

X-Ray Crystal Structure of the Industrial Bleaching Agent 'Sodium Percarbonate' [Sodium Carbonate-Hydrogen Peroxide (2/3)]

By Maria A. A. F. de C. T. Carrondo, William P. Griffith, D. Philip Jones, and Andrzej C. Skapski,*
Chemical Crystallography and Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY

The title compound crystallises in the orthorhombic system, with unit-cell dimensions $a = 9.183(1)$, $b = 15.745(1)$, $c = 6.730(1)$ Å, space group $Aba2$, and $Z = 8$. Diffractometer data have been used to solve the structure, and least-squares refinement with 486 independent reflections has reached R 0.029. Apart from sodium and carbonate ions, the structure determination has shown the presence of hydrogen peroxide molecules which are hydrogen-bonded to the carbonate ions, and therefore the compound is not a true 'percarbonate.' Within a strictly ordered ionic environment, the two crystallographically independent hydrogen peroxide sites show disorder. The molecules in the two types of sites are appreciably different. Thus eight molecules in the unit cell are skewed with a dihedral angle (ϕ) of *ca.* 125°, while the other four appear to be nearly planar (ϕ *ca.* 170°). Infrared and Raman studies on the normal and ^{13}C and ^2H isotopically substituted forms of the compound also suggest that there are two types of H_2O_2 , one being nearly planar and the other skewed.

THE product of reaction of dilute aqueous hydrogen peroxide with sodium carbonate is generally believed to contain hydrogen peroxide of crystallisation, *viz.* $\text{Na}_2[\text{CO}_3] \cdot 1.5\text{H}_2\text{O}_2$.^{1,2} However, it has also been formulated as $\text{Na}_2[\text{CO}_4] \cdot n\text{H}_2\text{O}$,³ and numerous hydrated sodium carbonate 'perhydrates' have been reported to exist.^{4,5} The present study was undertaken to establish the stoichiometry and structure of the compound, which is extensively used in the detergent industry as a bleaching agent under the name of 'sodium percarbonate,' and hence gain some insight into its mode of action.

EXPERIMENTAL

The crystals were prepared by slow evaporation in air of a solution of sodium carbonate in 10% aqueous hydrogen peroxide. The isotopically substituted forms $\text{Na}_2[\text{CO}_3] \cdot 1.5^2\text{H}_2\text{O}_2$ and $\text{Na}_2[^{13}\text{CO}_3] \cdot 1.5\text{H}_2\text{O}_2$ were made from the appropriately substituted reactants, using an excess of 15% hydrogen or deuterium peroxide and allowing the solution to stand for 1 h at -5°C before precipitating the compound with ethanol, washing with ethanol and diethyl ether, and drying in air (Found for $\text{Na}_2[\text{CO}_3] \cdot 1.5\text{H}_2\text{O}_2$: C, 7.8; H, 2.1; O_2^{2-} , 29.7. $\text{CH}_3\text{Na}_2\text{O}_6$ requires C, 7.7; H, 2.0; O_2^{2-} , 30.5%). Infrared spectra were recorded on a Perkin-Elmer 325 instrument in Nujol and Voltalef-3S mulls at -150 and 25°C from 600 to 4 000 cm^{-1} , and Raman spectra of the powdered solids over the same range and at the same temperatures on a Spex Ramolog 5 instrument with krypton-ion laser excitation at 5 682 Å.

Preliminary X-ray photographs showed the crystals of the title compound to be orthorhombic, with systematic absences: hkl , $k + l = 2n + 1$, $0kl$, $k = 2n + 1$, and $h0l$, $h = 2n + 1$. These absences are consistent with space groups $Acam$ (no. 64) and $Aba2$ (no. 41). Subsequent refinement of the structure showed the latter to be the correct one. Accurate unit-cell dimensions were obtained by a least-squares calculation based on 20 high-angle α_1 reflections measured on a diffractometer.

Crystal Data.— $\text{CH}_3\text{Na}_2\text{O}_6$, $M = 157.0$, Orthorhombic,

¹ T. A. Connor and R. E. Richards, *J. Chem. Soc.*, 1958, 289.

² E. H. Riesenfeld and W. Mau, *Ber.*, 1911, **44**, 3595.

³ J. R. Partington and A. H. Fathallah, *J. Chem. Soc.*, 1950, 1934.

⁴ S. Scholle and J. Duška, *Chem. prumysl.*, 1958, **8**, 169.

⁵ C. Rocchiccioli, *Compt. rend.*, 1965, **261**, 361.

⁶ F. H. Allen, D. Rogers, and P. G. H. Troughton, *Acta Cryst.*, 1971, **B27**, 1325.

$a = 9.183(1)$, $b = 15.745(1)$, $c = 6.730(1)$ Å, $U = 973.1$ Å³, $D_m = 2.15$ (by flotation), $Z = 8$, $D_c = 2.14$ g cm⁻³, $F(000) = 632$, space group $Aba2$ (no. 41), Cu- K_α radiation, $\lambda = 1.5418$ Å, $\mu(\text{Cu}-K_\alpha) = 36.9$ cm⁻¹.

A crystal of size *ca.* 0.11 × 0.08 × 0.04 mm was mounted about its c axis on a Siemens off-line four-circle diffractometer. A coat of picture varnish had been applied to the crystal to prevent loss of hydrogen peroxide under X-rays. Reflection intensities were measured with Cu- K_α radiation at a take-off angle of 3°, using a nickel β filter and an Na(Tl)I scintillation counter. The θ — 2θ scan technique was employed with a 'five-value' measuring procedure.⁶ A total of 490 independent reflections was measured to $\theta = 70^\circ$, and, of these, 75 were considered to be 'unobserved' having a net count $< 2.58\sigma$. The reflection 404 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). The data were scaled by use of the reference reflection, and Lorentz and polarisation corrections were applied.

Solution and Refinement of the Structure.—The 1972 version⁷ of the 'X-Ray '63' system⁸ was used for the solution and refinement of the structure. Calculations were carried out on the University of London CDC 7600 computer, and structural illustrations were drawn with the aid of the Imperial College CDC 6400 computer using the program ORTEP.⁹

Location of the sodium atoms from an origin-removed Patterson synthesis was quite difficult. Finally, a solution with two independent atoms gave R 0.49 after a few cycles of isotropic refinement. The subsequent difference-Fourier synthesis showed the location of the carbonate group and gave R 0.32.

The hydrogen peroxide molecules now appeared to be disordered in two independent sites: an eight-fold and a four-fold site. A considerable number of rounds of refinement were needed in order to show, first, whether the disorder was genuine or was an artefact caused by the symmetry of the sodium and carbonate ion arrangement, and, secondly, to establish the correct space group. Initially

⁷ J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, Technical Report TR 192, Computer Science Center, University of Maryland, 1972.

⁸ 'X-Ray '63' system of programs, J. M. Stewart, Technical Report TR 646, Computer Science Center, University of Maryland, 1964.

⁹ C. K. Johnson, ORTEP program, Oak Ridge National Laboratory, 1965, Report ORNL 3794.

refinement was carried out both in space group *Acam* and *Aba2*. In both space groups the disordered model was the only one tenable, and a refinement in space group *Aba2* with sodium and carbonate ions anisotropic and six oxygen atoms at half occupancy gave R 0.047. The positions of the Na^+ and $[\text{CO}_3]^{2-}$ ions were compatible with *Acam*, as were those of the hydrogen peroxide molecule in the eight-fold position. Although disorder had to be assumed, the centre of gravity of the molecule was on the apparent mirror plane also occupied by the $[\text{CO}_3]^{2-}$ ions. The disordered H_2O_2 in the four-fold position (astride a two-fold axis), however, had its centre of gravity to one side of the apparent mirror plane. The last comparative refinement in the two space groups *Acam* and *Aba2* gave R 0.073 and 0.038 respectively, and all subsequent calculations were in space group *Aba2*.

When the six half-hydrogen atoms were included in subsequent refinement as a fixed-atom contribution with isotropic temperature factors of their parent atoms, and anisotropic thermal parameters were extended to all the non-hydrogen atoms, R reached a value of 0.032. Data were corrected for absorption by the Gaussian-integration method¹⁰ with a $12 \times 12 \times 12$ grid, and with crystal path lengths determined by the vector-analysis procedure of Coppens *et al.*¹¹ A weighting scheme of the type suggested by Hughes¹² was applied where $w = 1$ for $F < F^*$ and $w^{\frac{1}{2}} = F^*/F$ for $F \geq F^*$, with $F^* = 30$ as the optimum value. Further full-matrix refinement in which these corrections were introduced, and where four strong low-angle reflections thought to be suffering from extinction were removed, reduced R to its final value of 0.029.

Atomic-scattering factors for sodium were from ref. 13,

TABLE 1
Atomic fractional co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
Na(1)	0.250 8(6)	0.010 9(1)	0.324 3(—)
Na(2)	0.000 1(5)	0.249 9(3)	0.323 2(10)
C(1)	0.249 6(3)	0.337 9(2)	0.073 4(17)
O(1)	0.176 8(2)	0.268 0(1)	0.082 2(18)
O(2)	0.182 7(2)	0.409 4(1)	0.075 3(15)
O(3)	0.389 4(2)	0.334 7(1)	0.076 5(17)
O(11) *	0.406 2(13)	0.114 8(8)	-0.020 1(20)
O(12)	0.345 6(20)	0.138 6(8)	0.166 6(21)
O(21)	0.334 7(14)	0.137 2(7)	-0.016 2(20)
O(22)	0.413 4(14)	0.110 7(11)	0.173 0(22)
O(31)	0.021 5(27)	0.024 8(12)	0.151 3(33)
O(32)	0.042 3(22)	0.032 7(10)	0.030 7(30)
H(11)	0.504	0.113	0.025
H(12)	0.288	0.188	0.125
H(21)	0.292	0.188	0.025
H(22)	0.510	0.110	0.125
H(31)	-0.029	0.075	0.120
H(32)	-0.021	0.079	0.045

* This and all the following atoms have a site population parameter of 0.5.

for oxygen and carbon from ref. 14, and for hydrogen from ref. 15, while the real and the imaginary parts of the anomalous dispersion correction for sodium and oxygen were those listed by Cromer and Liberman.¹⁶ Table 1 lists

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

¹⁰ W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

¹¹ P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

¹² E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

¹³ P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 390.

the final atomic fractional co-ordinates. The thermal parameters and the observed and the calculated structure amplitudes are listed in Supplementary Publication No. SUP 22142 (7 pp.).*

DISCUSSION

The structure determination has shown 'sodium percarbonate' to contain sodium and carbonate ions and hydrogen-bonded hydrogen peroxide molecules. A view of the structure is seen in Figure 1, while the more

TABLE 2

Selected interatomic distances (Å) and bond angles (°) with estimated standard deviations in parentheses

(a) Sodium ions			
Na(1)—O(2I)	2.408(7)	Na(1)—O(2II)	2.395(7)
Na(1)—O(11III)	2.419(13) or *	Na(1)—O(21III)	2.393(12)
Na(1)—O(12)	2.435(14) or	Na(1)—O(22)	2.394(16)
Na(1)—O(31)	2.416(25) or	Na(1)···O(31IV)	2.814(25)
Na(1)—O(32III)	2.379(21) ($\times \frac{1}{2}$)		
Na(1)···O(32)	2.772(21) ($\times \frac{1}{2}$)		
Na(2)—O(1)	2.312(11)	Na(2)—O(1V)	2.399(11)
Na(2)—O(3III)	2.392(10)	Na(2)—O(3VI)	2.359(10)
Na(2)—O(11III)	2.526(14) or	Na(2)—O(21III)	2.573(14)
Na(2)—O(12VI)	2.490(16) or	Na(2)—O(22VI)	2.544(17)
(b) Carbonate ion			
C(1)—O(1)	1.290(3)	O(1)—C(1)—O(2)	120.0(3)
C(1)—O(2)	1.283(3)	O(1)—C(1)—O(3)	118.9(2)
C(1)—O(3)	1.285(3)	O(2)—C(1)—O(3)	120.9(2)
Mean C—O	1.286		
(c) Hydrogen peroxide molecules			
O(11)—O(12)	1.42(2)	O(21)—O(22)	1.52(2)
O(31)—O(32IV)	1.35(3)	Mean O—O	1.43
Mean O—H	0.95	(Range 0.9—1.0)	
Mean O—O—H	100	(Range 96—102)	
(d) Hydrogen bonds			
O(1)···O(12)	2.622(16)	O(1)—H(12)—O(12)	172
or O(1)···O(21)	2.604(13)	O(1)—H(21)—O(21)	167
O(2)···O(11VI)	2.646(13)	O(2VII)—H(11)—O(11)	168
or O(2)···O(22VI)	2.578(14)	O(2VII)—H(22)—O(22)	167
O(3)···O(31VII)	2.572(21)	O(3VI)—H(31)—O(31)	176
or O(3)···O(32VII)	2.535(18)	O(3VI)—H(32)—O(32)	173

Superscripts refer to atoms in the following positions:

I $x, y - \frac{1}{2}, z + \frac{1}{2}$	II $\frac{1}{2} - x, y - \frac{1}{2}, z$
III $\frac{1}{2} - x, y, z + \frac{1}{2}$	IV $-x, -y, z$
V $-x, \frac{1}{2} - y, z + \frac{1}{2}$	VI $x - \frac{1}{2}, \frac{1}{2} - y, z$
VII $x + \frac{1}{2}, \frac{1}{2} - y, z$	

* When two bond lengths or angles are linked by ' or ' this signifies that an individual sodium atom or carbonate oxygen may be connected with either of two disordered positions, but not to both at the same time.

important bond lengths and bond angles are listed in Table 2.

The ionic components of the structure are arranged in layers, that of the sodium ions forming a hexagonal pattern clearly seen in Figure 1. Layers of carbonate and sodium ions alternate in the c direction, with an interplane separation of *ca.* $\frac{1}{4}c$. These layers form a strictly ordered framework into which the hydrogen peroxide molecules fit. These molecules lie close to the carbonate layer to which they are hydrogen bonded. The three-dimensional packing of these entities can be

¹⁴ D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

¹⁵ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

¹⁶ D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

seen in the stereoscopic drawing in Figure 2. Two crystallographically distinct sites are occupied by the hydrogen peroxide molecules: one general eight-fold

is made more severe by relatively weaker $\text{Na} \cdots \text{O}$ interactions (2.772 and 2.814 Å), giving possible 4 + 2, 5, 5 + 2, and 6 co-ordinations.

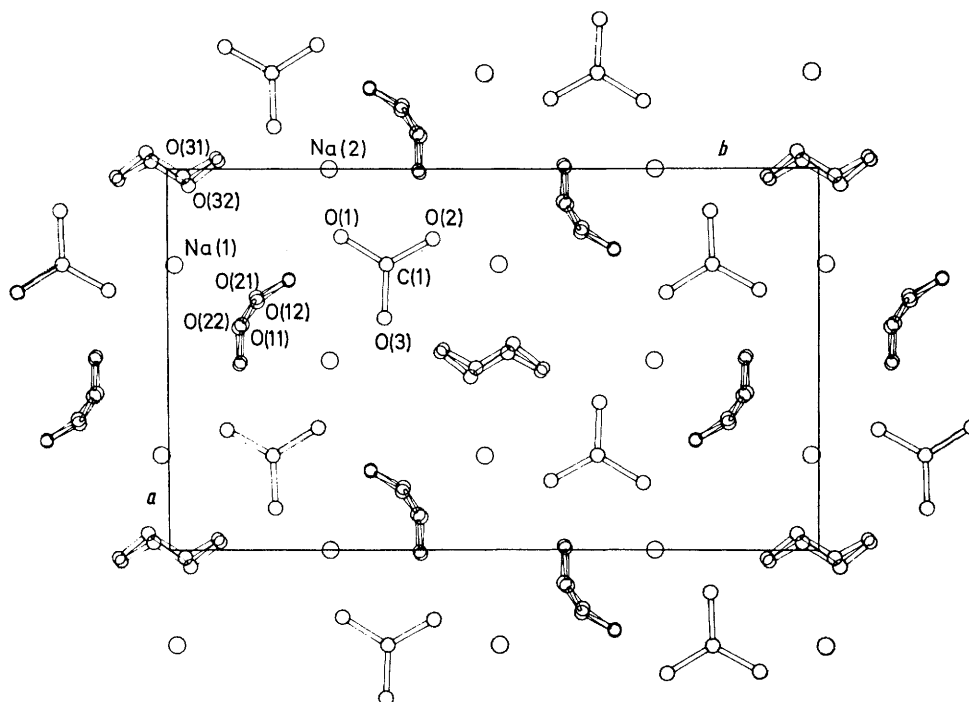


FIGURE 1 A [001] projection of the structure of $\text{Na}_2[\text{CO}_3] \cdot 1.5\text{H}_2\text{O}_2$ showing one layer of sodium ions and a layer of carbonate ions with its associated disordered hydrogen peroxide molecules

site and the other a special four-fold position astride a two-fold axis. Molecules in both sites are disordered. Of the crystallographically independent sodium ions

All three C-O distances in the carbonate ion are very similar (1.283–1.290 Å), with a mean of 1.286 Å. This is consistent with the fact that each carbonate oxygen

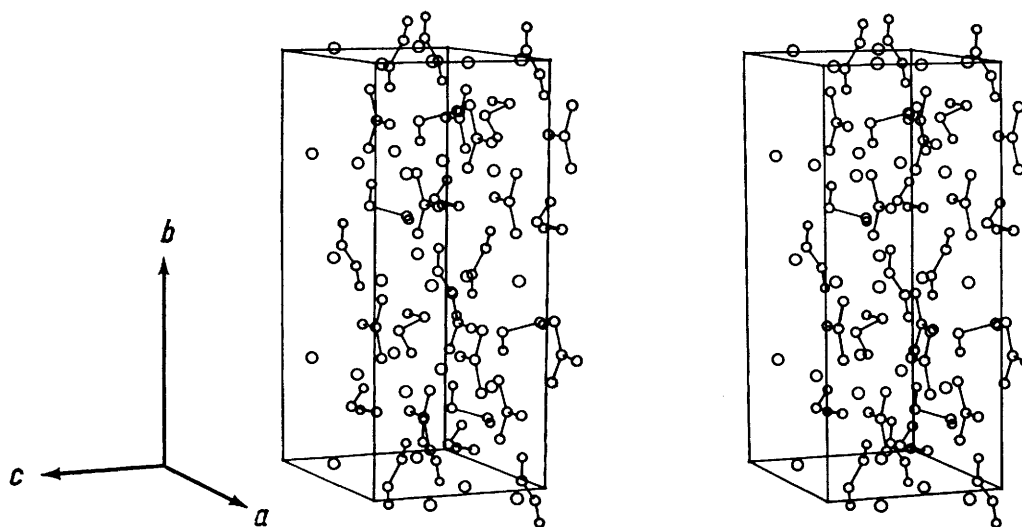


FIGURE 2 A stereoscopic view of the crystal structure. For the sake of clarity, only one possible orientation of the hydrogen peroxide molecules is shown for each site

$\text{Na}(2)$ has six close oxygen neighbours (after allowing for disorder) from carbonate ions and hydrogen peroxide molecules. Its co-ordination can be described as distorted octahedral. In the case of $\text{Na}(1)$ the distortion

atom forms one moderately strong hydrogen bond ($\text{O} \cdots \text{O}$ 2.54–2.65 Å) to a hydrogen peroxide molecule, and also forms part of the co-ordination sphere of two sodium ions. The C-O distances are similar to those

found for hydrogen-bonded C–O in $\text{Na}_2[\text{CO}_3]\cdot\text{H}_2\text{O}$ (1.285 and 1.299 Å)¹⁷ and in $\text{K}_2[\text{CO}_3]\cdot 1.5\text{H}_2\text{O}$ (1.288 and 1.296 Å).¹⁸

It is not surprising that the hydrogen peroxide molecules are disordered. Figure 3 shows that in both sites the molecule can adopt either of two positions with equal probability, being anchored to the same two carbonate ions (*via* hydrogen bonds). This disorder and the consequent difficulties in refinement reduce the accuracy with which this part of the structure can be described. Nevertheless, a clear difference in the dihedral angle ϕ of the molecules occupying the two sites

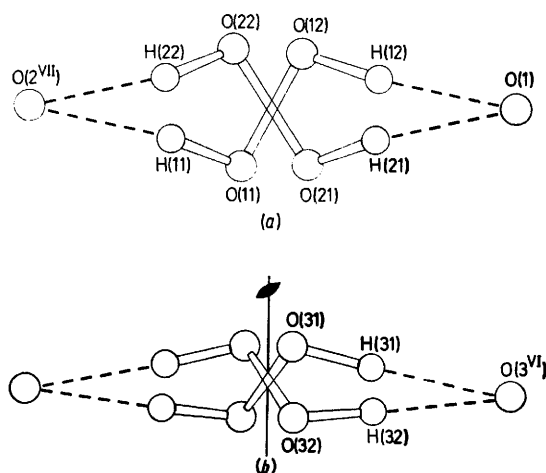


FIGURE 3 Disorder of the hydrogen peroxide molecules: (a) the general eight-fold position; (b) the four-fold position astride a two-fold axis. The hydrogen peroxide molecules are viewed normal to the *c* axis and to the line joining the two acceptor oxygen atoms. (Superscripts have the same meaning as in Table 2)

emerges. In the case of the eight-fold position the two independent values of ϕ are 120 and 129°, while for the other site ϕ is 168°, *i.e.* this molecule is nearly planar. If values of the dihedral angle involving the acceptor oxygens are calculated, the corresponding figures are 132 and 136°, and 173°. These are slightly larger than the equivalent ϕ , a situation found¹⁹ for instance in $[\text{NH}_4]_2[\text{C}_2\text{O}_4]\cdot\text{H}_2\text{O}_2$ where ϕ (acceptor) is larger than ϕ by 7°. Although the positions of the acceptor oxygen atoms are determinable much more precisely than those of the hydrogen atoms, there is no necessity for the O–H–O angle to be strictly 180°. The acceptor dihedral angle is therefore probably no more accurate a guide to the value of ϕ than the directly measured value.

Thus eight molecules in the unit cell are skewed with ϕ *ca.* 125°, while four are nearly planar with ϕ *ca.* 170°. This difference between the molecules can be related to their different interaction with sodium and carbonate ions. In the case of the skewed H_2O_2 , apart from taking

part in a hydrogen bond, each oxygen atom interacts with two sodium ions. On the other hand, for the nearly planar molecule, apart from hydrogen bonding, each oxygen atom interacts strongly with only one sodium ion, and this ion is fairly close to the 'plane' of the molecule.

Dihedral angles similar to those in this structure have been found¹⁹ for $[\text{NH}_4]_2[\text{C}_2\text{O}_4]\cdot\text{H}_2\text{O}_2$ (ϕ 121°), while strictly planar H_2O_2 molecules occur²⁰ in $\text{Li}_2[\text{C}_2\text{O}_4]\cdot\text{H}_2\text{O}_2$ and $\text{Na}_2[\text{C}_2\text{O}_4]\cdot\text{H}_2\text{O}_2$.²¹ The presence of both skewed and planar hydrogen peroxide within the same unit cell has not before been demonstrated. However, since the barrier to rotation of H_2O_2 from its preferred skewed conformation of 90.2° in the free molecule²² to the *trans*-planar form is only *ca.* 5 kJ mol⁻¹,²³ the adoption by the molecule of intermediate conformations due to hydrogen-bonding and ion–dipole interactions is not surprising.

Vibrational Spectra.—Since the disorder in the hydrogen peroxide molecules prevents as accurate a determination of their conformation as we would have wished, we have studied the vibrational spectra of solid $\text{Na}_2[\text{CO}_3]\cdot 1.5\text{H}_2\text{O}_2$, $\text{Na}_2[\text{CO}_3]\cdot 1.5^3\text{H}_2\text{O}_2$, and $\text{Na}_2[^{13}\text{CO}_3]\cdot 1.5\text{H}_2\text{O}_2$ at high resolution at –150 and 25 °C in order to supplement our data. In particular, we wished to establish whether the molecules in the four-fold positions are strictly planar or not.

The bands due to H_2O_2 in the compound are identified by their shifts on deuteration and immobility on ¹³C substitution. We follow previous practice in spectroscopic studies of 'perhydrates'^{24–26} by using the six normal modes²⁷ [symmetric and asymmetric O–H stretches (ν_1 and ν_5), deformations (ν_2 and ν_6), the torsion (ν_4), and the O–O stretch (ν_3)] of H_2O_2 as approximate descriptions for corresponding modes of the hydrogen-bonded H_2O_2 . The observed bands are listed in Table 3. The Raman modes are intrinsically weak and broad, with the exception of ν_3 , but the i.r. modes show a systematic splitting of each band into a doublet (with the exception of ν_6 which is obscured by the ν_3 carbonate vibration). The bands due to ν_1 – ν_3 each have a weak and a strong component, whereas those of ν_4 and ν_5 have components of comparable intensities.

These splittings could arise from site symmetry or intra-unit-cell coupling, but although neither possibility can be excluded such splitting is not observed in other 'perhydrates' (*e.g.* $\text{M}^I_2[\text{C}_2\text{O}_4]\cdot\text{H}_2\text{O}_2$ ^{24,25} and $\text{CO}(\text{NH}_2)_2\cdot\text{H}_2\text{O}_2$ ²⁶) where only one type of peroxide is present; nor would the observed alternation of intensities be expected. Instead, we attribute the effect to the presence of two types of peroxide. In the first, which gives rise to the strong i.r. components of ν_1 – ν_6 , the H_2O_2 is considerably skewed and the intensity of ν_3 relative to the

²² W. R. Busing and H. A. Levy, *J. Chem. Phys.*, 1965, **42**, 3054.

²³ C. S. Ewig and D. O. Harris, *J. Chem. Phys.*, 1970, **52**, 6268.

²⁴ B. F. Pedersen, *Acta Chem. Scand.*, 1967, **21**, 801.

²⁵ J. L. Arnau and P. A. Giguère, *Canad. J. Chem.*, 1969, **47**, 3745.

²⁶ J. L. Arnau and P. A. Giguère, *J. Mol. Structure*, 1969, **3**, 483.

²⁷ P. A. Giguère, *J. Chem. Phys.*, 1950, **18**, 88.

¹⁷ B. Dickens, F. A. Mauer, and W. E. Brown, *J. Res. Nat. Bur. Stand., Sect. A*, 1970, **74**, 319.

¹⁸ F. D. Hunter and G. A. Jeffrey, *J. Chem. Phys.*, 1967, **47**, 3297.

¹⁹ B. F. Pedersen, *Acta Cryst.*, 1972, **B28**, 746.

²⁰ B. F. Pedersen, *Acta Chem. Scand.*, 1969, **23**, 1871.

²¹ B. F. Pedersen and B. Pedersen, *Acta Chem. Scand.*, 1964, **18**, 1454.

other modes in the i.r. is comparable with that in $[\text{NH}_4]_2\text{[C}_2\text{O}_4]\cdot\text{H}_2\text{O}_2$ where ϕ is 121° .¹⁹ As expected for a skewed (C_2) H_2O_2 , all the six modes are active in the Raman and i.r. The second type of peroxide gives rise to the weaker components of $\nu_1-\nu_3$ in the i.r. and to the second of each of the split bands in ν_4 and ν_5 . For a truly

observed in the oxalate 'perhydrates',¹⁹ and in close agreement with the values obtained from the X-ray data.

Bleaching Action of the Compound.—The crystal structure shows unequivocally that the H_2O_2 is hydrogen bonded, and clearly will be instantly released when the compound is dissolved in water. Thus 'sodium per-

TABLE 3

Infrared and Raman spectra (cm^{-1}) of $\text{Na}_2[\text{CO}_3]\cdot 1.5\text{H}_2\text{O}_2$ and its deuterate recorded at 25°C . Raman bands are given in parentheses

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$\text{Na}_2[\text{CO}_3]\cdot 1.5\text{H}_2\text{O}_2$	3 050w, 2 900m (2 900w)	1 550m ^a (1 552w)	873vw, 868w (873s, 869vs)	985m, 960s (988w)	2 720 (sh), 2 490s, 2 350m (2 600w)	<i>b</i>
$\text{Na}_2[\text{CO}_3]\cdot 1.5^2\text{H}_2\text{O}_2$	2 470w, 2 210m (2 200w)	1 130m ^a (1 136w)	873vw, 869w (871s, 869vs)	660m, 635s (670w, 655w)	1 940 (sh), 1 890s, 1 820m (1 970w)	1 040s, 1 035m <i>b</i>

^a Splits at -150°C into bands at 1 570w and 1 550 cm^{-1} (1 140w and 1 135 cm^{-1} for the deuterate). ^b Obscured by carbonate vibrations.

trans-planar (C_{2h}) H_2O_2 molecule, as found in $\text{Li}_2[\text{C}_2\text{O}_4]\cdot\text{H}_2\text{O}_2$ ²⁰ and $\text{Na}_2[\text{C}_2\text{O}_4]\cdot\text{H}_2\text{O}_2$,²¹ $\nu_1-\nu_3$ will be i.r. inactive (with $\nu_4-\nu_6$ i.r. active only); the fact that $\nu_1-\nu_3$ are present as weak bands only while their $\nu_4-\nu_6$ components are stronger is suggestive of a group in which the dihedral angle approaches 180° but does not reach it, *i.e.* a quasi-planar molecule. Thus the spectroscopic data support the X-ray evidence for the second H_2O_2 molecule being almost, but not quite, planar.

The positions of the bands are similar to those found in the oxalate 'perhydrates'; the low values of ν_1 and ν_5 suggest an O-H...O distance much shorter than in crystalline H_2O_2 ,²² comparable with the *ca.* 2.62 Å

carbonate' in this context is effectively a portable form of hydrogen peroxide. 'Sodium perborate,' which is used for similar purposes in some detergents, contains direct boron-peroxide bonds²⁸ rather than H_2O_2 of crystallisation so its mode of action could be somewhat different.

We thank Professor D. Rogers for the use of a diffractometer, Interlox Chemicals Ltd. and the S.R.C. for a C.A.S.E. award (to D. P. J.), and Comissão Permanente INVOTAN for the award of a Postgraduate Scholarship (to M. A. A. F. de C. T. C.).

[7/730 Received, 2nd May, 1977]

²⁸ A. Hansson, *Acta Chem. Scand.*, 1961, **15**, 934.