·081

[a] This site is void to the extent of 0·175.

Of major interest, however, is the apparently linear O–B–O grouping at a centre of symmetry in each of these crystals. The oxygen atom positions correspond to one pair of mirror-related OH in hydroxyapatite. The rotation of the phosphate groups also enlarges the volume near the site of the O–B–O unit. The B–O bond lengths are 1·252(10), 1·263(18), 1·244(18), and 1·23(1) Å in sample 1, 2, 3, and 5 respectively. In the latter two cases the B atoms have an apparent amplitude of vibration of *ca.* 0·5 Å in the plane perpendicular to the B–O bond. Crystals from batch 4 showed fairly sharp diffuse peaks at various values of $h + 1/2$, $k + 1/2$, l suggestive of a continuous phase transformation to an enlarged cell with doubled a and b axes. However, in the Sr member the vibration amplitude of B is *ca.* 0·1 Å and comparable to that of P. Thus the O–B–O bond angle is precisely 180° in the ground state and without any indication of positional disorder. A linear metaborate ion was reported in solution as a result of an early Raman study[5] and at the time, concern was voiced regarding the absence of such grouping in the solid state. Although O–B–O groupings are known in the vapour phase[1] this is the first confirmed appearance in the solid state.

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