The X-ray structure of a sodium peroxide hydrate, $Na_2O_2 \cdot 8H_2O$, and its reactions with carbon dioxide: relevance to the brightening of mechanical pulps

Geoffrey S. Hill, David G. Holah, Stephen D. Kinrade, Vincent R. Magnuson, Valery Polyakov, and Todd A. Sloan

Abstract: The main component of the solid originally believed to be a peroxosilicate with pulp-brightening properties has been shown to be $Na_2O_2 \cdot 8H_2O$. The solid crystallizes in the monoclinic space group *C2/c*, with an empirical formula H_8O_5Na, and with a = 14.335(3), b = 6.461(1), c = 11.432(2) Å, β = 118.28(3)°, and Z = 8. The centrosymmetric structure consists of a peroxide anion with an O—O distance of 1.499(2) Å. Each of these oxygen atoms is at the apex of an approximate square-based pyramid, the base of which consists of four oxygen atoms of water molecules. The bases of the two pyramids are staggered when viewed down the peroxide bond. Each sodium is at the centre of an approximate octahedron of water molecules, four of which bridge other sodium atoms and two bridge to the peroxide anions. One hydrogen atom of each of these two water molecules is terminal and the other two are hydrogen bonded to peroxide oxygen atoms. The compound reacts very rapidly with CO_2 in moist air to form Na_2CO_3, but in drier conditions, formation of the carbonate can take many days and proceeds via a percarbonate, believed to be Na_2CO_4. This has been identified by infrared spectroscopy and X-ray powder diffraction and can persist for long periods in dry air.

Key words: sodium peroxide hydrate, sodium percarbonate, pulp brightening, X-ray diffraction, infrared.

Résumé : On démontre que le produit principal d'un solide, auquel on avait originalement attribué la structure d'un peroxosilicate ayant des propriétés de blanchiment de la pulpe, est formé de $Na_2O_2 \cdot 8H_2O$. Le solide, de formule empirique de H_8O_5Na, cristallise dans le groupe d'espace monoclinique *C2/c*, avec a = 14,335(3), b = 6,461(1), et c = 11,432(2) Å, β = 118,28(3)°, et Z = 8. La structure centrosymétrique comporte un anion peroxyde dans lequel la longueur de la liaison O—O est égale à 1,499(2) Å. Chacun de ces atomes d'oxygène se trouve au sommet d'une pyramide à base approximativement carrée dont la base est formée de quatre atomes d'oxygène des molécules d'eau. Lorsqu'on les regarde le long de la liaison du peroxyde, les bases des deux pyramides sont décalées. Chaque atome de sodium se trouve approximativement au centre d'un octaèdre de molécules d'eau, dont quatre forment des ponts avec d'autres atomes de sodium et deux forment des ponts avec des anions peroxydes. L'un des atomes d'hydrogène de chacune de ces molécules d'eau est terminal et les deux autres forment des liaisons hydrogènes avec les atomes d'oxygène du peroxyde. Le composé réagit rapidement avec le CO_2, dans l'air humide, pour conduire à la formation de Na_2CO_3; toutefois, dans des conditions plus sèches, la formation du carbonate nécessite plusieurs jours et elle implique un intermédiaire percarbonate que l'on croit être le Na_2CO_4. Celui-ci a été identifié par spectroscopie infrarouge et par diffraction de poudre des rayons X et il peut exister pour de longues périodes dans de l'air sec.

Mots clés : hydrate de peroxyde de sodium; percarbonate de sodium; blanchiment de la pulpe; diffraction des rayons X; infrarouge.

[Traduit par la rédaction]

Introduction

The work described here arose during research aimed at improving the procedures for the lignin-preserving brightening of mechanical wood pulps. (Bleaching more often refers to the production of pure cellulose by delignification with reagents such as Cl_2, ClO_2, O_2, etc. in Kraft pulps; for a general reference, see Smook (1)). The most widely used brightening reagent is an alkaline solution of hydrogen peroxide and its successful use in mills requires the presence of a variety of additional reagents (2) whose primary goals are to stabilize the peroxide and minimize its autodecomposition and its decomposition catalyzed by transition metal ions in the wood (2, 3). The most common additives include sodium silicate, magnesium ions, and the sodium salt of diethylenetriaminepentaacetic acid. Because of the enormous amounts of mechanical pulps being produced, and since hydrogen peroxide is the most expensive chemical used in such mills, it is of consider-

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Fig. 1. The structure of $Na_2O_2 \cdot 8H_2O$ showing the environment of the Na atoms.

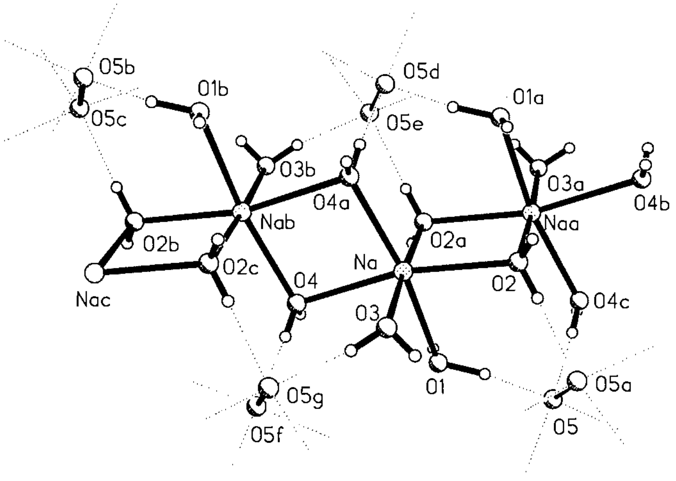
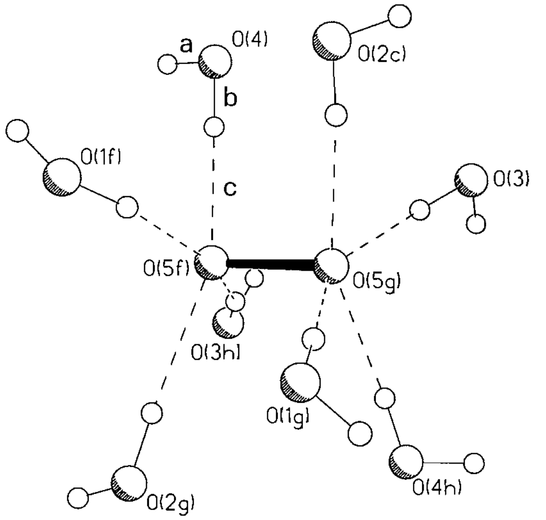


Fig. 2. The structure of $Na_2O_2 \cdot 8H_2O$ showing the environment of the peroxide anion.



able economic importance to understand the chemistry involved in these processes so that peroxide losses can be minimized. For example, there has been much discussion and speculation on the specific role(s) of the silicate (4). It has been shown (3) that a major (but not total (5)) function is the deactivation of metal cations involved in catalyzing peroxide decomposition. In addition, it has long been suspected that peroxosilicates are involved (3), and there are several reports describing the solid obtained when solutions of hydrogen peroxide and sodium silicate solutions are mixed at high pH values as $Na_2SiO_3 \cdot xH_2O_2$ (6), sodium persilicate (7), and sodium peroxysilicate (3, 8, 9). The solid has brightening properties (7, 8), but no evidence has been presented to support any of the above formulations. This paper describes the structure of the only crystalline compound, $Na_2O_2 \cdot 8H_2O$, present in the solid and its reactions with CO_2.

Results and discussion

The presence of silicon in the very unstable solid obtained in bulk from solutions containing silicate, hydrogen peroxide, and sodium hydroxide, and generally referred to as a peroxosilicate, has been confirmed by strong signals in the ^{29}Si nmr spectra, by ir spectroscopy, and by energy-dispersive X-ray microanalysis. Since this solid shows brightening properties (7, 8), and is of unknown composition, it was of importance to establish its composition. We have shown previously (4) that, compared to pure silicate, there are minor changes in the ^{29}Si nmr spectra of solutions from which the solid crystallizes and that these are probably due to the formation of labile complexes of dissolved silicates and radical H_2O_2 decomposition products. No evidence for the existence of peroxide coordinated to silicate was found in such solutions.

Well-formed crystals were obtained from a variety of solutions (especially at very high pH) containing NaOH, SiO_2, and H_2O_2, prepared in connection with the ^{29}Si nmr studies (4). These crystals are colourless, transparent plates that become opaque very rapidly when removed from the mother liquor in air. Decomposition is slightly less rapid under nitrogen at room temperature, but to preserve a crystal for data collection, it was necessary to transfer crystals rapidly, under nitrogen, to sealed Lindemann capillaries for storage at liquid nitrogen temperatures.

Results from the structural determination (see below) show that the compound is $Na_2O_2 \cdot 8H_2O$, which was made previously (10) either by reacting sodium peroxide with water or, more conveniently (11), from mixtures of hydrogen peroxide and sodium hydroxide. It is reported as a white powder that reacts readily with carbon dioxide and water vapour. The stabilization of this compound for industrial use has formed the subject of patents (12).

Views of the structure, showing the arrangement of the water molecules about each Na atom and about each peroxide ion, are shown in Figs. 1 and 2, with selected bond lengths and angles recorded in Table 1. From Fig. 1, it can be seen that each Na (Nab for example) is surrounded by O atoms from six water molecules. Four of these (O2b, O2c, O4a, and O4) are from water molecules that essentially act as bridges to other Na atoms. Two (O1b and O3b) serve to bridge Nab to O5b and O5e, the oxygen atoms of peroxide anions. Na—O distances are in the range 2.376(12)–2.508(12) Å, and the O-Na-O angles approximate to 90° so that each Na ion is in the centre of an approximate octahedron.

Effects of hydrogen bonding can be seen by considering the distances labelled ***a***, ***b***, and ***c*** in Fig. 2 and tabulated below.

	a	*b*	*c*	*d*
O1	0.787(25)	1.032(31)	1.555(1)	2.582(1)
O2	0.768(25)	0.847(25)	1.897(1)	2.742(1)
O3	0.791(22)	0.855(27)	1.788(1)	2.622(1)
O4	0.795(25)	0.865(25)	1.802(1)	2.665(2)

Distance ***b*** is greater than distance ***a*** for all lattice waters. This fact is consistent with the H atom oriented towards the peroxide being hydrogen bonded to the peroxide O atom, whereas the second H atom is terminal, with little or no hydrogen bonding as distances range from 1.958 to 2.581 Å. It is apparent from Fig. 2 and from a comparison of ***d***, the peroxide O to

Table 1. Selected bond lengths (Å) and angles (°). See supplementary material for complete data.

Na—O(4a)	2.3710(12)
Na—O(3)	2.3913(13)
Na—O(2a)	2.4160(13)
Na—O(2)	2.4223(12)
Na—O(1)	2.4428(12)
Na—O(4)	2.5009(12)
Na—Na(a)	3.5229(12)
Na—Na(b)	3.6366(12)
O5—O5(a)	1.499(2)
O(4a)-Na-O(3)	93.15(3)
O(4a)-Na-O(2a)	88.49(5)
O(3)-Na-O(2a)	177.13(4)
O(4a)-Na-O(2)	109.64(4)
O(3)-Na-O(2)	90.69(4)
O(2a)-Na-O(2)	86.54(4)
O(4a)-Na-O(1)	166.15(4)
O(3)-Na-O(1)	94.88(5)
O(2a)-Na-O(1)	83.98(5)
O(2)-Na-O(1)	81.56(4)
O(4a)-Na-O(4)	83.47(4)
O(3)-Na-O(4)	88.96(4)
O(2a)-Na-O(4)	93.57(4)
O(2)-Na-O(4)	166.90(4)
O(1)-Na-O(4)	85.41(4)
O(4a)-Na-Na(a)	102.29(4)
O(3)-Na-Na(a)	133.89(4)
O(2a)-Na-Na(a)	43.34(3)
O(2)-Na-Na(a)	43.20(3)
O(1)-Na-Na(a)	80.05(3)
O(4)-Na-Na(a)	135.43(4)
O(4a)-Na-Na(b)	43.10(3)
O(3)-Na-Na(b)	91.34(4)
O(2a)-Na-Na(b)	91.47(4)
O(2)-Na-Na(b)	152.72(4)
O(1)-Na-Na(b)	125.31(4)
O(4)-Na-Na(b)	40.37(3)
Na(a)-Na-Na(b)	128.95(4)
Na(a)-O(2)-Na	93.46(4)
Na(b)-O(4)-Na	96.53(4)

water O distance, with the sum of ***b*** and ***c*** that the hydrogen bond is approximately linear (angles range from 164.4° to 176.2°).

The environment of the anions can also be seen in Fig. 1 and, more clearly, in Fig. 2. Each O atom of the O_2^{2-} is approximately 0.5 Å above a plane formed by four O atoms from neighbouring water molecules. When viewed down the O—O bond, the eight O atoms are in a staggered configuration. Distances from a peroxide O to its closest four water O atoms are 2.582(2)–2.742(1) Å, with angles of the type O(5f)-O(5g)-O(2c) ranging between 100° and 110°. The O—O distance of 1.499(2) Å is comparable to that found in the related $SrO_2 \cdot 8H_2O$ and in fact the two structures are quite similar (10, 13). In previous work, the space group of $Na_2O_2 \cdot 8H_2O$ was reported as either *Cc* or *C*2/*c*, with a unit cell of a = 13.5, b = 6.5, c = 11.5 Å, β = 100.5 and Z = 4 (14).

The solid obtained by literature methods (7, 8) in high yields from mixtures of NaOH, Na_2SiO_3, and H_2O_2 is very sticky because of the high NaOH content. After washing with small amounts of ethanol and H_2O_2, small well-formed crystals are clearly visible in the bulk solid, suggesting that the original precipitate is a mixture. The powder diffraction patterns of several samples at various stages of washing are the same as that of the pure octahydrate (see experimental section). The observed pattern agrees very closely with that calculated from the single crystal data and is only slightly different from that on file (15) in the ICDD data bank. Data from ir, nmr, and energy-dispersive X-ray spectrometry suggest that the amorphous, silicon-containing contaminant is sodium silicate, which is more soluble in water (16) or H_2O_2 than is $Na_2O_2 \cdot 8H_2O$ and explains why the pure octahydrate is the only solid remaining after washing.

There is a clear phase change when the pure octahydrate is pumped under vacuum for 5 h, and the powder pattern of the new phase corresponds to that reported for the dihydrate (15), obtained when the octahydrate is allowed to stand over desiccants (11).

Because decomposition of the peroxide begins as soon as the solid is exposed to atmosphere, samples for ir measurements were handled under dry nitrogen. The ir spectrum (Fig. 3) consists of a series of broad absorptions due to the lattice water and peaks in the 500–1000 cm^{-1} region. The peak at 985 cm^{-1} is possibly due to νO—O, which is typically (17) found in this region. There are additional peaks in the 500–850 cm^{-1} region but, significantly, no peaks between 1000 and 1600 cm^{-1}, and therefore the sample is carbonate free at this point (18).

The rate of decomposition and the product formed greatly depend on the amount of moisture present in the atmosphere. Exposure to moist air (relative humidity ~80%) results in the rapid (within minutes) appearance of the very intense signal at ~1450 cm^{-1} due to CO_3^{2-} (18). Transformation is complete in a few hours. This accounts for the previously published spectra (19) of both $Na_2O_2 \cdot 8H_2O$ and $Na_2O_2 \cdot 8D_2O$, which are dominated by absorptions due to water (~3000 cm^{-1}) and to sodium carbonate at ~1450 cm^{-1} (very strong), ~880, and ~700 (very weak) cm^{-1} (18). In fact there is little evidence of any peroxide remaining in the samples used to record these spectra, which were also used to argue that the structure of $Na_2O_2 \cdot 8H_2O$ does not consist of units of $2NaOH \cdot H_2O_2 \cdot 6H_2O$.

However, in drier air (relative humidity ~20%), dehydration is accompanied by the appearance, within minutes, of new signals that continue to grow in intensity over several hours. The changes after 20 h are shown in Fig. 3. There is little peroxide remaining, almost all the water has been lost, and a small amount of CO_3^{2-} is present. The three peaks due to the latter continue to increase with time, but many days are required for complete conversion to CO_3^{2-}. The remaining peaks in the spectrum in Fig. 3 are most likely due to a surprisingly stable, colourless sodium percarbonate.

A detailed analysis of ir and Raman spectra of various percarbonates suggests that the spectra of most species are best interpreted on the basis of the centrosymmetric $(C_2O_6)^{2-}$ anion (20). The ir spectra of $Na_2C_2O_6 \cdot nH_2O$ (n = 0–1) and three coloured (orange and blue) forms of $K_2C_2O_6$, prepared by reactions between CO_2, KOH, and H_2O_2, have been analyzed (20). In addition, ("yellowish") $Na_2C_2O_6$ has been reported from $Na_2O_2 \cdot 8H_2O$ and CO_2 (21). Percarbonates formulated as

CO_4^{2-} are less well known. Attempts to prove the existence of Li_2CO_4 by X-ray powder diffraction methods were unsuccessful and it was concluded that the compound does not exist at room temperature (22). It was later obtained from LiOH–H_2O_2–CO_2 mixtures and characterized by elemental analysis and ir spectroscopy (20); its (unpublished) powder pattern does not contain lines due to Li_2CO_3, LiOH, LiO_2H, or Li_2O_2 (20). There is a report of CO_4^{2-} coordinated to Pt (23).

The ir spectrum of the colourless percarbonate shown in Fig. 3 closely resembles that of $Li_2CO_4 \cdot H_2O$. The one difference is that the very strong 1350 cm^{-1} peak in the Li compound, assigned to the C--O stretching vibration (20), appears as a doublet at 1371 and 1339 cm^{-1} in Fig. 3. These may be the symmetric and antisymmetric modes. The spectrum is quite different from that of $Na_2C_2O_6$ (20). The X-ray powder pattern of this sample (see experimental section) shows it to be mostly the percarbonate, contaminated by approximately 5% Na_2CO_3, with no detectable amount of $Na_2O_2 \cdot 8H_2O$. The pattern is also quite different from that reported for $Na_2C_2O_6$ (21) and is therefore probably due to Na_2CO_4.

There is a variety of adducts of H_2O_2 and Na_2CO_3 (20, 24) and it appears to be common practice in the literature (see, for example, ref. 25) to refer to these, particularly the important bleaching agent $Na_2CO_3 \cdot 1.5H_2O_2$, as percarbonates. The crystal structure of the latter (24, 26) shows that it contains H_2O_2 molecules hydrogen bonded to CO_3^{2-}, and is therefore not a percarbonate. Its powder pattern and ir spectrum (20) are quite different from the compound prepared in this work.

Relationship to pulp brightening

All the evidence now points to the fact that the bulk solid obtained from NaOH, H_2O_2, and Na_2SiO_3 mixtures, previously described as sodium peroxysilicate (3, 8, 9) with pulp-brightening properties (7, 8), is in fact a mixture of $Na_2O_2 \cdot 8H_2O$ and amorphous Na_2SiO_3. The pulp-brightening properties of such solids are due to the title compound. The presence of other known crystalline species, such as $Na_2O_2 \cdot xH_2O_2 \cdot yH_2O$ ($x = 2$, $y = 4$ and $x = 4$, $y = 0$) (27), $Na_2(HO_2)_2 \cdot H_2O_2$ (10), and $Na_2SiO_3 \cdot xH_2O_2 \cdot yH_2O$ (particularly with $x = 3$, $y = 0$ (7) and $x = 2$, $y = 1$ (28)) can be also ruled out from powder pattern data. The compound containing the hydroperoxide anion would be particularly important since this anion is believed to be the major active pulp-brightening agent (1). Isolation of peroxide adducts of silicate require that silicate–peroxide solutions be taken to dryness under vacuum (6, 28). In addition, they are very water soluble when first formed and therefore would likely not precipitate under the conditions studied in this work.

Experimental

Physical measurements and syntheses

Infrared spectra as both Nujol mulls and KBr discs were recorded on a Bruker IFS 66 FTIR spectrophotometer. Scanning electron microscopy (SEM) spectra were collected from a Hitachi 570 energy-dispersive X-ray microanalysis instrument equipped with a Tracor Northern 5502 energy-dispersive X-ray spectrometer. X-ray powder data were recorded on a 114.83 mm diameter Debye–Scherrer camera using Ni-filtered Cu-K_α radiation from a Phillips PW 1010 generator. Samples were contained in sealed Lindemann capillaries.

The title compound was made by the literature method (11), and also obtained from mixtures of NaOH, Na_2SiO_3, and H_2O_2 (7, 8) by careful washing with H_2O_2. Optimum conditions for the growth of single crystals suitable for structural determination occur when solutions contain 3.0 mol dm^{-3} SiO_2, 2.0 mol dm^{-3} H_2O_2, and 6.5–7.0 mol dm^{-3} NaOH, crystallization being complete after 48 h; ir (KBr): 3625, 3533, 3446, 3305 (w on broad background, νOH), 2920 (w,vb), 1918 (w,b), 1672 (m, δHOH), 985 (s, νO–O), 833 (sh), 717 (m), 627 (m), 537 (m) cm^{-1}. When exposed to air new peaks due to CO_4^{2-} occur at 1664 (vs, νC═O), 1645 (sh, δHOH?), 1369, 1342 (d,s), 1016 (m), 877 (m), 818 (m), 724 (m) cm^{-1}. In addition, peaks due to CO_3^{2-} occur at 1450 (vs,b), 878 (m) and 724 (w) cm^{-1}.

The first 25 lines in the powder pattern of Na_2CO_4, *d*-spacing in Å (relative intensities): 5.10(2), 4.88(2), 4.30(1), 3.7395), 3.65(2), 3.42(2), 3.29(5), 3.08(20), 2.99(10), 2.915(20), 2.800(2), 2.750(5), 2.700(100), 2.610(2), 2.530(80) br, 2.37(5), 2.300(100), 2.275(5), 2.205(5).

X-ray crystallography

A small crystal was mounted in a sealed Lindemann capillary under nitrogen, and immediately placed in liquid nitrogen.

Data were collected on an Enraf–Nonius CAD4 diffractometer using graphite-monchromatized Mo-K_α radiation at 173 K; 1343 independent reflections were measured in the range $-20 \leq h \leq 17, 0 \leq k \leq 9, 0 \leq l \leq 6$ with a 2θ (max) = 59.96°. Of these, 1064 had $F_o > 4\sigma(F_o)$ and were used for further computation of $wR2$. The Enraf–Nonius peak search, centering, and indexing program was used to determine the initial choice for crystal class and space group. Unit cell parameters were obtained by least-squares analysis of 25 low-angle reflections. The stability of the crystal was measured by periodically monitoring three standard reflections; no systematic intensity variations were observed. Intensity data were corrected for Lorentz and polarization factors. NRCVAX programs (29; PC version of the system) were used for scaling and data reduction. Atomic scattering factors were taken from tabulated values (30).

Crystal data were as follows: H_8O_5Na, $F_w = 111.05$, monoclinic, $C2/c$; $a = 14.335(3)$, $b = 6.461(1)$, $c = 11.432(2)$ Å, $\beta = 118.28(3)°$, $V = 932.44$ Å^3, $Z = 8$, $D_c = 1.582$ g cm^{-3}, $F(000) = 472.0$, $\lambda = 0.71073$ Å, μ(Mo-K_α) = 0.24 mm^{-1}, $T = 173$ K.

The structure was solved by a combination of direct methods and difference Fourier cycles. The Na and the O atoms were refined anisotropically and H atoms were refined isotropically. Coordinates of all atoms were refined. Full-matrix least-squares refinement on F^2, for 1064 data ($F_o > 4\sigma(F_o)$), 0 restraints, and 87 parameters resulted in a gof on $F^2 = 1.129$, $R1 = 0.0313$, and $wR2 = 0.0760$.[2] The largest peaks in the final difference Fourier were 0.243 and -0.223 e/Å^3. Positional thermal parameters are shown in Table 2.[3]

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[2] $R1 = \sigma||F_o|-|F_c||/\sigma|F_o|$ and $wR2 = [\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]]^{0.5}$.

[3] Tables of atomic coordinates and displacement parameters, complete bond lengths and angles, and other refinement data may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. This supplementary material has also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

Fig. 3. IR spectra of $Na_2O_2 \cdot 8H_2O$ (dotted line) and, probably, Na_2CO_4 (solid line). Contamination by Na_2CO_3 is revealed by the very strong band marked by * due to ν_3 of CO_3^{2-}. Arrows indicate the positions of the peaks in the spectrum of the analogous $Li_2CO_4 \cdot H_2O$; relative peak intensities are also very similar (20).

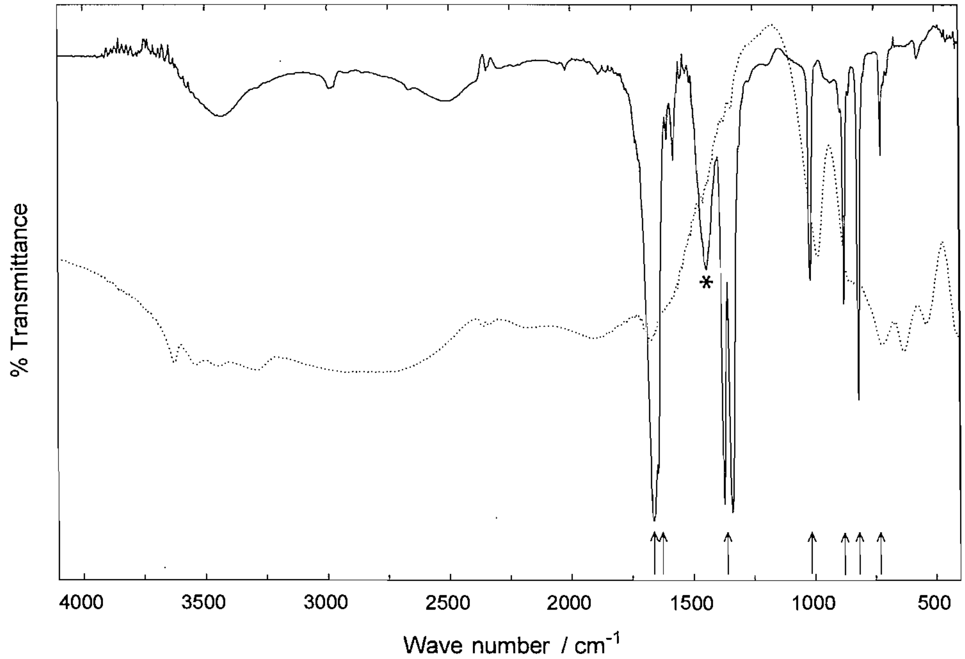

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	$U_{(eq)}$
Na	3002(1)	49(1)	682(1)	20(1)
O(1)	4603(1)	1634(2)	834(1)	22(1)
O(2)	2844(1)	3414(2)	1505(1)	22(1)
O(3)	3855(1)	−1302(2)	2894(1)	21(1)
O(4)	3566(1)	−3115(2)	−79(1)	23(1)
O(5)	5203(1)	5174(2)	2004(1)	21(1)
H(11)	4398(16)	1803(32)	53(22)	46(6)
H(12)	4794(19)	3022(41)	1231(23)	69(8)
H(21)	2469(16)	3553(29)	1801(19)	35(5)
H(22)	3439(17)	4003(33)	2002(20)	45(6)
H(31)	4288(15)	−443(30)	3225(19)	31(5)
H(32)	4225(17)	−2364(39)	2857(21)	62(7)
H(41)	3769(16)	−2769(35)	−582(20)	45(6)
H(42)	4109(17)	−3635(33)	600(21)	47(6)

Refinement calculations were carried out on a PC Express computer with the SHELX program system (31) .

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