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Refinement of the X-ray Crystal Structure of the Industrial Bleaching Agent Disodium Tetrahydroxo-di-μ-peroxo-diborate Hexahydrate, $Na_2[B_2(O_2)_2(OH)_4].6H_2O$

BY MARIA A. A. F. DE C. T. CARRONDO AND ANDRZEJ C. SKAPSKI

Chemical Crystallography Laboratory, Imperial College, London SW7 2AY, England

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Disodium tetrahydroxo-di-μ-peroxo-diborate hexahydrate is triclinic with $a = 6{\cdot}837\,(1)$, $b = 7{\cdot}370\,(1)$, $c = 7{\cdot}283\,(1)$ Å, $\alpha = 98{\cdot}77\,(1)$, $\beta = 101{\cdot}85\,(1)$, $\gamma = 120{\cdot}33\,(1)°$, space group $P\bar{1}$ and $Z = 1$. Least-squares refinement of 1116 independent reflections measured on a diffractometer reached a final R value of 0·027. The structure contains Na^+ ions, water molecules, and the centrosymmetric cyclic $[B_2(O_2)_2(OH)_4]^{2-}$ anion. In the anion the B atoms are joined by two peroxo bridges, and their tetrahedral coordination is completed by terminal OH groups. Mean B—OH and B—O distances are 1·442 and 1·495 Å respectively. The O—O distance is 1·480 Å, and the acute peroxo dihedral angle of 60·0° is a consequence of the chair conformation adopted by the six-membered ring. Water molecules and OH groups surround the Na^+ ions to give them an octahedral coordination.

Introduction

The title compound and 'sodium percarbonate' ($Na_2CO_3.1\frac{1}{2}H_2O_2$) are the two most important industrial bleaching agents used in solid detergents. The peroxoborate had been variously described as $NaBO_3.4H_2O$ or $NaBO_2.H_2O_2.3H_2O$, until its nature was determined crystallographically by Hansson (1961), who showed it to contain the cyclic $[B_2(O_2)_2(OH)_4]^{2-}$ anion. His report, however, was based on unrefined data and no R was quoted. The unique structure of the anion and our interest in these compounds (Carrondo, Griffith, Jones & Skapski, 1977) have prompted us to carry out an accurate determination based on diffractometer data. Our work has essentially confirmed the original structure, but we find one water molecule to have been misplaced by 0·7 Å.

Experimental

Crystals of $Na_2[B_2(O_2)_2(OH)_4].6H_2O$ were obtained as colourless irregular prisms by the method of Hansson (1961). (Composition: found: H 5·2, O_2^{2-} 20·9%; $B_2H_{16}Na_2O_{14}$ requires: H 5·2, O_2^{2-} 20·8%.)

Photographs confirmed that the crystals were triclinic, and the space group was shown to be $P\bar{1}$ by the successful refinement of the structure. Measurement of 27 high-angle α_1 reflections on a diffractometer, followed by a least-squares calculation, gave the following morphologically convenient cell: $a = 6{\cdot}837\,(1)$, $b = 7{\cdot}084\,(1)$, $c = 8{\cdot}907\,(1)$ Å, $\alpha = 87{\cdot}38\,(1)$, $\beta = 126{\cdot}85\,(1)$, $\gamma = 116{\cdot}10\,(1)°$.

Intensities were measured on a Siemens off-line automatic diffractometer. A crystal 0·30 × 0·15 × 0·10 mm was mounted about **c**, and a layer of picture varnish was applied to prevent decomposition under X-rays. Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) at a take-off angle of 3·0°, a Ni filter, and a Na(Tl)I scintillation counter were used. The θ–2θ technique was employed with a five-value measuring procedure (Allen, Rogers & Troughton, 1971). 1122 independent reflections were measured (to $\theta = 70°$), of which 29 were judged to be unobserved with $I < 2{\cdot}58\sigma(I)$. The $3\bar{3}0$ reflection was monitored as a reference every 50 reflections, and its net count did not alter noticeably over the period of data collection (*ca* 2 d). Data were scaled by the use of the reference reflection, and Lorentz and polarization corrections were applied. No absorption correction was applied, because of the low value of μ and the difficulty of indexing with any accuracy the faces of the transparent crystal when covered in varnish.

A Delauney reduction was now carried out on the unit cell to give $a = 6{\cdot}837\,(1)$, $b = 7{\cdot}370\,(1)$, $c = 7{\cdot}283\,(1)$ Å, $\alpha = 98{\cdot}77\,(1)$, $\beta = 101{\cdot}85\,(1)$, $\gamma = 120{\cdot}33\,(1)^\circ$, $U = 295{\cdot}4$ Å^3 (at 10°C), and after applying the corresponding transformation ($h_r = -h$, $k_r = k + h$, $l_r = h + l$) to the reflection indices the reduced cell was used in all subsequent calculations. Other crystal data are: space group $P\bar{1}$, $D_c = 1{\cdot}73$ g cm^{-3} for $Z = 1$ and a molecular formula $B_2H_{16}Na_2O_{14}$, $M_r = 307{\cdot}7$, $F(000) = 158$, $\mu(\text{Cu } K\alpha) = 20{\cdot}7$ cm^{-1}.

Refinement of the structure

Cell dimensions reported by Hansson (1961), $a = 7{\cdot}34$, $b = 6{\cdot}81$, $c = 8{\cdot}15$ Å, $\alpha = 101$, $\beta = 110$, $\gamma = 120^\circ$, after Delauney reduction, gave a similar cell to that obtained in the present work. After applying the appropriate transformation to the reported coordinates for Na, O and B atoms, with these as starting parameters, isotropic refinement gave $R = 0{\cdot}077$. All the atoms refined well, except O(2) and O(4) which moved 0·70 and 0·24 Å respectively, and O(2) needed two rounds of refinement to stabilize in its new position.

Anisotropic refinement reduced R to 0·051. All H atoms were now located from a difference synthesis, and when included with isotropic temperature factors led to a further drop in R to 0·029. Introduction of the anomalous-dispersion correction for Na and O, and of a weighting scheme gave $R = 0{\cdot}028$. Finally the six strongest reflections, thought to be affected by extinction, were removed from refinement to give $R = 0{\cdot}027$. The final difference synthesis was featureless, with all remaining peaks $<0{\cdot}2$ e Å^{-3}.

The June 1974 update of the XRAY 72 system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the refinement. Calculations were performed on the University of London CDC 7600 computer; structure illustrations were drawn with the aid of the Imperial College CDC6500 computer. In the final stages of refinement the weighting scheme suggested by Hughes (1941) was used, where $w = 1$ for $F < F^*$, $w^{1/2} = F^*/F$ for $F \geq F^*$, with $F^* = 10$ as the optimum value. Scattering factors of Doyle & Turner (1968) and for H of Stewart, Davidson & Simpson (1965) were used, while the real and the imaginary anomalous-dispersion corrections for Na and O were from Cromer & Liberman (1970).

Table 1 lists the atomic coordinates as well as the transformed coordinates of Hansson (1961).†

Description of the structure and discussion

This study has confirmed that the structure of the title compound is made up of centrosymmetric $[B_2(O_2)_2(OH)_4]^{2-}$ anions, Na^+ cations and water molecules, as reported by Hansson (1961). The water molecules, OH groups, and peroxo groups form a network of hydrogen

Table 1. *Atomic coordinates with e.s.d.'s in parentheses*

For comparison, the coordinates listed on the lower line in italics have been derived from those of Hansson (1961), x_H, y_H, z_H, by use of the transformations: $x = -y_H + z_H$, $y = -x_H + z_H$, $z = z_H$.

	x	y	z
Na(1)	0	0	0
	0	*0*	*0*
Na(2)	½	0	0
	½	*0*	*0*
O(1)	−0·1966 (2)	0·0087 (2)	0·2547 (2)
	−0·200	*0·005*	*0·245*
O(2)	0·2699 (2)	−0·0465 (2)	0·2088 (2)
	0·315	*0·060*	*0·265*
O(3)	0·6972 (2)	0·3899 (2)	0·1076 (2)
	0·725	*0·400*	*0·105*
O(4)	0·2777 (2)	0·3854 (2)	0·1795 (1)
	0·235	*0·370*	*0·170*
O(5)	0·1767 (2)	0·6019 (2)	0·3694 (2)
	0·175	*0·600*	*0·365*
O(6)	0·5766 (2)	0·7073 (1)	0·4645 (1)
	0·575	*0·705*	*0·470*
O(7)	0·2605 (2)	0·3698 (2)	0·5035 (1)
	0·270	*0·380*	*0·520*
B(1)	0·3224 (3)	0·5109 (2)	0·3712 (2)
	0·315	*0·505*	*0·385*
H(11)*	−0·258 (4)	−0·082 (4)	0·309 (4)
H(12)	−0·071 (5)	0·110 (5)	0·333 (4)
H(21)	0·240 (3)	−0·151 (3)	0·247 (3)
H(22)	0·324 (4)	0·057 (4)	0·303 (4)
H(31)	0·633 (5)	0·428 (4)	0·163 (4)
H(32)	0·840 (5)	0·452 (4)	0·181 (4)
H(4)	0·287 (4)	0·451 (3)	0·112 (3)
H(5)	0·197 (4)	0·665 (3)	0·472 (3)

* The first digit of the H atoms is the same as that of the parent O atom.

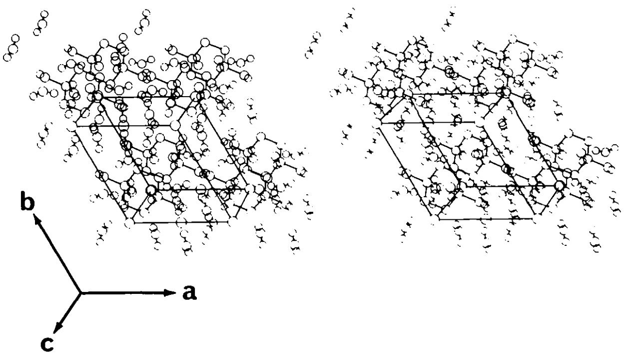

Fig. 1. A stereoscopic view showing the packing of the ions and water molecules in the unit cell. H atoms are also included in the diagram.

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33866 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds, and the three-dimensional packing of all the structure components can be seen in Fig. 1. The arrangement of the atoms in the cyclic anion and the thermal-vibration ellipsoids (Johnson, 1965) are shown in Fig. 2. This arrangement consists of two centrosymmetrically related B atoms, each tetrahedrally coordinated to two OH groups and to two peroxide groups which act as bridges between the B atoms. The resulting six-membered ring adopts a chair conformation.

Table 2 lists the more important interatomic distances and bond angles. The means of the two B—O and two B—OH distances are significantly different, 1·495 and 1·442 Å respectively. There are no comparable structurally characterized peroxoborate compounds. However, this relation (mean B—O > mean B—OH) is in contrast to the data available for similar compounds. For instance, in $Na_3[B_3O_5(OH)_2]$ one of the B atoms has a tetrahedral coordination and is bonded to two terminal OH groups and to two bridging O atoms which are also linked to other B atoms. For this compound, B—O and B—OH distances have mean values of 1·465 and 1·488 Å respectively (Corazza, Menchetti & Sabelli, 1975). The same kind of relation is also found in the structure of γ-HBO_2, which is formed from a three-dimensional network of $BO_2(OH)_2$ tetrahedra. Mean values for B—O and B—OH distances are 1·451 and 1·499 Å respectively (Zachariasen, 1963*a*).

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

(*a*) $[B_2(O_2)_2(OH)_4]^{2-}$ anion			
B(1)—O(4)	1·430 (2)	O(4)—B(1)—O(5)	112·8 (1)
B(1)—O(5)	1·454 (3)	O(4)—B(1)—O(6)	113·0 (1)
Mean B—OH	1·442	O(4)—B(1)—O(7)	110·9 (1)
B(1)—O(6)	1·500 (2)	O(5)—B(1)—O(6)	104·7 (1)
B(1)—O(7)	1·489 (2)	O(5)—B(1)—O(7)	105·3 (1)
Mean B—O	1·495	O(6)—B(1)—O(7)	109·7 (1)
O(6)—O(7^{I})	1·480 (2)	B(1)—O(6)—O(7^{I})	109·1 (1)
		B(1)—O(7)—O(6^{I})	109·3 (1)
(*b*) Sodium cations			
Na(1)—O(1)	2·515 (2)	Na(2)—O(1^{II})	2·449 (2)
Na(1)—O(2)	2·341 (1)	Na(2)—O(2)	2·345 (1)
Na(1)—O(4)	2·405 (1)	Na(2)—O(3)	2·378 (1)
	cis O—Na(1)—O range 83·0–97·0		
	cis O—Na(2)—O range 87·2–92·8		
(*c*) Hydrogen bonds			
O(1)···O(6^{III})	2·864	O(1)—H(11)—O(6^{III})	174
O(1)···O(7)	2·817	O(1)—H(12)—O(7)	173
O(2)···O(5^{IV})	2·838	O(2)—H(21)—O(5^{IV})	175
O(2)···O(6^{I})	2·743	O(2)—H(22)—O(6^{I})	174
O(3)···O(5^{II})	2·859	O(3)—H(32)—O(5^{II})	177
O(4)···O(3^{V})	2·839	O(4)—H(4)—O(3^{V})	174

Symmetry code
(I) $1-x, 1-y, 1-z$
(II) $1+x, y, z$
(III) $x-1, y-1, z$
(IV) $x, y-1, z$
(V) $1-x, 1-y, -z$

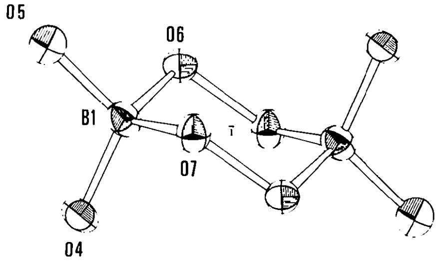

Fig. 2. Structure of the cyclic $[B_2(O_2)_2(OH)_4]^{2-}$ anion. Thermal-vibration ellipsoids are scaled to enclose 50% probability.

The bond angles centred on the B atom range between 104·7 and 113·0°, showing a slight distortion from ideal tetrahedral geometry. On the other hand, both B—O(6)—O(7^{I}) and B—O(7)—O(6^{I}) angles are very close to those expected for sp^3 hybridization in each O atom. The accepted O—O single-bond distance is 1·48 Å (Pedersen, 1972), and the O(6)—O(7^{I}) distance (1·480 Å) in the peroxo bridge of the title compound is identical to that value. The dihedral angle of the bridge is 60·0°, and is much more acute than those found in other compounds containing O—O linkages (Table 11.4 in Wells, 1975). Its acuteness is a consequence of the chair conformation of the ring system and of the tetrahedral angles at the B atoms.

Comparing the results obtained in this work with those published by Hansson (1961), one can see that the present ranges of bond lengths and angles are less wide and are more consistent with the geometry of the anion. Thus B—O distances are in the range 1·43–1·50 Å as against 1·42–1·54 Å, and O—B—O angles 105–113° as against 101–116°. In particular, the movement of O(4) now places the two B—O(hydroxo) distances into a separate category compared with the two B—O-(peroxo) distances. Within each category the longer bond length is to the O atom involved in two hydrogen bonds, as against one for the shorter length.

The placement of O(4) and especially the water O(2) in their correct positions has also improved the description of the octahedral coordinations about the two crystallographically independent Na^+ ions, where previously for Na(1) the coordination was rather distorted with *cis* O—Na—O angles in the range 72–108°. The cations form linear chains along **a** with the octahedra sharing opposite edges. As the Na^+ ions lie on centres of symmetry, each has three independent Na—O distances: in the ranges 2·341–2·515 Å for Na(1) and 2·345–2·449 Å for Na(2).

The three-dimensional network of hydrogen bonds is composed of six independent O···O distances in a fairly narrow range of 2·74–2·86 Å, and with all O—H—O angles close to 180°. Although the length of hydrogen bonds can vary considerably from one structure to another, these distances are typical of those observed in other inorganic borates (Zachariasen, 1963*b*). In the other important bleaching agent used in solid detergents, $Na_2CO_3.1\frac{1}{2}H_2O_2$, these bonds are slightly stronger, as suggested by the shorter O···O distances in the range 2·54–2·65 Å (Carrondo, Griffith, Jones & Skapski, 1977).

The bleaching action of the title compound must clearly be different from that of 'sodium percarbonate', which can be regarded as a portable form of hydrogen peroxide, since in the former covalent B–O bonds have to be broken in order to release the peroxide.

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Barium Tin Chromium Oxide, A New Hollandite Phase

By M. C. Cadée and G. C. Verschoor

Gorlaeus Laboratories, University of Leiden, PO Box 9502, 2300 *RA Leiden, The Netherlands*

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The crystal structure and composition of barium tin chromium oxide were determined by single-crystal X-ray techniques. The composition was determined as $Ba_xSn_{4-2x}Cr_{2x}O_8$, with $x = 0{\cdot}70$, and checked by preparing a pure powder sample of this composition. The compound has a hollandite structure and crystallizes in the space group $I2/m$ with $a = 10{\cdot}532$ (2), $b = 3{\cdot}108$ (1), $c = 10{\cdot}012$ (2) Å, $\beta = 91{\cdot}56$ (1)°, and $Z = 2$. Transformed to space group $C2/m$ the unit-cell parameters are $a = 14{\cdot}728$, $b = 3{\cdot}108$, $c = 10{\cdot}012$ Å, $\beta = 134{\cdot}37$°, and $Z = 2$. Data were collected with a three-circle diffractometer using Mo $K\alpha$ radiation. Full-matrix least-squares refinement of 991 observed symmetry-independent reflexions gave a conventional R index of 0·037 ($R_w = 0{\cdot}049$). Sn and Cr are octahedrally coordinated, Ba has tenfold coordination. Several isomorphs have been prepared. A number of unsuccessful attempts to prepare isomorphs are also reported.

Introduction

In an investigation of some Ba–M^{4+}–M^{3+}–O systems, unknown phases with identical X-ray powder diffraction patterns were found. Because of the unknown composition we could not prepare a pure sample to index the diffraction pattern. Fortunately, needle-shaped crystals suitable for single-crystal diffraction formed in the Ba–Sn–Cr–O system.

Experimental

All starting materials were of AR quality. $BaCO_3$, SnO_2 and Cr_2O_3 were thoroughly mixed under acetone in an agate mortar in the ratio 1:3:1. The mixture was dried and heated for several days at 1450°C in air. The reaction product consisted of numerous thin needle-shaped crystals. X-ray powder diffraction showed the unknown phase to be dominant, with $BaCrO_4$ as