

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 Br , in which the halide anions orchestrate extended orientation sequences of H_2O_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 H_2O_2 solvate can be clearly seen. Although H_2O_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 H_2O_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 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 Na^+ , Cl^- and SO_4^{2-} ions can be seen, but in which the H_2O_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 H_2O_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 ₄ ClNa ₉ O ₂₀ S ₄	H ₄ BrNa ₉ O ₂₀ S ₄
<i>M_r</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 ³)	7402.61 (14)	1869.20 (10)
<i>Z</i>	16	4
<i>D_x</i> (Mg m ⁻³)	2.493	2.626
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	87 529	5097
θ range (°)	1.0–27.5	1.0–32.0
μ (mm ⁻¹)	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_{min}</i>	0.909	0.618
<i>T_{max}</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_{int}</i>	0.090	0.049
θ_{max} (°)	27.5	32.0
Range of <i>h</i> , <i>k</i> , <i>l</i>	–38 ⇒ <i>h</i> ⇒ 37 –38 ⇒ <i>k</i> ⇒ 38 –10 ⇒ <i>l</i> ⇒ 10	–18 ⇒ <i>h</i> ⇒ 21 –22 ⇒ <i>k</i> ⇒ 12 –12 ⇒ <i>l</i> ⇒ 8
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <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) _{max}	0.011	0.001
Δρ _{max} , Δρ _{min} (e Å ⁻³)	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 *K*α radiation ($\lambda = 0.71073$ Å). Details of cell parameters, data collection and refinement are summarized in Table 1,¹ 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,

¹ 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*². 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

Na₉[SO₄]₄X·2H₂O₂, 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 H₂O₂ 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 H₂O₂ sites. The H₂O₂ orientation sequence leads to the chloride *a* and *b* axes being double those of the bromide and 8^{1/2} those of the chloride

substructure.

In order to answer the question of why the chloride and bromide structures have different H₂O₂ orientation sequences, it is useful to focus on the distorted cubes with corners defined by six-coordinate Na⁺ that form a sublattice (4 × 4 × 2 cubes for the bromide and 8 × 8 × 2 for the chloride). Each cube houses an SO₄²⁻, X⁻, or Na⁺ ion, or an H₂O₂ molecule. Sulfate anions form adjacent cubes from an eight-coordinate shell around each central Na⁺ ion (Fig. 5). The SO₄²⁻ and H₂O₂ cubes each form stacks, generated by non-crystallographic glides down *c*. Those cubes containing central Na⁺ and X⁻ ions also stack down *c*, alternating their Na⁺ and X⁻ 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⁺ 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 H₂O₂ 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 Cl₂, which has C₄ symmetry, and Cl₄ with S₄ symmetry, are seen in the bromide

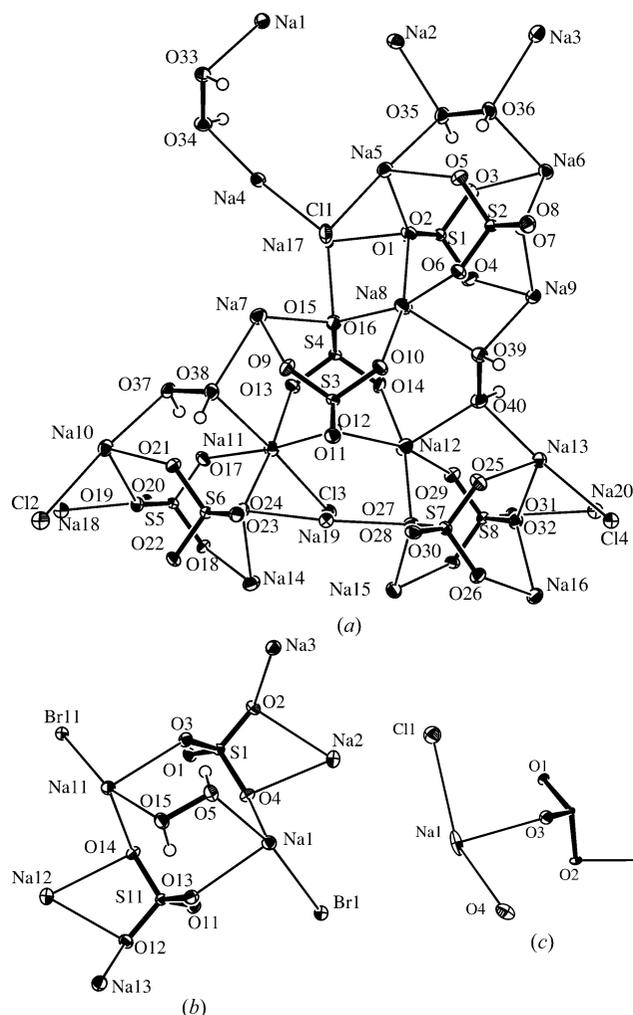


Figure 1
Asymmetric unit of Na₉[SO₄]₄Cl·2H₂O₂ (top), its bromide analogue (bottom left) and subcell structure (bottom right)

Table 2

(a) Hydrogen bonds (Å, °) and Na—O coordination bonds (Å) involving H₂O₂; (b) H₂O₂ 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 ⁱ	1.00 (6)	1.70 (6)	2.676 (4)	164 (5)	2.413 (3), 2.364 (3)	
O34—H34···O14 ⁱⁱ	0.97 (6)	1.81 (5)	2.706 (4)	152 (5)	2.408 (3), 2.408 (3)	
O35—H35···O3	0.85 (4)	1.83 (4)	2.677 (4)	169 (4)	2.353 (3), 2.403 (3)	
O36—H36···O5	0.82 (5)	1.92 (5)	2.711 (4)	162 (5)	2.399 (3), 2.413 (3)	
O37—H37···O17	0.95 (6)	1.77 (6)	2.700 (4)	167 (5)	2.410 (3), 2.406 (3)	
O38—H38···O21	0.98 (7)	1.71 (7)	2.677 (4)	171 (5)	2.420 (3), 2.363 (3)	
O39—H39···O26 ⁱⁱⁱ	0.89 (5)	1.84 (5)	2.696 (4)	159 (5)	2.407 (3), 2.394 (3)	
O40—H40···O30 ^{iv}	1.03 (7)	1.71 (6)	2.687 (4)	157 (6)	2.374 (3), 2.414 (3)	
Br						
O5—H5···O3	0.85 (2)	1.86 (3)	2.695 (2)	166 (3)	2.399 (2), 2.391 (2)	
O15—H15···O13	0.86 (4)	1.86 (4)	2.688 (2)	161 (4)	2.380 (2), 2.379 (2)	

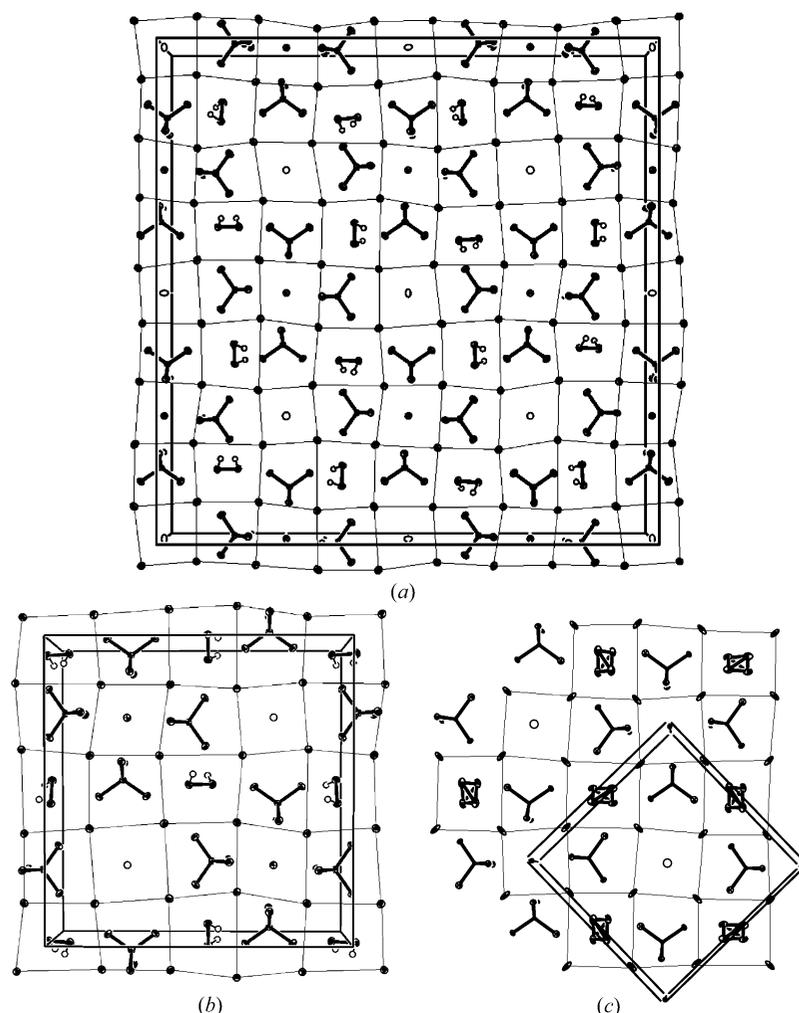
(b)

	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⁺ cations than the smaller chloride anion in the C₄ site. The difference between the bromide and chloride structure seems to hinge on the larger halide's tendency to promote C₄ coordination, which would, however, destroy the crystal's tetragonal symmetry if used exclusively. The combination of C₄ and S₄ 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 H₂O₂. In sodium percarbonate dynamic H₂O₂ disorder becomes complete above 240 K, however, no disorder is observed in Na₉[SO₄]₄Cl·2H₂O₂, 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 Na^+ cubes, has been highlighted in each case. Na^+ ions are represented by filled ellipses and the 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 H_2O_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 °, 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].² 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 H_2O_2 orientations within the above structures, each H_2O_2 site is identical (or nearly identical) as well as optimal in terms of H_2O_2 conformation, coordination and hydrogen bonding. In contrast to the alkali metal oxalate perhydrates, the title perhydrates do not form analogous hydrates. H_2O_2 must template these structures

² 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

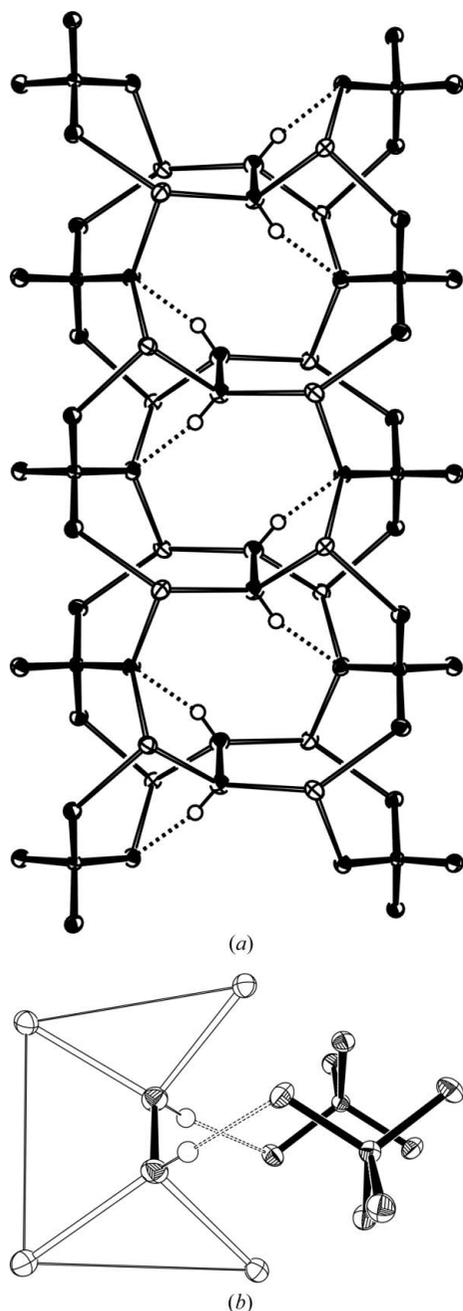


Figure 3
 H_2O_2 environment in $\text{Na}_9[\text{SO}_4]_4\text{X}\cdot 2\text{H}_2\text{O}_2$. Projections down (a) **a** and (b) **b**. The *c* axis is directed up the page in the top view.

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,

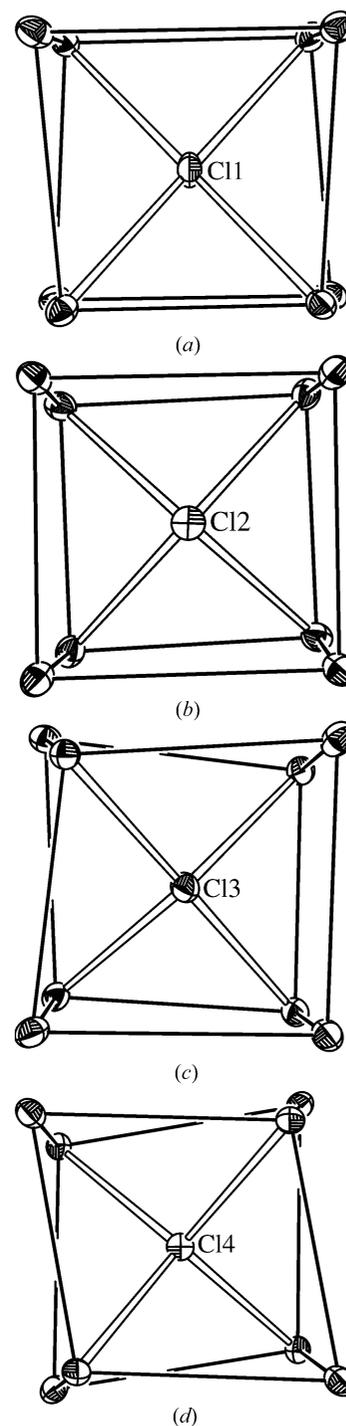


Figure 4
 The four Cl^- environments in $\text{Na}_9[\text{SO}_4]_4\text{Cl}\cdot 2\text{H}_2\text{O}_2$ viewed down **c**. Referring to how many Na^+ are pushed in on the top and bottom faces of the cube, the four configurations are 2–2, 0–4, 1–3 and diagonal 2–2.

Table 3
Na–X bond lengths (Å) in the C₄ and S₄ sites of Na₉[SO₄]₄X·2H₂O₂.

C ₄ site		S ₄ 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)

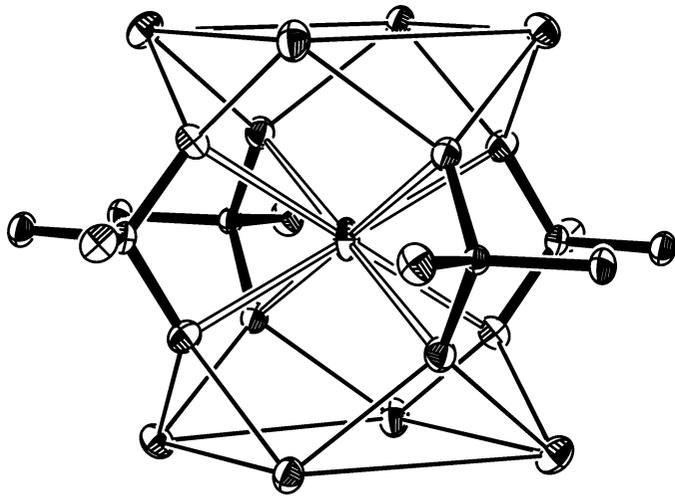


Figure 5
Eight-fold coordination shell of central sodium cation involving four SO₄²⁻ anions.

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 Na₉[SO₄]₄Br·2H₂O₂ as a combined H₂O₂/Br⁻ source.

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