

# Structures of $\text{Na}_9[\text{SO}_4]_4\text{X}\cdot 2\text{H}_2\text{O}_2$ , where $\text{X} = \text{Cl}$ or $\text{Br}$ , in which the halide anions orchestrate extended orientation sequences of $\text{H}_2\text{O}_2$ solvate molecules

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Detailed structures of nonasodium tetrakis(sulfate) chloride diperhydrate,  $\text{Na}_9[\text{SO}_4]_4\text{Cl}\cdot 2\text{H}_2\text{O}_2$ , and its novel bromide analogue are compared. Hydrogen peroxide could not be resolved in a previously reported  $\text{Na}_9[\text{SO}_4]_4\text{Cl}\cdot 2\text{H}_2\text{O}_2$  substructure [tetragonal,  $P4/mnc$ ; Adams *et al.* (1978), *J. Chem. Soc. Chem. Commun.* p. 288; Adams & Pritchard (1978), *Acta Cryst.* B34, 1428–1432]. However, on lowering the symmetry to  $P4/n$ , and using reflection data based on full unit-cells, the  $\text{H}_2\text{O}_2$  solvate can be clearly seen. Although  $\text{H}_2\text{O}_2$  molecules are not directly bonded to the halide anions, they exert considerable influence on the eight sodium cations that constitute each halide's coordination shell so that  $\text{H}_2\text{O}_2$  ordering can be linked to halide dimensions.

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## 1. Introduction

The title compounds belong to a class of solids in which hydrogen peroxide simultaneously coordinates to alkali metal cations and hydrogen bonds to oxy-acid anions. These include commercially important sodium percarbonate,  $\text{Na}_2(\text{CO}_3)\cdot 1.5\text{H}_2\text{O}_2$  (Pritchard & Islam, 2003), and the extensively studied alkali metal oxalates  $M_2(\text{C}_2\text{O}_4)\cdot \text{H}_2\text{O}_2$  ( $M = \text{Li}, \text{Na}, \text{K}$  and  $\text{Rb}$ ; Pedersen, 1969; Pedersen & Pedersen, 1964; Pedersen & Kvick, 1989, 1990; Adams *et al.*, 1980*a,b*). A previous crystallographic investigation of  $\text{Na}_9[\text{SO}_4]_4\text{Cl}\cdot 2\text{H}_2\text{O}_2$  yielded a subcell structure (Adams *et al.*, 1978; Adams & Pritchard, 1978) in which the  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions can be seen, but in which the  $\text{H}_2\text{O}_2$  site is obscured by disorder. This led to continued speculation (Adams *et al.*, 1981; Cosgrove & Jones, 1998*a,b,c*) about the role of  $\text{H}_2\text{O}_2$  in the architecture of this exceptionally stable compound (Kao Soap Co. Ltd & Nippon Peroxide Co. Ltd, 1975).

The current investigation was initiated in order to address this last point and extended to include the bromide analogue, which was discovered during preliminary crystallization studies.

## 2. Experimental

### 2.1. Synthesis

The title compounds were prepared by dissolving sodium sulfate and sodium halide in 4:1 molar ratios in 30% w/w hydrogen peroxide and leaving the solution to evaporate over 48 h.

**Table 1**  
Experimental details.

|  | Cl  | Br   |
|--|---|--|
| Crystal data   |   |  |
| Chemical formula   | H <sub>4</sub> ClNa <sub>9</sub> O <sub>20</sub> S <sub>4</sub>                     | H <sub>4</sub> BrNa <sub>9</sub> O <sub>20</sub> S <sub>4</sub>                    |
| <i>M<sub>r</sub></i>   | 694.63  | 739.09   |
| Cell setting, space group  | Tetragonal, <i>P4/n</i>   | Tetragonal, <i>P4/n</i>  |
| <i>a</i> , <i>c</i> (Å)  | 29.6829 (3), 8.40180 (10)   | 14.9126 (5), 8.4052 (2)  |
| <i>V</i> (Å <sup>3</sup> )   | 7402.61 (14)  | 1869.20 (10)   |
| <i>Z</i>   | 16  | 4  |
| <i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )   | 2.493   | 2.626  |
| Radiation type   | Mo <i>Kα</i>  | Mo <i>Kα</i>   |
| No. of reflections for cell parameters   | 87 529  | 5097   |
| $\theta$ range (°)   | 1.0–27.5  | 1.0–32.0   |
| $\mu$ (mm <sup>-1</sup> )  | 0.97  | 2.96   |
| Temperature (K)  | 150 (2)   | 150 (2)  |
| Crystal form, colour   | Plate, colourless   | Prism, colourless  |
| Crystal size (mm)  | 0.1 × 0.1 × 0.05  | 0.18 × 0.18 × 0.07   |
| Data collection  |   |  |
| Diffractometer   | KappaCCD  | KappaCCD   |
| Data collection method   | CCD rotation images, thick slices   | CCD rotation images, thick slices  |
| Absorption correction  | Multi-scan (based on symmetry-related measurements)                                 | Multi-scan (based on symmetry-related measurements)                                |
| <i>T<sub>min</sub></i>   | 0.909   | 0.618  |
| <i>T<sub>max</sub></i>   | 0.953   | 0.820  |
| No. of measured, independent and observed reflections  | 65 291, 8402, 4855  | 8459, 3226, 2368   |
| Criterion for observed reflections   | <i>I</i> > 2σ( <i>I</i> )   | <i>I</i> > 2σ( <i>I</i> )  |
| <i>R<sub>int</sub></i>   | 0.090   | 0.049  |
| $\theta_{max}$ (°)   | 27.5  | 32.0   |
| Range of <i>h</i> , <i>k</i> , <i>l</i>  | –38 ⇒ <i>h</i> ⇒ 37<br>–38 ⇒ <i>k</i> ⇒ 38<br>–10 ⇒ <i>l</i> ⇒ 10                   | –18 ⇒ <i>h</i> ⇒ 21<br>–22 ⇒ <i>k</i> ⇒ 12<br>–12 ⇒ <i>l</i> ⇒ 8                   |
| Refinement   |   |  |
| Refinement on  | <i>F</i> <sup>2</sup>   | <i>F</i> <sup>2</sup>  |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.061, 0.147, 1.24  | 0.040, 0.093, 1.07   |
| No. of reflections   | 8402  | 3226   |
| No. of parameters  | 649   | 164  |
| H-atom treatment   | Mixture of independent and constrained refinement                                   | Mixture of independent and constrained refinement                                  |
| Weighting scheme   | $w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 19.2938P]$ , where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 1.5967P]$ , where $P = (F_o^2 + 2F_c^2)/3$ |
| (Δ/σ) <sub>max</sub>   | 0.011   | 0.001  |
| Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )   | 0.59, –0.53   | 0.59, –0.64  |
| Extinction method  | None  | <i>SHELXL</i>  |
| Extinction coefficient   |   | 0.0047 (5)   |

Computer programs used: *Kappa-CCD* server software (Nonius, 1997), *COLLECT* (Nonius, 1998), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 1997), *SHELXL97* (Sheldrick, 1997), *Wingx* (Farrugia, 1999), *ORTEP* (Farrugia, 1997), *SORTAV* (Blessing, 1995, 1997).

## 2.2. Data collection, structure solution and refinement

All measurements were carried out using a Nonius Kappa-CCD diffractometer with graphite-monochromated Mo *Kα* radiation ( $\lambda = 0.71073$  Å). Details of cell parameters, data collection and refinement are summarized in Table 1,<sup>1</sup> together with a listing of the software employed.

Systematic absences and statistical tests clearly indicate the space group *P4/n* for both the chloride and bromide structures,

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE5022). Services for accessing these data are described at the back of the journal.

even though the diffraction patterns have very low intensity in regions that are not governed by the subcell.

The structures were solved by direct methods and refined with all data on *F*<sup>2</sup>. A weighting scheme based on  $P = [F_o^2 + 2F_c^2]/3$  was employed in order to reduce statistical bias (Wilson, 1976).

It did not prove necessary to restrain or constrain the refinements in any way, despite the pseudo-symmetric appearance of the structures.

## 3. Results and discussion

### 3.1. Crystallization characteristics

Na<sub>9</sub>[SO<sub>4</sub>]<sub>4</sub>X·2H<sub>2</sub>O<sub>2</sub>, where X = Cl or Br, crystallize as colourless squares when sodium sulfate and the appropriate sodium halide are dissolved in 30% w/w aqueous hydrogen peroxide and allowed to evaporate to dryness. Once formed the crystals are stable under ambient conditions.

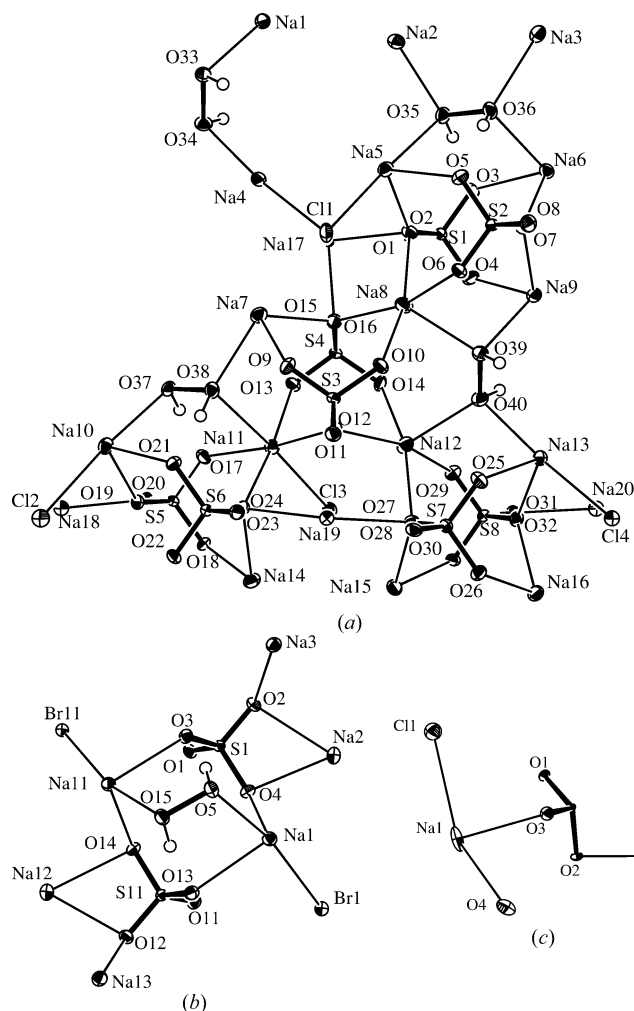
### 3.2. Supramolecular structures

Fig. 1 shows the asymmetric units of the title chloride and bromide structures as well as the previously reported chloride substructure. It clearly illustrates how the resolution of the H<sub>2</sub>O<sub>2</sub> molecules has dramatically increased the number of parameters that are needed to describe the structures. Interestingly, on application of the space-group symmetry the resulting packing diagrams, shown in Fig. 2, are almost identical except for the H<sub>2</sub>O<sub>2</sub> sites. The H<sub>2</sub>O<sub>2</sub> orientation sequence leads to the chloride *a* and *b* axes being double those of the bromide and 8<sup>1/2</sup> those of the chloride

substructure.

In order to answer the question of why the chloride and bromide structures have different H<sub>2</sub>O<sub>2</sub> orientation sequences, it is useful to focus on the distorted cubes with corners defined by six-coordinate Na<sup>+</sup> that form a sublattice (4 × 4 × 2 cubes for the bromide and 8 × 8 × 2 for the chloride). Each cube houses an SO<sub>4</sub><sup>2-</sup>, X<sup>-</sup>, or Na<sup>+</sup> ion, or an H<sub>2</sub>O<sub>2</sub> molecule. Sulfate anions form adjacent cubes from an eight-coordinate shell around each central Na<sup>+</sup> ion (Fig. 5). The SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>O<sub>2</sub> cubes each form stacks, generated by non-crystallographic glides down *c*. Those cubes containing central Na<sup>+</sup> and X<sup>-</sup> ions also stack down *c*, alternating their Na<sup>+</sup> and X<sup>-</sup> contents.

Importantly, the halide and hydrogen peroxide cubes share edges parallel to *c* (Fig. 2). Also, each hydrogen peroxide molecule is not located centrally within its cube, but straddles the top (*i.e.* perpendicular to the *c* axis) square face where it coordinates to four sodium cations and hydrogen bonds to two sulfate anions (Fig. 3, Table 2). The side of the Na<sup>+</sup> square over which the hydrogen bonding is directed distends and impinges on the corners of two neighbouring halide-containing cubes, distorting the halide environments. Travelling along an H<sub>2</sub>O<sub>2</sub> stack, *i.e.* along *c*, the direction of the hydrogen bonding is reversed at each level and hence the side of the square that is elongated, and is also reversed (Fig. 3). This has two repercussions on the shape of the halide-bearing sodium cubes: firstly, if a top corner is pushed in, the corner directly below is not; secondly, only half the corners of any cube can be pushed in. The four unique chloride ions and their surrounding sodium cubes are shown in Fig. 4 and, given the above conditions, represent all the possible distortions. In contrast, only distortions of the type seen around Cl<sub>2</sub>, which has *C*<sub>4</sub> symmetry, and Cl<sub>4</sub> with *S*<sub>4</sub> symmetry, are seen in the bromide



**Figure 1**  
Asymmetric unit of Na<sub>9</sub>[SO<sub>4</sub>]<sub>4</sub>Cl·2H<sub>2</sub>O<sub>2</sub> (top), its bromide analogue (bottom left) and subcell structure (bottom right)

**Table 2**

(a) Hydrogen bonds (Å, °) and Na—O coordination bonds (Å) involving H<sub>2</sub>O<sub>2</sub>; (b) H<sub>2</sub>O<sub>2</sub> geometry (Å, °).

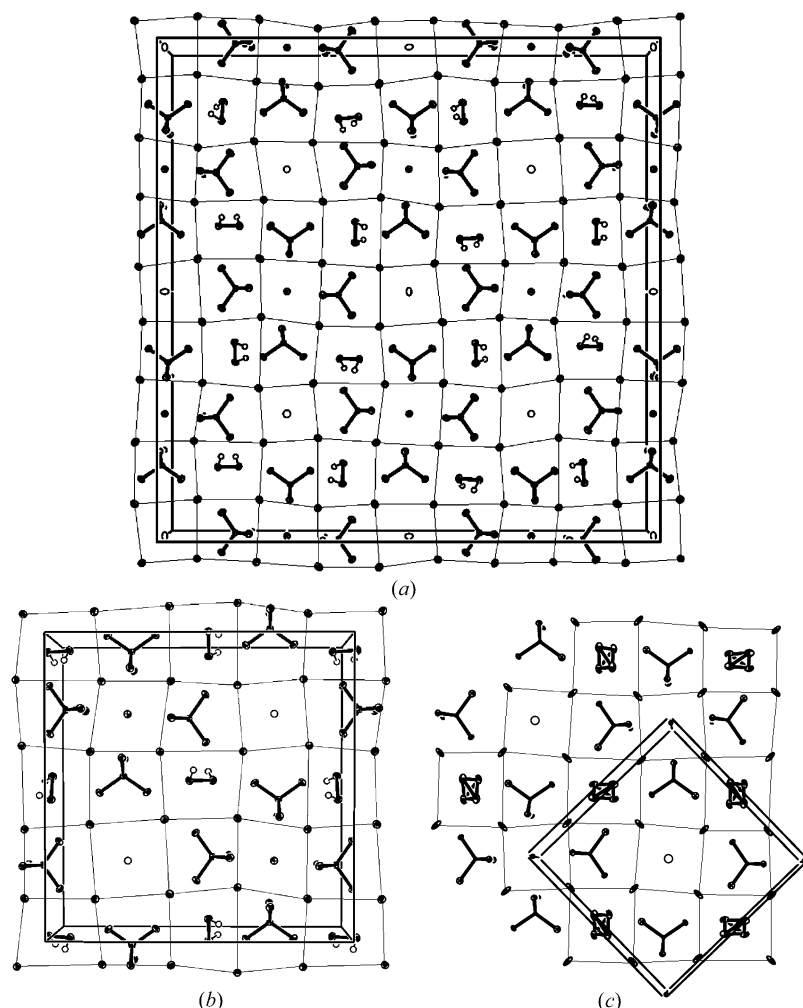
| (a)                          | <i>D</i> —H··· <i>A</i> | <i>d</i> ( <i>D</i> —H) | <i>d</i> (H··· <i>A</i> ) | <i>d</i> ( <i>D</i> ··· <i>A</i> ) | ∠( <i>D</i> H <i>A</i> ) | Na—O |
|------------------------------|-------------------------|-------------------------|---------------------------|------------------------------------|--------------------------|------|
| Cl                           |                         |                         |                           |                                    |                          |      |
| O33—H33···O10 <sup>i</sup>   | 1.00 (6)                | 1.70 (6)                | 2.676 (4)                 | 164 (5)                            | 2.413 (3),<br>2.364 (3)  |      |
| O34—H34···O14 <sup>ii</sup>  | 0.97 (6)                | 1.81 (5)                | 2.706 (4)                 | 152 (5)                            | 2.408 (3),<br>2.408 (3)  |      |
| O35—H35···O3                 | 0.85 (4)                | 1.83 (4)                | 2.677 (4)                 | 169 (4)                            | 2.353 (3),<br>2.403 (3)  |      |
| O36—H36···O5                 | 0.82 (5)                | 1.92 (5)                | 2.711 (4)                 | 162 (5)                            | 2.399 (3),<br>2.413 (3)  |      |
| O37—H37···O17                | 0.95 (6)                | 1.77 (6)                | 2.700 (4)                 | 167 (5)                            | 2.410 (3),<br>2.406 (3)  |      |
| O38—H38···O21                | 0.98 (7)                | 1.71 (7)                | 2.677 (4)                 | 171 (5)                            | 2.420 (3),<br>2.363 (3)  |      |
| O39—H39···O26 <sup>iii</sup> | 0.89 (5)                | 1.84 (5)                | 2.696 (4)                 | 159 (5)                            | 2.407 (3),<br>2.394 (3)  |      |
| O40—H40···O30 <sup>iv</sup>  | 1.03 (7)                | 1.71 (6)                | 2.687 (4)                 | 157 (6)                            | 2.374 (3),<br>2.414 (3)  |      |
| Br                           |                         |                         |                           |                                    |                          |      |
| O5—H5···O3                   | 0.85 (2)                | 1.86 (3)                | 2.695 (2)                 | 166 (3)                            | 2.399 (2),<br>2.391 (2)  |      |
| O15—H15···O13                | 0.86 (4)                | 1.86 (4)                | 2.688 (2)                 | 161 (4)                            | 2.380 (2),<br>2.379 (2)  |      |

| (b)      | O—O       | O—O—H            | H—O—O—H (°) |
|----------|-----------|------------------|-------------|
| Cl       |           |                  |             |
| O33, O34 | 1.465 (3) | 98 (3), 105 (3)  | −114 (3)    |
| O35, O36 | 1.466 (3) | 97 (3), 101 (3)  | −107 (3)    |
| O37, O38 | 1.465 (3) | 100 (3), 100 (4) | −98 (4)     |
| O39, O40 | 1.459 (3) | 101 (3), 105 (3) | −112 (3)    |
| Br       |           |                  |             |
| O5, O15  | 1.458 (2) | 102 (2), 102 (3) | 106 (3)     |

Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $1 - x, 1 - y, -z$ ; (iii)  $\frac{1}{2} + y, 1 - x, 1 - z$ ; (iv)  $\frac{1}{2} + y, 1 - x, -z$ .

structure. A comparison of the Na—*X* bond lengths from these two sites, presented in Table 3, show that the larger bromide anion is able to interact more effectively with all eight Na<sup>+</sup> cations than the smaller chloride anion in the *C*<sub>4</sub> site. The difference between the bromide and chloride structure seems to hinge on the larger halide's tendency to promote *C*<sub>4</sub> coordination, which would, however, destroy the crystal's tetragonal symmetry if used exclusively. The combination of *C*<sub>4</sub> and *S*<sub>4</sub> sites seen in the bromide enable it to retain tetragonal symmetry, whilst doubling the occurrence of what is, presumably, a favourable halide environment for the larger bromide anion.

Unlike sodium percarbonate (Pritchard & Islam, 2003), the current structures show no evidence of disordered H<sub>2</sub>O<sub>2</sub>. In sodium percarbonate dynamic H<sub>2</sub>O<sub>2</sub> disorder becomes complete above 240 K, however, no disorder is observed in Na<sub>9</sub>[SO<sub>4</sub>]<sub>4</sub>Cl·2H<sub>2</sub>O<sub>2</sub>, even when the temperature is raised to 300 K.


**Figure 2**

Perspective view of half a unit cell of  $\text{Na}_9[\text{SO}_4]_4\text{Cl}\cdot 2\text{H}_2\text{O}_2$  ( $c/2$ ) on the  $ab$  plane (top), bromide analogue (bottom left) and subcell structure (bottom right). The sublattice, defined by distorted  $\text{Na}^+$  cubes, has been highlighted in each case.  $\text{Na}^+$  ions are represented by filled ellipses and the  $\text{X}^-$  ions by empty ellipses.

### 3.3. Molecular conformations and dimensions

Although the sulfate anions in both structures conform to the expected tetrahedral geometry they all display minor systematic deviations, which are related to crystal packing interactions.

In the chloride the 32 crystallographically unique S—O bonds can be divided into two groups with those involved in hydrogen bonding to  $\text{H}_2\text{O}_2$  being longer [1.488 (3)–1.492 (3) Å] than the remainder [1.456 (3)–1.484 (3) Å]. A similar picture is seen in the bromide where the hydrogen-bonding S—O bonds of 1.492 (2) and 1.494 (2) Å are clearly distinguished from the shorter non-hydrogen bonding variety of 1.467 (2)–1.479 (2) Å.

The O—S—O angles do not deviate substantially from the expected tetrahedral value, falling in the range 108.1 (2)–110.6 (2)°, however, there is a demarcation within this group with sulfate O atoms that participate in the eight-fold coordination of sodium cations (Fig. 5) subtending the smaller O—S—O bond angles [108.1 (2)–108.7 (2)°]. An identical situa-

tion arises in the bromide, where the O—S—O angles range from 108.5 (1) to 110.1 (1)°, but those involved in the eightfold coordination of sodium are both 108.5 (1)°.

The peroxide O—O bond lengths are presented in Table 2 and show that the chloride values of 1.459 (3)–1.466 (3) Å, average 1.464 Å, are in good agreement with the single bromide O—O bond of 1.458 (2) Å. All these bonds are slightly shorter than an equivalent bond in sodium percarbonate, which was determined to be 1.4785 (8) Å at 150 K, but are well within the range, 1.439 (15)–1.509 (7) Å, defined by alkali-metal oxalate monoperhydrates.

HOOH torsion angles vary from  $-98$  (4) to  $-114$  (3)° in the chloride, but their average,  $-108^\circ$ , is a good match for the bromide value of  $106$  (3)°. All these values coincide with the staggered minimum energy conformation that was identified

from gas-phase spectroscopic measurements (Hunt *et al.*, 1965).

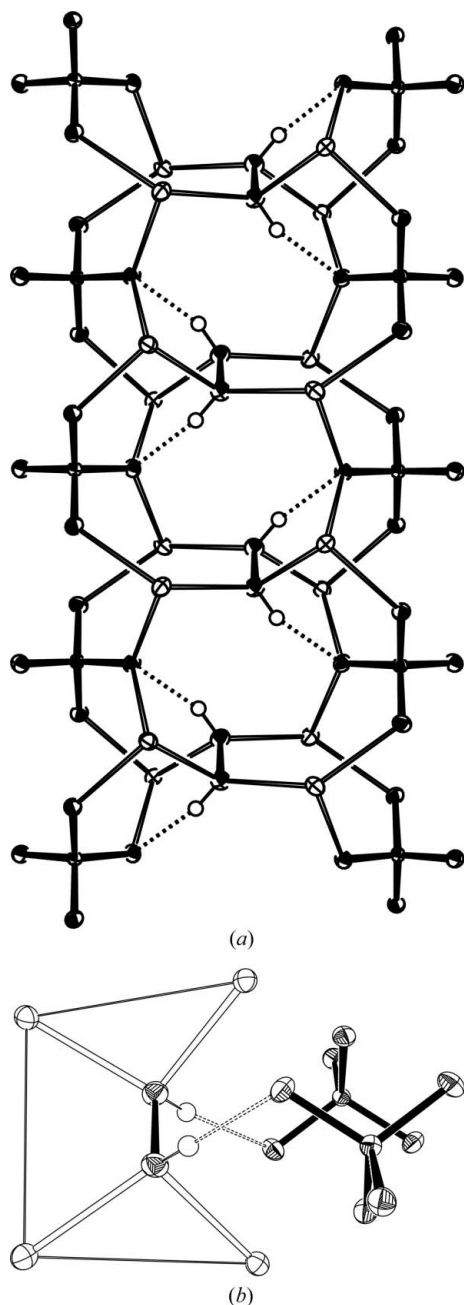
The O—H bonds fall in the range 0.82 (5)–1.03 (7) Å in the chloride and 0.85 (2), 0.86 (4) Å in the bromide, showing good agreement with the analogous bonds in the oxalate perhydrates [0.83 (10)–1.0117 (5) Å].<sup>2</sup> Also at 97 (3)–105 (3)° in the chloride and 102 (3)° in the bromide the OOH angles show excellent agreement with the oxalate values of 97 (3)–104 (5)°.

## 4. Conclusions

Despite the rather elaborate pattern of  $\text{H}_2\text{O}_2$  orientations within the above structures, each  $\text{H}_2\text{O}_2$  site is identical (or nearly identical) as well as optimal in terms of  $\text{H}_2\text{O}_2$  conformation, coordination and hydrogen bonding. In contrast to the alkali metal oxalate perhydrates, the title perhydrates do not form analogous hydrates.  $\text{H}_2\text{O}_2$  must template these structures

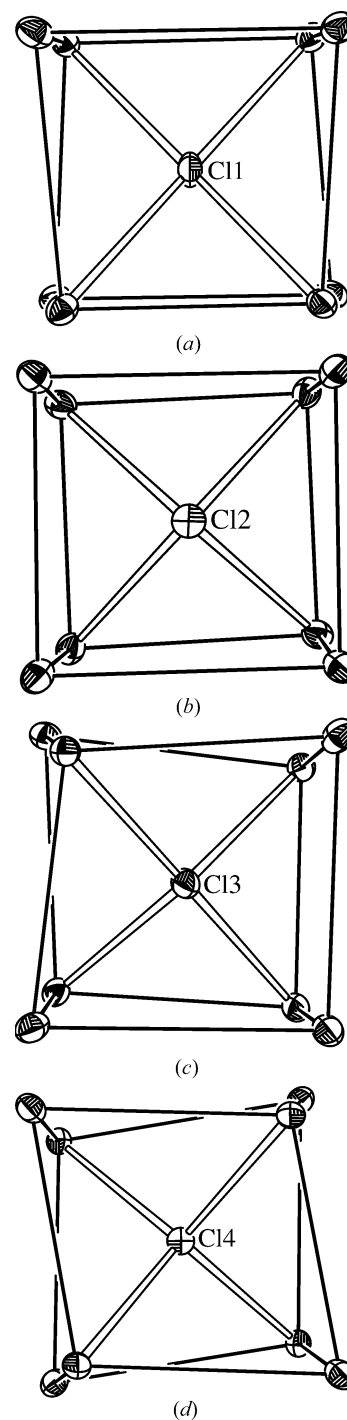
<sup>2</sup> Determined using neutrons.

in a very specific way as crystallization from water yields a mixture of sodium halide and sodium sulfate. This is somewhat surprising, given that both sodium sulfate fluoride [Kogarkoite,  $\text{Na}_3(\text{SO}_4)\text{F}$ ]; Fanfani *et al.*, 1980] and sodium sulfate fluoride chloride [ $[\text{Na}_6(\text{SO}_4)_2\text{FCl}$ , sulphohalite; Sakamoto, 1968] are known. In these structures the halide is octahedrally coordinated by sodium cations, matching its geometry in NaF or NaCl. Also, as each sulfate coordinates to 12 sodium cations (three per oxygen), an octahedral geometry is maintained around each cation. The sodium octahedra that surround each halide share faces with the 12-pointed polyhedra that encase



**Figure 3**  
 $\text{H}_2\text{O}_2$  environment in  $\text{Na}_9[\text{SO}_4]_4\text{X}\cdot 2\text{H}_2\text{O}_2$ . Projections down (a) **a** and (b) **b**. The *c* axis is directed up the page in the top view.

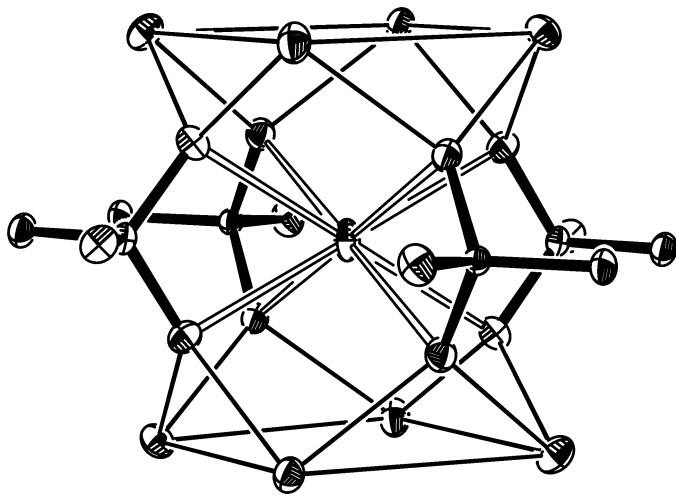
the sulfate anions, a truncated trigonal bipyramid for Kogarkoite and truncated cube for sulphohalite. In sulphohalite the halide octahedra share corners to form a three-dimensional orthogonal grid with alternating F and Cl anions so that the unit-cell dimension in this cubic structure corresponds directly to the sum of the bond distances in the Na–Cl–Na–F–Na sequence. If fluoride is replaced with chloride the unit cell and,



**Figure 4**  
 The four  $\text{Cl}^-$  environments in  $\text{Na}_9[\text{SO}_4]_4\text{Cl}\cdot 2\text{H}_2\text{O}_2$  viewed down **c**. Referring to how many  $\text{Na}^+$  are pushed in on the top and bottom faces of the cube, the four configurations are 2–2, 0–4, 1–3 and diagonal 2–2.

**Table 3**  
Na—X bond lengths (Å) in the C<sub>4</sub> and S<sub>4</sub> sites of Na<sub>9</sub>[SO<sub>4</sub>]<sub>4</sub>X·2H<sub>2</sub>O<sub>2</sub>.

| C <sub>4</sub> site |           | S <sub>4</sub> site |           |
|---------------------|-----------|---------------------|-----------|
| Cl2—Na10            | 2.845 (2) | Cl4—Na13            | 2.747 (2) |
| Cl2—Na3             | 3.186 (2) | Cl4—Na16            | 3.309 (2) |
| Br11—Na11           | 2.942 (1) | Br1—Na1             | 2.847 (1) |
| Br11—Na13           | 3.177 (1) | Br1—Na3             | 3.287 (1) |



**Figure 5**  
Eight-fold coordination shell of central sodium cation involving four SO<sub>4</sub><sup>2-</sup> anions.

consequently, the sodium polyhedra around the sulfate would expand, making it harder for the sulfate to span all 12 cations. This does not happen and, given the scenario of a system where full coordination of the cations becomes difficult due to steric effects, it is not surprising that hydrogen peroxide, with its excess of lone pairs, is able to create a niche for itself.

Initially, interest in perhydrates centred on their commercial application as bleaches, but more recent research has employed them as a convenient and safe method of introducing anhydrous hydrogen peroxide to chemical reactions (Jones, 1999). This work included extensive studies on their use in the presence of bromide ions to oxidize and brominate substituted toluenes (Jones *et al.*, 1996) and suggests that it

would be worthwhile to test Na<sub>9</sub>[SO<sub>4</sub>]<sub>4</sub>Br·2H<sub>2</sub>O<sub>2</sub> as a combined H<sub>2</sub>O<sub>2</sub>/Br<sup>-</sup> source.

We would like to thank the EPSRC for purchasing the Nonius Kappa CCD diffractometer.

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