nent une nette augmentation des paramètres de maille. La position particulière des atomes de rhénium (0,392;0;0,287) ainsi que la géométrie des polyèdres ReO_5 conduisent à un groupe d'espace plus symétrique ($P6_3cm$) que celui des apatites classiques ($P6_3/m$).

Les deux positions trouvées pour les atomes de chlore ($z = 0{,}076$ et $z = -0{,}057$) sont, comme dans les chlorapatites, situées sensiblement au $\frac{1}{3}$ et au $\frac{2}{3}$ de la distance entre les plans de baryum Ba(2).

La similitude des spectres de poudre entre les cristaux broyés de $Ba_5(ReO_5)_3Cl$ et la phase $Ba_3Re_2O_{10}$ obtenue en ampoule scellée sous vide permet de penser que ce deuxième composé est une apatite lacunaire en baryum de formule $Ba_9\square(ReO_5)_6$. Il est possible que ce composé renferme quelques ions hydroxyle, l'oxyde de baryum étant très hygroscopique.

La cristallogénèse de la chlorapatite dans un flux de chlorure de baryum peut ainsi s'expliquer par le processus réactionnel suivant:

$$Ba_9\square(ReO_5)_6 + BaCl_2 \rightarrow Ba_{10}(ReO_5)_6Cl_2.$$

La section relativement importante des tunnels parallèles à l'axe c, due à la présence des groupements ReO_5, devrait nous permettre de préparer des composés analogues contenant des halogènes volumineux tels que le brome et l'iode.

Dans ces apatites il est également possible de substituer le rhénium par le technétium 99 dont les propriétés chimiques sont très voisines. La présence de ce radioélément dans les apatites semble susceptible d'applications pour le dépistage de métastases cancéreuses dans les tissus osseux.

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Neutron Profile Refinement and Deuterium Positions in $Na_2CO_3.1\frac{1}{2}D_2O_2$

BY J. M. ADAMS AND R. G. PRITCHARD

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE, Wales

AND A. W. HEWAT

Institut Laue–Langevin, 156X, 38042 Grenoble CEDEX, France

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Abstract

Data obtained at 300 K with 1·9 Å radiation have been refined to $R_I = 5{\cdot}8\%$ with isotropic temperature factors. It has been confirmed that there are two disordered D_2O_2 orientations at each deuterium peroxide site. The e.s.d.'s of the heavy-atom positions are comparable with the best X-ray determination but the D atom positions are much more accurate and the definition of the hydrogen-bonding geometry has been improved considerably. In contrast to the X-ray structure, the dihedral angles within the three distinct types of D_2O_2 molecules have been found to be very similar at 157, 158 and 164°.

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Introduction

Sodium percarbonate ($Na_2CO_3.1\frac{1}{2}H_2O_2$) is an industrial bleach, the structure of which was determined simultaneously by Adams & Pritchard (1977) and Carrondo, Griffith, Jones & Skapski (1977), hereafter AP and CGJS, although the latter diffractometer-data refinement was more accurate. The main interest in the

structure is in the hydrogen-bonding pattern of the H_2O_2 molecules. There are two distinct sites for these; one is fourfold, the other eightfold. Both refinements agreed that there were two disordered orientations of the H_2O_2 in the fourfold site; the CGJS data additionally showed similar disorder at the eightfold site. Since this material is of considerable technological importance (its extremely high stability is very unusual) it was considered that more precise hydrogen-bonding parameters would be of interest.

Experimental

The preparation of the sample was carried out in a glove box under dry nitrogen. 25 g Na_2CO_3 (previously dried at 403 K for 2 h and then allowed to cool in a desiccator) were dissolved in 120 ml D_2O. 10 ml of 87% (w/w) H_2O_2 solution was diluted with 30 ml D_2O. The two solutions were mixed and after 5 min the crystals which had formed were filtered off and dried over P_2O_5. The maximum isotropic % D for samples prepared by this method is ~95%. Refinement of the data later showed 90% deuteration.

The sample was packed inside a vanadium tube and the neutron data collected at 300 K with 1·9094 Å neutrons for 22 h on the high-resolution powder diffractometer D1A at the Institut Laue–Langevin, Grenoble (Hewat & Bailey, 1976). The angular range (2θ) studied was 6 to 160° in steps of 0·05°.

Structure refinement

The starting point of the refinement used the coordinates given by AP. The whole refinement was made with Hewat's (1973*a*,*b*) development of the original Rietveld (1969) neutron-profile-refinement program. The background points were estimated at regions of the diffraction diagram where peaks were known to be absent. Some small regions of the diffraction trace where impurity peaks occurred were omitted. Refinement of the scale factor, counter zero point and cell dimensions reduced R_I to 48%.* A difference synthesis enabled the D atoms to be located and isotropic refinement proceeded smoothly to an R_I of 10·6%. A further difference map then showed that in addition to the disordered D_2O_2 at the fourfold position (a feature of both the X-ray refinements of AP and CGJS) there was disorder at the eightfold site consistent with that found by CGJS. With this modification of the model further isotropic refinement proceeded rapidly to a final R_I of 5·8%. Scattering lengths used were from *International Tables for X-ray Crystallography* (1974). The site occupancy of the observed peroxide O atoms was fixed at 0·5 throughout but that of the D atoms was refined to allow for the unknown (*a priori*) D/H substitution. An attempt at anisotropic refinement was abandoned since there was a deterioration in R_I and in the e.s.d.'s of the atoms. The final coordinates are given in Table 1. A comparison of the observed and calculated diffraction profiles is given in Fig. 1.

* R_I is defined as $\sum|I(\text{obs.}) - (1/c)I(\text{calc.})|/\sum I(\text{obs.})$, where c is the scale factor and I(obs.) and I(calc.) are the observed and calculated intensities. The observed intensities are integrated for each reflection at the end of the refinement. The observed counts are divided between overlapping reflections according to the relative contribution of these reflections computed from the fitted structure (Rietveld, 1969).

Table 1. *Fractional atomic coordinates and isotropic temperature factors with their e.s.d.'s*

	x	y	z	B (Å^2)
Na(1)	0·2512 (15)	0·9888 (3)	0·257 (3)	1·8 (1)
Na(2)	0·9943 (16)	0·2460 (9)	0·243 (2)	1·6 (1)
C(1)	0·2494 (3)	0·1626 (2)	0·000 (fixed)	0·90 (5)
O(1)	0·1823 (4)	0·0911 (2)	−0·016 (1)	1·7 (1)
O(2)	0·3911 (4)	0·1640 (2)	0·001 (2)	1·8 (1)
O(3)	0·1769 (4)	0·2314 (2)	−0·003 (2)	1·6 (1)
O(4)*	0·5458 (9)	0·0319 (6)	−0·032 (2)	1·9 (1)
O(44)*	0·5096 (11)	0·0261 (5)	0·091 (2)	1·9
O(5)*	0·9052 (21)	0·1109 (15)	−0·105 (3)	2·3 (1)
O(55)*	0·9060 (20)	0·1131 (14)	0·085 (3)	2·3
O(6)*	0·8382 (20)	0·1372 (11)	0·102 (2)	2·2 (1)
O(66)*	0·8379 (18)	0·1412 (11)	−0·084 (2)	2·2
H(1)*†	0·0107 (23)	0·1077 (11)	−0·062 (3)	2·5 (3)
H(11)*†	0·0152 (21)	0·0988 (11)	0·032 (3)	2·5
H(2)*†	0·2834 (14)	0·3051 (7)	−0·054 (2)	1·4 (2)
H(22)*†	0·2684 (15)	0·3203 (7)	0·035 (3)	1·4
H(3)*†	0·4650 (12)	0·0755 (7)	−0·052 (2)	1·4 (2)
H(33)*†	0·4843 (11)	0·0908 (6)	0·026 (2)	1·4

* Site occupancy 0·5.

† The apparent site occupancy at the hydrogen positions [0·422 (4)] corresponds to (0·450D + 0·050H) with $b_D = 0·663$, $b_H = -0·372$.

Results and discussion

The overall structure of $Na_2CO_3.1\frac{1}{2}H_2O_2$ has been described by AP and CGJS (Fig. 2). They have assigned the space group as $Aba2$ with $Z = 8$. The cell parameters derived from this profile technique are of much higher accuracy than those given by conventional single-crystal X-ray methods: a = 9·1824 (5), b = 15·7513 (2), c = 6·7272 (1) Å. However, these errors do not include the uncertainty in the neutron wavelength. The bond lengths and angles (Tables 2 and 3) of the carbonate group and the coordination around the Na ions agree reasonably well with the X-ray results except perhaps in the O(5)—O(6) and O(55)—O(66) distances. The e.s.d.'s of these heavy-atom parameters are slightly worse than those of CGJS. The H (D) positions have, however, been improved considerably; the e.s.d.'s of these atoms are comparable with those of the O atoms to which they are bonded.

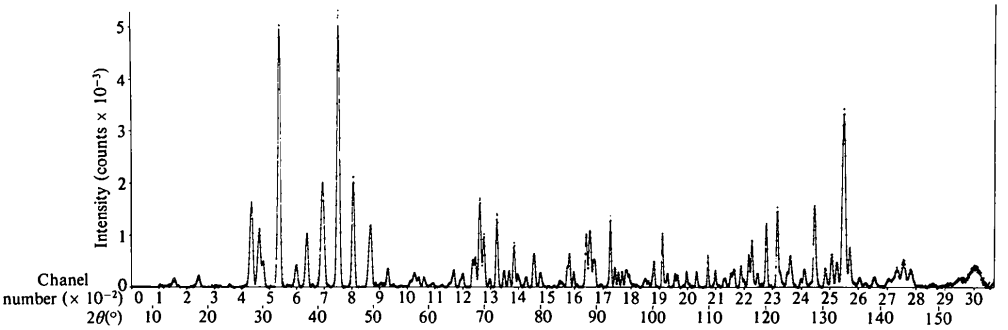

Fig. 1. Observed (· · ·) and calculated (—) diffraction profiles from 6 to 160° 2θ.

The parameters for the D_2O_2 molecules in this study are the best obtained to date except for the study of solid H_2O_2 itself by single-crystal neutron diffraction (Busing & Levy, 1965). The mean O—H distance and OOH angle given by CGJS are 0·95 Å and 100°. The values for D_2O_2 derived here are 1·048 Å and 102·3°, which compare well with those of 1·008 Å and 102·7° given for H_2O_2 by Busing & Levy (1965). With X-rays, the O—H bond is usually found to be 0·10 Å shorter than in a neutron determination because of the transfer of electrons towards the O atom. In addition there are three distinct D_2O_2 molecules in this structure, each having two OOD angles. It has been demonstrated that the OOD angle can deviate considerably from the expected tetrahedral angle: the range is from 91·5 to 109·6°. The dihedral angle (φ) found for the H_2O_2 molecule in the solid state can vary between large limits since the hindering potential for rotation in the free molecule is small (Hunt, Leacock, Peters & Hecht, 1965), 4·6 kJ mol^{-1} between φ = 80 and 280°. In previous studies, summarized by Pedersen (1969), dihedral angles ranging from 93 to 180° have been found. In the X-ray determination of CGJS it was considered that the values of φ derived from the H-atom positions were less than those derived from acceptor O atoms where linear H-bonds are assumed by ~7° [*i.e.* 168° (fourfold site) and 120, 129° compared with 173° (fourfold) and 132 and 136°]. This was consistent with the results obtained for

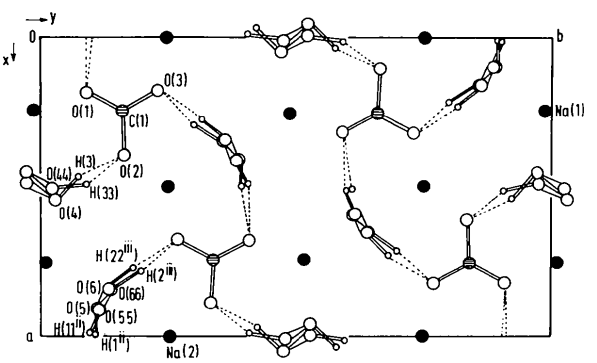

Fig. 2. Projection of the structure on to (001), from $z = -0{\cdot}2$ to $z = +0{\cdot}3$. One layer of sodium ions and one layer of carbonate ions are shown together with the disordered hydrogen peroxide molecules.

Table 2. *Geometry of the carbonate and* H_2O_2 *groups*

(*a*) Carbonate ion

		CGJS
C(1)—O(1)	1·287 (4) Å	1·283 (3) Å
C(1)—O(2)	1·301 (5)	1·283 (3)
C(1)—O(3)	1·273 (5)	1·293 (3)
O(1)—C(1)—O(2)	119·6 (3)°	120·9 (2)°
O(1)—C(1)—O(3)	119·5 (3)	120·0 (3)
O(2)—C(1)—O(3)	120·6 (3)	118·9 (2)

(*b*) H_2O_2 molecule sited across the twofold axis

		CGJS
O(4)—O(44^{i})	1·33 (2) Å	1·35 (3) Å
H(3)—O(4)	1·02 (2)	
O(44^{i})—H(33^{i})	1·13 (1)	
H(3)—O(4)—O(44^{i})	105 (1)°	
O(4)—O(44^{i})—H(33^{i})	107 (1)	
Dihedral angle	157 (2)°	168°

(*c*) Remaining H_2O_2 molecules

		CGJS
O(5)—O(6)	1·58 (3) Å	1·42 (2) Å
H(1^{ii})—O(5)	1·01 (3)	
O(6)—H(22^{iii})	1·03 (2)	
H(1^{ii})—O(5)—O(6)	98 (2)°	
O(5)—O(6)—H(22^{iii})	92 (2)	
Dihedral angle	164 (2)°	129°
O(55)—O(66)	1·37 (3) Å	1·52 (2) Å
H(11^{ii})—O(55)	1·09 (3)	
O(66)—H(2^{iii})	1·00 (2)	
H(11^{ii})—O(55)—O(66)	102 (2)°	
O(55)—O(66)—H(2^{iii})	110 (2)	
Dihedral angle	158 (2)°	120°

Symmetry code (applies also to Tables 3 and 4)

(i)	$1-x, -y, z$	(vi)	$1-x, 1-y, z$
(ii)	$1+x, y, z$	(vii)	$-\frac{1}{2}+x, 1-y, \frac{1}{2}+z$
(iii)	$\frac{1}{2}+x, \frac{1}{2}-y, z$	(viii)	$1\frac{1}{2}-x, y, \frac{1}{2}+z$
(iv)	$x, 1+y, z$	(ix)	$1-x, \frac{1}{2}-y, \frac{1}{2}+z$
(v)	$\frac{1}{2}-x, 1+y, \frac{1}{2}+z$	(x)	$2-x, \frac{1}{2}-y, \frac{1}{2}+z$

Table 3. *Coordination distances around the sodium ions* (Å)

		CGJS
Na(1)–O(1^{iv})	2·52 (2)	2·408 (7)
Na(1)–O(1^{v})	2·30 (1)	2·395 (7)
Na(1)–O(4^{iv})	3·40 (2)	
or Na(1)–O(44^{vi})	2·47 (2)	2·42 (3)
Na(1)–O(4^{vi})	2·71 (2)	2·77 (2)
or Na(1)–O(44^{iv})	2·69 (2)	2·81 (3)
Na(1)–O(4^{v})	3·15 (2)	
or Na(1)–O(44^{vii})	3·17 (2)	
Na(1)–O(4^{vii})	2·38 (2)	2·38 (2)
or Na(1)–O(44^{v})	3·34 (2)	
Na(1)–O(5^{vii})	2·31 (2)	2·42 (1)
or Na(1)–O(66^{vii})	2·44 (2)	2·39 (1)
Na(1)–O(55^{vi})	2·45 (2)	2·39 (2)
or Na(1)–O(6^{vi})	2·39 (2)	2·44 (1)
Na(2)–O(2^{viii})	2·40 (2)	2·39 (1)
Na(2)–O(2^{iii})	2·36 (2)	2·36 (1)
Na(2)–O(3^{ix})	2·35 (2)	2·31 (1)
Na(2)–O(3^{ii})	2·37 (2)	2·40 (1)
Na(2)–O(5^{x})	2·64 (3)	2·53 (1)
or Na(2)–O(66^{x})	2·63 (2)	2·57 (1)
Na(2)–O(55)	2·49 (3)	2·54 (2)
or Na(2)–O(6)	2·43 (2)	2·49 (2)

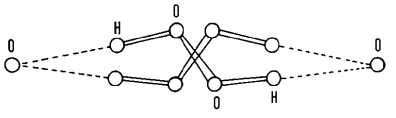

Fig. 3. Arrangement of disordered hydrogen peroxide groups at each site. Both molecules have site occupancy of 0·5. The hydrogen-bonding parameters are similar for both disordered positions. In the fourfold site the two H_2O_2 molecules are related by a twofold axis. In the eightfold site the two peroxide molecules are not related by symmetry.

$(NH_4)_2C_2O_4.H_2O_2$ by Pedersen (1972). It was found in the X-ray study of CGJS that φ was apparently different for the H_2O_2 molecule in the fourfold site than for the molecule in the eightfold site, although it should be noted that there are large uncertainties in these values because of the imprecise location of the H atoms. In contrast, the more precise neutron determination has shown that the value of φ derived from the D atom positions is ~16° less than that predicted from the acceptor O atom positions (linear hydrogen bond assumption) for the fourfold site and is ~26° greater for the molecules in the eightfold site. In addition, the three distinct types of D_2O_2 molecule gave φ = 157, 158 and 164°. Fig. 3 shows the arrangement of the disordered hydrogen peroxide groups.

Each peroxide D atom is involved in one hydrogen bond (Table 4). The O···O distances agree well with those of AP and CGJS, while the H···O distances and OHO angle are now precisely defined. The O···O distances are near the shorter limit of those found previously for perhydrates (*e.g.* Pedersen, 1969; Adams & Pritchard, 1976, 1978). The maximum deviation from linearity found here is ~30°, even with such short hydrogen bonds. Pedersen (1969) had concluded from PMR data that for the alkali-metal oxalate perhydrates with bonds of 2·6 Å (comparable with those found here) such deviations would be small.

Table 4. *Hydrogen-bond geometry*

a–*b*···*c*	*a*···*c*	*b*···*c*	∠*a*–*b*···*c*
O(4)–H(3)···O(2)	2·53 (1) Å	1·59 (1) Å	151 (7)°
O(44)–H(33)···O(2)	2·51 (1)	1·45 (1)	152 (1)
O(5)–H(1^{ii})···O(1^{ii})	2·63 (2)	1·63 (2)	172 (2)
O(55)–H(11^{ii})···O(1^{ii})	2·65 (2)	1·57 (2)	169 (2)
O(6)–H(22^{iii})···O(3^{iii})	2·64 (2)	1·65 (1)	159 (2)
O(66)–H(2^{iii})···O(3^{iii})	2·55 (2)	1·56 (1)	171 (2)

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