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Structure of Sodium Tetrahydroxyborate

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Abstract. $NaB(OH)_4$, $M_r = 101.83$, monoclinic, $P2_1/a$, $a = 5.886$ (3), $b = 10.566$ (6), $c = 6.146$ (3) Å, $\beta = 111.60$ (4)°, $V = 355.4$ (3) Å^3, $Z = 4$, $D_x = 1.903$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.27$ mm^{-1}, $F(000) = 208$, room temperature, $R = 0.030$ for 882 observed reflections with $I > 3\sigma(I)$. The structure consists of six-coordinate Na^+ in cavities in a hydrogen-bonded framework of BO_4 tetrahedra. Only three of the four H atoms of the anions are involved in O—H···O bonding.

Introduction. In the course of a systematic study of the system $CaO–B_2O_3–Na_2O–H_2O$, the title compound was prepared in a form suitable for X-ray structure analysis, which was carried out in order to characterize the material more fully. Chemical analysis suggested the presence of a small amount of Ca but recourse to the Crystal Identification File (CDIF) component of the Chemical Databank Service suggested that the material was very similar to the compound $NaB(OH)_4$, as variously formulated by Menzel & Schulz (1943) and Krc (1951), but for which no structural data are presently available. The structure analysis described here is on the basis of the ideal formula $NaB(OH)_4$.

Experimental. The compound was prepared by mixing analytical reagent grades of NaOH, H_3BO_3 and $Ca(OH)_2$ (14.5, 9.0 and 10.7 wt%, respectively; balance water) and letting the resultant mixture, sealed to protect it from CO_2 uptake, stand for 180 d at 293 K. The resulting product was drained, washed with water and gently dried in warm air. X-ray diffraction data were obtained from a suitable crystal (*ca* 0.2 × 0.6 × 0.6 mm) on a Nicolet *P*3 four-circle diffractometer with Mo $K\alpha$ radiation and graphite monochromator.

Cell dimensions were determined using 14 reflections at 17–25° in 2θ. The intensities of 1180 reflections with $2\theta \leq 60°$, h 0–8, k 0–14 and l $\bar{8}$–8, were measured from ω scans with a fixed width of 0.6°, scan rates in the range 1.0–29.3° min^{-1} related to pre-scan intensity, and stationary crystal–stationary counter background counts taken at ± 1.0° in ω from the calculated position of the Bragg peak. No correction for absorption or extinction was applied. Two reference reflections, monitored periodically, showed no significant variation in intensity. The data were reduced to structure amplitudes in the usual way to yield a total of 1039 unique reflections ($R_{\text{int}} = 0.023$). The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990) to yield starting positions for all of the atoms. On refinement with *SHELX*76 (Sheldrick, 1976), H(4) was found to have been wrongly positioned and was relocated by means of a difference map. Full-matrix least-squares refinement was based on F for the parameters of all atoms, anisotropic displacement parameters were used except for B and H atoms (66 parameters). Refinement converged at $R = 0.030$ and $wR = 0.037$ $\{w = 1.0/[\sigma^2(F_o) + 0.00356(F_o)^2]\}$ for 882 reflections with $I > 3\sigma(I)$. Maximum shift/e.s.d. = 0.06 and $(\Delta\rho)_{\min} = -0.45$, $(\Delta\rho)_{\max} = 0.23$ e Å^{-3}. Atomic parameters are given in Table 1.† Calculations were carried out on a SUN SPARC 480 system of the Computing Centre of the University of Aberdeen. The scattering curve for neutral Na was taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). For B, H and O atoms the values installed in *SHELX*76 were used. *STRUPLO*82 (Fischer, 1982) was used to prepare Figs. 1 and 2.

Discussion. Na is in a distorted six-coordinated environment with Na—O distances in the range 2.308 (1)–2.615 (1) Å and O—Na—O angles 57.46 (3)–166.86 (4)° (Table 2). Each Na is in contact with four distinct $B(OH)_4$ anions (Fig. 2). The anion is relatively regular in shape, with B—O and O—H in the ranges 1.463 (2)–1.483 (1) and 0.76 (2)–0.85 (3) Å, respectively, and O—B—O and B—O—H in the ranges 106.94 (9)–112.34 (9) and 104 (2)–114 (2)° (Table 2). The $B(OH)_4$ units are interconnected in three dimensions by O—H···O interactions involving H(1), H(2) and H(3) but not H(4)

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† Lists of anisotropic thermal vibration parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55858 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1036]

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Table 1. *Coordinates* ($\times 10^5$ *for* Na *and* O, $\times 10^4$ *for* B *and* H) *and isotropic or equivalent isotropic thermal vibration parameters* ($\text{Å}^2 \times 10^4$ *for* Na, O *and* B, $\times 10^3$ for H)

$U_{\rm eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ except for B and H where $U_{\rm iso}$ is given.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Na	24896 (8)	48030 (5)	75745 (8)	216 (2)
O(1)	18791 (15)	54208 (8)	32753 (15)	187 (2)
O(2)	38478 (15)	40168 (8)	14256 (15)	189 (2)
O(3)	− 1942 (14)	35407 (8)	14764 (16)	198 (2)
O(4)	33257 (16)	34264 (8)	50498 (14)	218 (2)
B	2248 (2)	4084 (1)	2766 (2)	157 (3)
H(1)	3141 (34)	5764 (20)	3586 (34)	35 (5)
H(2)	4215 (40)	3236 (24)	1467 (35)	41 (5)
H(3)	− 598 (40)	3722 (17)	118 (38)	39 (5)
H(4)	3348 (42)	2715 (19)	4958 (42)	46 (6)

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and hydrogen-bond geometry* (Å, °)

Na coordination			
Na—O(1)	2.615 (1)	Na—O(4)	2.308 (1)
Na—O($2^{\rm i}$)	2.353 (1)	Na—O($1^{\rm ii}$)	2.440 (1)
Na—O($2^{\rm iii}$)	2.367 (1)	Na—O($3^{\rm ii}$)	2.410 (1)
O(1)—Na—O(4)	57.46 (3)	O(4)—Na—O($2^{\rm i}$)	112.09 (4)
—O($2^{\rm i}$)	166.86 (4)	—O($1^{\rm ii}$)	105.29 (4)
—O($1^{\rm ii}$)	93.78 (3)	—O($2^{\rm iii}$)	96.16 (4)
—O($2^{\rm iii}$)	84.50 (3)	—O($3^{\rm ii}$)	153.83 (4)
—O($3^{\rm ii}$)	100.52 (3)	O(2′)—Na—O($1^{\rm ii}$)	97.02 (4)
O($1^{\rm ii}$)—Na—O($2^{\rm iii}$)	153.37 (4)	—O($2^{\rm iii}$)	89.15 (4)
—O($3^{\rm ii}$)	58.78 (3)	—O($3^{\rm ii}$)	91.49 (4)
O($2^{\rm iii}$)—Na—O($3^{\rm ii}$)	95.32 (4)		
$B(OH)_4$ anion			
B—O(1)	1.481 (1)	B—O(2)	1.463 (2)
B—O(3)	1.478 (2)	B—O(4)	1.483 (1)
O(1)—H(1)	0.79 (2)	O(2)—H(2)	0.85 (3)
O(3)—H(3)	0.80 (2)	O(4)—H(4)	0.76 (2)
O(1)—B—O(2)	109.87 (9)	O(2)—B—O(3)	112.34 (9)
—O(3)	107.12 (9)	—O(4)	111.75 (9)
—O(4)	106.94 (9)	O(3)—B—O(4)	108.58 (9)
B—O(1)—H(1)	107 (2)	B—O(2)—H(2)	104 (2)
B—O(3)—H(3)	109 (2)	B—O(4)—H(4)	114 (2)
Hydrogen bonds			
O—H···O′	H···O′	O···O′	O—H···O′
O(1)—H(1)···O($4^{\rm iii}$)	2.11 (2)	2.893 (1)	171 (2)
O(2)—H(2)···O($3^{\rm iv}$)	1.91 (3)	2.758 (1)	176 (2)
O(3)—H(3)···O($1^{\rm v}$)	2.14 (2)	2.930 (1)	168 (2)

Symmetry code: (i) $x, y, 1+z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (v) $-x, 1-y, -z$.

(Fig. 1, Table 2). The geometry, particularly the H···O and O···O distances associated with these interactions, suggests that H(2) certainly participates in hydrogen bonding in the classical sense [see, for example, Pauling (1960)]; (H1) and H(3) exhibit progressively weaker interactions.

Wet chemical analysis for Ca, Na and B and thermal analysis for water indicated the formula $CaO{:}24Na_2O{:}25B_2O_3{:}85H_2O$ for the bulk material from which the crystal was selected. There is no compelling evidence in the results of the structure analysis for any form of replacement of Na by Ca but the extent of such replacement required to accommodate the chemical analytical formula would in any case by very small (approximately 2% Ca in the total Ca + Na atom count) and therefore probably not detectable by X-ray structure analysis. Ignoring the possible presence of Ca, the water content (determined by thermogravimetric analysis) is about 15% too low compared with the ideal formula $NaB(OH)_4$. It is concluded that the compound is essentially $NaB(OH)_4$. Reasons for the

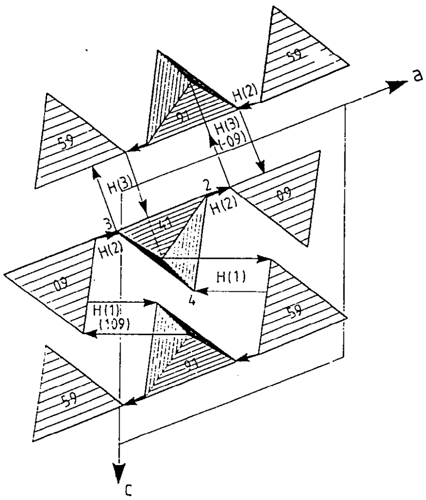

Fig. 1. The hydrogen-bonded anionic framework of $NaB(OH)_4$. O atoms are centred on the vertices of the tetrahedra. Na, B and H atoms have been omitted for clarity. Atoms O(2)–O(4) are designated by number. The two digit numbers are the heights of the tetrahedra ($10^2 \times y$ of the central B atom). The O—H···O′ interactions are indicated by arrows directed towards O′ and labelled in terms of the H atoms involved. The values in parentheses associated with one of each of the H(1) and H(3) interactions are the heights of the tetrahedra outside the cell, which is outlined, actually participating in the interaction in these cases.

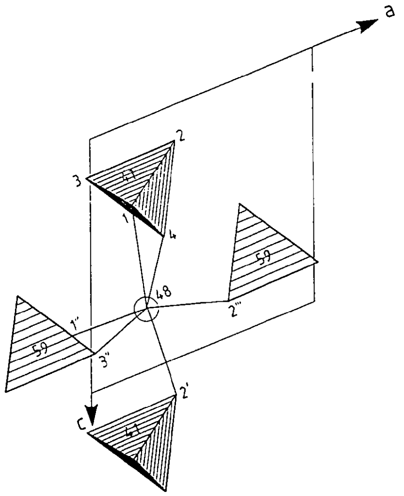

Fig. 2. The Na coordination in $NaB(OH)_4$; the same view of the structure as in Fig. 1 but only those BO_4 tetrahedra in contact with the single representative Na are shown. The numbering scheme for O atoms is as in Table 2.

apparently low water content are not known, but it is possible that powders lose some weakly bonded water on exposure to the laboratory atmosphere, although the single crystals did not exhibit loss during the course of the structure determination.

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Structure of *catena*-Poly[tris(pyridine)copper-μ-{*N*-(2-hydroxyiminopropionyl)-L-methioninato(1−)-*O''*,*N'*:*O*}] Nitrate Ethanol Solvate

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Abstract. $[Cu(C_8H_{13}N_2O_4S)(C_5H_5N)_3]NO_3.C_2H_6O$, $M_r = 642.19$, tetragonal, $P4_3$, $a = 9.264\,(3)$, $c = 35.503\,(12)$ Å, $V = 3047$ Å^3, $D_x = 1.398$ g cm^{-3}, $Z = 4$, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 20.8$ cm^{-1}, $F(000) = 1340$, $T = 293$ K, final $R = 0.043$ for 2256 independent reflections. The crystal is built up from complex cations linked into polymeric chains, the outer sphere being occupied by nitrate anions and ethanol solvate molecules. The coordination around Cu is a distorted square bipyramid generated by three pyridine molecules and the oxime-containing anion acting simultaneously in a chelating bidentate mode (*via* the amide O atom and the hydroxyimino N atom) and in a bridging mode (*via* the carboxyl O atom).

Introduction. In continuation of our studies on pyruvoyl amino acid oximes and their metal complexes (Skopenko, Lampeka & Fritsky, 1990), the crystal structure determination of the title complex was carried out. Earlier we reported the preparation and structural study of three ligands of this class: pyruvoylglycine oxime (Lampeka, Dvorkin, Simonov, Fritsky & Skopenko, 1989), pyruvoyl-L-alanine oxime (Dvorkin, Fritsky, Simonov, Lampeka, Mazus & Malinowsky, 1990) and pyruvoyl-L-methionine oxime (H_3Mt) (Dvorkin, Simonov, Skopenko, Fritsky & Lampeka, 1990). It was shown that the mentioned ligands can enter the inner sphere of the metal ions in different ionic forms. A recently performed X-ray investigation of trisodium bis[*N*-(2-hydroxyiminopropionyl)glycinato]cobaltate(III) (Fritsky, Lampeka, Skopenko, Simonov, Dvorkin & Malinowsky, 1993) identified an *N*,*N*,*O*-tridentate chelating mode for the triply charged acido ligand in the complex anion. The present paper reports the structure determination of the mixed ligand complex in which the other possible coordination mode of pyruvoyl amino acid oxime is observed.

Experimental. The complex was synthesized according to the following scheme:

$$Cu(NO_3)_2.3H_2O + H_3Mt + 4py = [Cu(H_2Mt)py_3]NO_3 + (pyH)NO_3 + 3H_2O.$$

A mixture of $Cu(NO_3)_2.3H_2O$ (0.302 g, 1.25 μmol) and pyridine (0.8 ml) in 10 ml of ethanol was added to H_3Mt (0.293 g, 1.25 μmol) dissolved in 5 ml of

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