Unusual hydrogen bonding in some hydrated borate structures. By JOAN R. CLARK and C. L. CHRIST, *US*

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The hydrogen-bonding scheme in the structure reported for $KBO_2.\frac{4}{3}H_2O$ suggests the possibility of a new class of water molecule with four cations oriented in a directed way about the lone-pair orbitals. Short hydrogen bonds ($\sim$2·4 Å) in the structures of two other hydrated borates also merit further investigation.

Information about this structure, which was solved by Zviedre, Ozols & Ievins (1974), is given in Table 1. These authors assigned the structural formula $K_3[B_3O_4(OH)_4].2H_2O$, a plausible assignment and possibly the best formula that can be written. Nevertheless, examination of the environments of oxygens O(9) and O(10), designated as water molecules, and of oxygen O(8)', designated as O^{2-} (completing the borate triangle, linked to one boron only), reveals two unusual features.

First, both O(9) and O(10) have six neighbors each (Fig. 1). A maximum of five for water molecules is indicated in a survey of water-molecule environments by Ferraris & Franchini-Angela (1972), *i.e.* two acceptor atoms for the water protons, and three cations (including hydrogen) oriented around the lone-pair orbitals of the water molecule either in a directed way (their class 3) or in an undirected way (their class 4). Our illustration (Fig. 1) and some calculations (Table 2) suggest that if O(9) and O(10) are truly water molecules they represent a new class where (using the Ferraris & Franchini-Angela notation) C1 and C4 lie approximately in the plane of the water molecule (π)

and C2 and C3 are approximately perpendicular to π. Specific designations for the most probable acceptor and C atoms for both O(9) and O(10) are given in Table 2. Obviously, hydrogen positions need to be determined in order to define this situation.

A second unusual feature is that O(8)' accepts four hydrogen bonds (Fig. 1), as well as coordinating K(1)' at 3·22 Å and contacting K(1) at 3·46 Å. In a recent review of hydrated borate structures, Christ & Clark (1977) point out that in such structures the expected sequence for protonation of oxygen atoms, either free or attached to only one boron of a polyanion, is, first, to the free oxygens to form free hydroxyls, second, to tetrahedral oxygens of the polyanion, third, to triangular oxygens of the polyanion, and last, to free hydroxyls to form water molecules. In the structure of $KBO_2.\frac{4}{3}H_2O$ there are not enough protons to complete both steps three and four, so those available are shared in such a way that O(8)', by acquiring about one-quarter proton from each of four donors, effectively accumulates one proton. It is not exactly an hydroxyl ion, just as O(9) and O(10) may not be proper water molecules. Possibly all three atoms are in a hybrid state somewhere between water molecule and
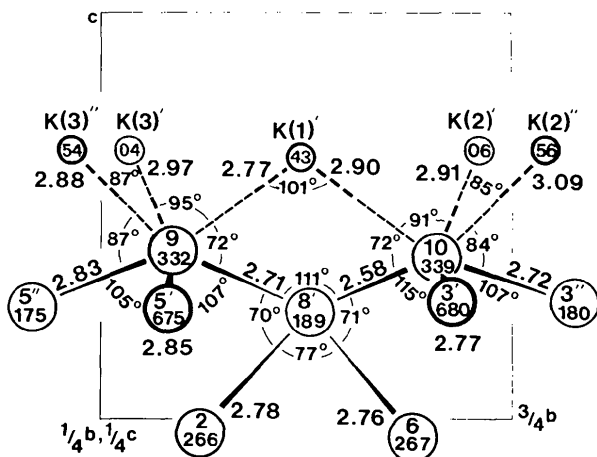

Fig. 1. View along **a** of the O(8)', O(9), and O(10) environments in $KBO_2.\frac{4}{3}H_2O$. Bond distances are in Å (see also Table 2); H-bonds are indicated by solid lines, K–O bonds by dashed lines, except that the 3·22 Å distance between K(1)'–O(8)' is not marked. The small numerals show heights in decimal fractions of *a*. Cell constants and atomic coordinates are in Table 1; distances and angles were calculated as described in the footnote to Table 2. Primes relate atoms to the basic set (Table 1) as follows: (') 2_1 operation, $1-x$, $1-y$, $\frac{1}{2}+z$; ('') *n* glide, $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$. Other O–O–O angles are: O(6)–O(8)'–O(9), 134°; O(2)–O(8)'–O(10), 133°.

Table 1. *Crystallographic data for* $KBO_2.\frac{4}{3}H_2O$ (*Zviedre, Ozols & Ievins,* 1974)

Orthorhombic, $Pna2_1$, $a = 7·81$, $b = 13·71$, $c = 8·80$ Å, $Z = 12[KBO_2.\frac{4}{3}H_2O]$. Conventional $R = 12·4\%$ for 736 *hkl* (individual, isotropic temperature factors). Hydrogen atoms were not located; no errors are given.

Positional parameters ($\times 10^3$)

	x	*y*	*z*		*x*	*y*	*z*
O(1)	57	412	25	$H_2O(9)$	332	339	571
OH(2)	266	373	224	$H_2O(10)$	339	657	559
OH(3)	320	325	−25	K(1)	568	506	252
O(4),△	332	496	33	K(2)	941	292	262
OH(5)	325	667	−39	K(3)	964	716	265
OH(6)	267	625	216	B(1),*T*	242	407	64
O(7),△	63	586	17	B(2),*T*	246	590	58
O(8),△	−189	497	−44	B(3),△	−22	499	−7

The structure contains isolated borate polyanions, each composed of two tetrahedra (*T*) joined at O(1) and a triangle (△) sharing corners O(4) and O(7) to form a trimer ring. There are three crystallographically distinct potassium polyhedra sharing edges and corners to form a network. K(1) and K(2) are best described as nine-coordinated with average K–O, respectively, 2·92 and 2·89 Å; each contacts one more oxygen at about 3·4 Å. K(3) is eight-coordinated, average K–O 2·86 Å, and contacts two additional oxygens, each at a distance of about 3·3 Å.

Table 2. *Water molecule environment in* $KBO_2.\frac{4}{3}H_2O$
(Zviedre, Ozols & Ievins, 1974)

Bond distances (Å)

Atom role		$H_2O(9)$		$H_2O(10)$	
Proton	O(8)'	2·71	O(8)'	2·58
acceptors	OH(5)'	2·85	OH(3)'	2·77
C1	K(3)'	2·97	K(2)'	2·91
C4	K(3)''	2·88	K(2)''	3·09
C2	OH(5)''	2·83	OH(3)''	2·72
C3	K(1)'	2·77	K(1)'	2·90

Bond angles (°)

$H_2O(9)$

O(8)', OH(5)'	107	K(3)', K(3)''	87
O(8)', K(3)'	96	OH(5)'', K(1)'	164
OH(5)', K(3)'	157	K(3)', OH(5)''	69
O(8)', K(3)''	159	K(3)', K(1)'	95
OH(5)', K(3)''	70	K(3)'', OH(5)''	87
O(8)', OH(5)''	113	K(3)'', K(1)'	87
OH(5)', OH(5)''	105	Planes	
O(8)', K(1)'	72	π-C1, C4	21
OH(5)', K(1)'	87	π-C2, C3	76
		C1, C4-C2, C3	94

$H_2O(10)$

O(8)', OH(3)'	115	K(2)', K(2)''	85
O(8)', K(2)'	94	OH(3)'', K(1)'	158
OH(3)', K(2)'	150	K(2)', OH(3)''	68
O(8)', K(2)''	161	K(2)', K(1)'	91
OH(3)', K(2)''	64	K(2)'', OH(3)''	84
O(8)', OH(3)''	113	K(2)'', K(1)'	89
OH(3)', OH(3)''	107	Planes	
O(8)', K(1)'	72	π-C1, C4	21
OH(3)', K(1)'	89	π-C2, C3	76
		C1, C4-C2, C3	89

Bond distances and angles were recalculated (*BONDLA*, Stewart, Kruger, Ammon, Dickinson & Hall, 1972) from the coordinates given by Zviedre *et al.*; the values are not always the same as those reported by them [*e.g.* they give O(8)'—O(10) as 2·64 Å]. Our assignment of proton acceptors and C atoms is considered the most probable; notation follows that of Ferraris & Franchini-Angela (1972). The π plane was defined as that of the water oxygen atom and its two proton acceptors. For usage of primes, see Fig. 1.

hydroxyl ion. Further experimental data are needed to determine the precise character of this group of oxygen atoms.

Kaliborite and preobrazhenskite

Two other borate structures have been reported with another kind of unusual hydrogen bond. In both cases the proton appears to be located between two ring oxygen atoms of tetrahedra in adjacent borate rings, and the O···O distance is about 2·4 Å. Such oxygen atoms are charge-deficient by approximately 0·5 v.u., so their bonding to a proton is reasonable. For the structure of kaliborite, $HKMg_2[B_5O_7-(OH)_3.OB(OH)_2]_2.4H_2O$ (Corazza & Sabelli, 1966; formula from Christ & Clark, 1977), most hydrogen atoms were located from a three-dimensional difference synthesis. However, the hydrogen H(10) associated with the 2·412 Å bond (and lying on a twofold axis) could not be found in this way. Possibly H(10) is a resonating proton and hence the residual electron density is smeared out. The structure of preobrazhenskite, $HMg_3\{B_9O_{12}(OH)_4.[O_2B(OH)_2]_2\}$ (Rumanova, Razmanova & Belov, 1972; formula from Christ & Clark, 1977), has a similar bond. No hydrogen atoms were located in that study. Again, experimental determinations of hydrogen positions in both these structures would provide further useful information about this kind of hydrogen bond.

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Book Review

Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.

Atlas of steroid structure. Vol. 1. Edited by W. L. DUAX and DORITA A. NORTON. Pp. xiii + 572. New York, Washington and London: IFI/Plenum, 1975. Price $59.40, £31.19.

This book, modestly termed an 'Atlas', is a superbly organized reference work on the detailed structures of those steroids that have been studied by X-ray crystallography. Written by crystallographers, it is intended primarily for a *non-crystallographic* readership: workers in organic chemistry, biochemistry, biology and medicine.

Dr Duax points out in his preface that the average crystallographic paper presents results in terms of atomic coordinates, from which many other molecular parameters