A Novel Tunnel Structure Containing Enclathrated Hydrogen Peroxide: $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$

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Summary A new type of tunnel structure is described in which guest molecules are disordered along, but tend to order in directions perpendicular to, the tunnel axis; one of the nine Na^+ ions in the asymmetric unit displays 8-fold co-ordination of a kind hitherto reported for this ion only in macrocyclic antibiotics.

WHEN sodium sulphate, sodium chloride, and hydrogen peroxide are combined [*e.g.*, 3 g NaCl dissolved in 20 cm^3 50% (w/w) H_2O_2 at 45 °C followed by addition of 5 g Na_2SO_4] a crystalline solid ($4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$) separates;[1] it possesses the remarkable property of being able to withstand a temperature of *ca.* 160 °C before the peroxide is evolved. We here report its crystal structure, which has been determined from microdensitometer data (1950 reflections reduced to 350 unique intensities) using MULTAN 76[2] and refined with CRYLSQ.[3] The space group is $P4/mnc$ ($P4nc$ gave poorer agreement with less satisfactory bond lengths), $a = 10{\cdot}53(1)$, $c = 8{\cdot}42(1)$ Å, $Z = 2$; $D_m = 2{\cdot}44$, $D_c = 2{\cdot}47$ g cm^{-3}; $R = 0{\cdot}071$. The crystal structure has several noteworthy features.

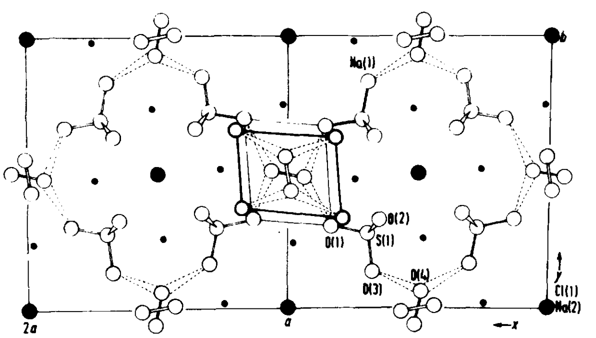

FIGURE 1. Projection of the structure onto (001) from $z = 0{\cdot}0$ to $z = 0{\cdot}5$. A left-handed system of axes has been used. Positive c is therefore towards the reader. Around one of the sets of disordered hydrogen peroxide guests the full number of the cage oxygen atoms is shown. (The four oxygen atoms in bold lines are from sulphate groups at $\frac{1}{2}+z$ relative to those depicted in full). The dotted lines represent hydrogen bond distances from the H_2O_2 oxygen atoms. It is noteworthy that each peroxide oxygen is close to two distinct tunnel oxygens (2·71 and 2·86 Å).

Firstly (see Figure 1), although eight of the nine Na^+ ions in the molecule possess the expected distorted octahedral co-ordination [five oxygen atoms, r(Na · · · O) range from 2·25(2) to 2·65(2) Å; one chlorine atom, r(Na · · · Cl) = 3·016(9) Å], the other has a co-ordination number of eight [a tetragonal prismatic array of oxygen atoms, r(Na · · · O) = 2·565(8) Å] not hitherto reported for sodium ions in such simple compounds (contrast the 8-fold co-ordination with six coplanar oxygen atoms displayed by the Na^+–crown ether complexes[4]). Such a co-ordination does, however, occur around Na^+ and K^+ ions in certain macrocyclic antibiotics.[5]

Secondly, the tunnels (lined with oxygen atoms of the sulphate groups) running parallel to c (see Figure 2), contain H_2O_2 in an apparently disordered state. Preliminary dielectric loss measurement indicates that reorientation of the guest species occurs at *ca.* 10^3 Hz at room temperature. Thirdly, there are strong superlattices in both directions perpendicular to c, each dimension of the superlattice being four times that of the subcell (*i.e.*, the structure reported here) mesh, *i.e.*, 42·06 Å. The implication is that some ordering of the hydrogen peroxide occurs parallel to a and b. This is consistent with the lack of evidence of diffuse reflections and it is therefore possible that the apparent disorder of the H_2O_2 is an artefact due to this structure being a subcell of the true structure.

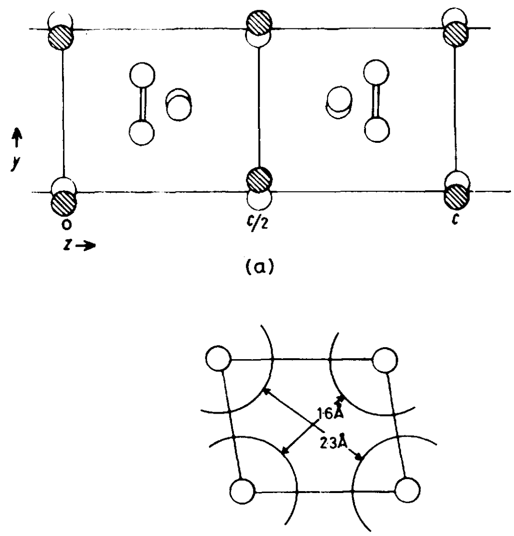

FIGURE 2. (a) Projection of one of the tunnels onto (100). (There is only one H_2O_2 molecule at each site; to convey the nature of the disorder, however, two are shown). (b) A section through the four oxygen atoms defining the tunnel at height $z = 0$ [see (a)]. It can be seen that the space available is too small to allow the free passage of H_2O_2 molecules along the tunnel (see also central part of Figure 1).

All attempts to form other alkali metal halide analogues of this compound, and to enclathrate other guests into the sulphate–chloride host have failed. Fuller accounts of the structure, as well as of the dielectric properties of the solid will be published elsewhere.

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The structure of the industrial bleach, sodium percarbonate ($Na_2CO_3 . 1\frac{1}{2}H_2O_2$) has recently been reported[6] and is similar to the title compound in that the hydrogen peroxide molecules are again orientationally disordered.

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[1] German Patent Application: 2,530,539, Kao Soap Co. Ltd. and Nippon Peroxide Co. Ltd., 9th July 1975. (We are grateful to Dr. T. G. Jones and his colleagues for drawing our attention to this reference).
[2] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.
[3] J. M. Stewart, G. J. Kruger, H. L. Ammon, C. H. Dickinson, and S. R. Hall, The XRAY System—version of June 1972, update of April 1974, Technical Report TR-192, Computer Science Center, University of Maryland, College Park, Maryland.
[4] M. Mercer and M. R. Truter, *J.C.S. Dalton*, 1973, 2215.
[5] B. T. Kilbourne, J. D. Dunitz, L. A. R. Pioda, and W. Simon, *J. Mol. Biol.*, 1967, **30**, 559; M. Dobler and R. P. Phizackerley, *Helv. Chim. Acta*, 1974, **57**, 664; T. Sakamaki, Y. Iitaka, and Y. Nawata, *Acta Cryst.*, 1976, **B32**, 768.
[6] J. M. Adams and R. G. Pritchard, *Acta Cryst.*, 1977, **B33**, 3650; M. A. A. F. de C. T. Carrondo, W. P. Griffith, D. P. Jones, and A. C. Skapski, *J.C.S. Dalton*, 1977, 2323.