Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Na₂O₂.8H₂O†

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Abstract

The structure of sodium peroxide octahydrate has been determined from single-crystal X-ray data and contains $Na(H_2O)_6^+$ octahedra, forming chains by two different types of edge-sharing. The chains are connected by the peroxide ion *via* hydrogen bonding.

Comment

As a by-product of an oxidation with H_2O_2, we obtained colourless crystals. The composition $Na_2O_2.8H_2O$ was verified by X-ray analysis. The first crystallographic studies of this compound were reported in 1939, giving a cell, from film data, of the same volume and space group as reported here, but with slightly different cell dimensions (Kotov, 1939). The structure of $Na_2O_2.8H_2O$ contains slightly distorted $Na(H_2O)_6^+$ octahedra which are linked by their edges [O(1)–O(1') and O(4)–O(4')] to form staggered chains, as shown in Fig. 1.

The Na—O distances are in the range 2.371 (1)–2.512 (1) Å. The Na···Na distance within two O(1)–O(1') linked $Na(H_2O)_6^+$ octahedra is 3.637 (1) Å. This

† Dedicated to Mr R. M. Schulze on the occasion of his 65th birthday.
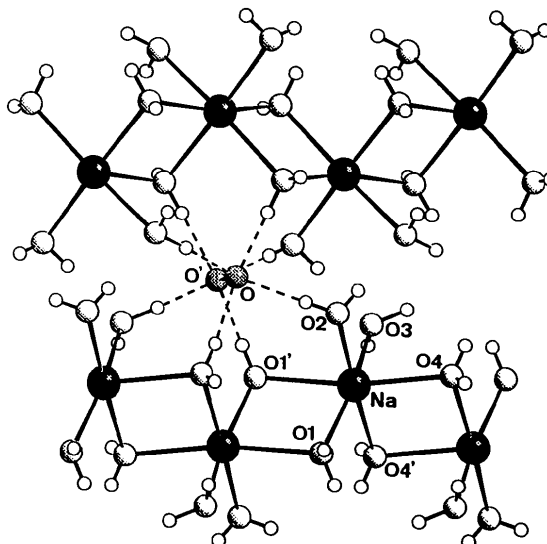

Fig. 1. Hydrogen-bonding scheme with numbering of the atoms.

distance is 0.106 Å longer than the interatomic Na···Na distance within two O(4)–O(4') edge-sharing octahedra. The distance between the O atoms of each peroxide group is 1.499 (2) Å, which is in good agreement with published data (Olovsson & Templeton, 1960; Busing & Levy, 1965). The peroxide anion is fixed by hydrogen bonds to the water molecules between the Na(H₂O)$_6^+$ chains. The shortest H···O distance is 1.63 (2) Å, the next 1.79 (2) Å. There are also weak hydrogen-bonding interactions between the water molecules of two different Na(H₂O)$_6^+$ chains (Table 2). The other H···O distances do not indicate any hydrogen bonding. A comparison with the structures of alkaline earth peroxide octahydrates (Vannerberg, 1959) shows similar bonding schemes between the peroxide anions and the water molecules. Each cation is surrounded by eight water molecules in the case of Sr₂O₂.8H₂O, and forms isolated square Archimedean antiprisms in contrast to the Na(H₂O)$_6^+$ chains of the title compound.
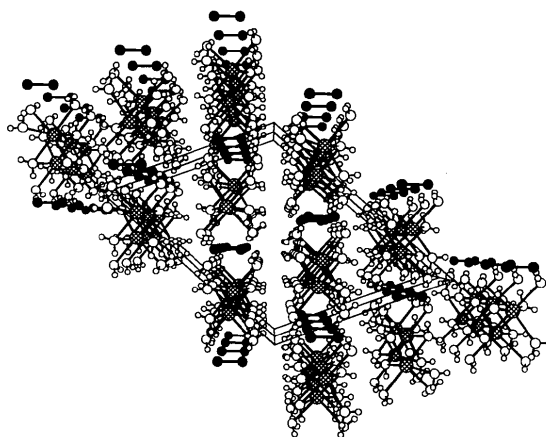

Fig. 2. View of the cell down **b**.

Experimental

Crystal data

Na₂O₂.8H₂O
$M_r = 222.10$
Monoclinic
$C2/c$
$a = 14.351 (3)$ Å
$b = 6.468 (1)$ Å
$c = 11.498 (2)$ Å
$\beta = 118.42 (1)°$
$V = 938.6 (3)$ Å³
$Z = 4$
$D_x = 1.572$ Mg m⁻³

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.08–18.56°$
$\mu = 0.242$ mm⁻¹
$T = 293$ K
Irregular
$0.4 \times 0.3 \times 0.2$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans

$h = -17 \rightarrow 0$
$k = 0 \rightarrow 8$
$l = -12 \rightarrow 14$

Absorption correction:
  none
1014 measured reflections
953 independent reflections
815 observed reflections
  $[I \geq 2\sigma(I)]$
$R_{int} = 0.0108$
$\theta_{max} = 26.33°$

Standard reflections:
  3 monitored every
    120 min for intensity
  2 monitored every
    250 reflections for
    orientation
  intensity decay: within
    statistical fluctuation

Refinement

Refinement on F^2
$R(F) = 0.0241$
$wR(F^2) = 0.0700$
$S = 1.208$
953 reflections
88 parameters
All H-atom parameters
  refined
$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 0.44P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.159$ e Å⁻³
$\Delta\rho_{min} = -0.136$ e Å⁻³
Extinction correction:
  $F_c^* = kF_c[1 + (0.001\chi \times F_c^2\lambda^3/\sin2\theta)]^{-1/4}$
Extinction coefficient:
  $\chi = 0.029 (2)$
Atomic scattering factors
  from International Tables
  for Crystallography (1992,
  Vol. C)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å²)

U_{iso} for H atoms; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	U_{iso}/U_{eq}
Na	0.30029 (4)	−0.00453 (8)	0.06811 (5)	0.028 (1)
O	0.4795 (1)	0.4837 (2)	0.2990 (1)	0.029 (1)
O(1)	0.1429 (1)	0.1869 (2)	0.0073 (1)	0.032 (1)
O(2)	0.3852 (1)	0.1309 (2)	0.2880 (1)	0.029 (1)
O(3)	0.4605 (1)	−0.1637 (2)	0.0833 (1)	0.031 (1)
O(4)	0.2840 (1)	−0.3415 (2)	0.1500 (1)	0.030 (1)
H(11)	0.125 (2)	0.215 (4)	0.059 (2)	0.064 (7)
H(12)	0.088 (2)	0.130 (3)	−0.060 (2)	0.055 (6)
H(21)	0.415 (2)	0.240 (4)	0.289 (2)	0.053 (6)
H(22)	0.432 (2)	0.040 (3)	0.323 (2)	0.044 (5)
H(31)	0.481 (2)	−0.296 (4)	0.125 (2)	0.064 (6)
H(32)	0.442 (2)	−0.181 (3)	0.006 (2)	0.051 (6)
H(41)	0.249 (2)	−0.356 (3)	0.180 (2)	0.046 (6)
H(42)	0.344 (2)	−0.404 (3)	0.200 (2)	0.056 (6)

Table 2. *Selected geometric parameters* (Å, °)

Na coordination sphere

Na—O(1)	2.371 (1)	Na—O(2)	2.390 (1)
Na—O(4^i)	2.420 (1)	Na—O(4)	2.429 (1)
Na—O(3)	2.448 (1)	Na—O(1^{ii})	2.512 (1)
Na···Na^i	3.531 (1)	Na···Na^{ii}	3.637 (1)
O(1)—Na—O(2)	93.16 (5)	O(1)—Na—O(4^i)	88.46 (5)
O(2)—Na—O(4^i)	177.19 (5)	O(1)—Na—O(4)	109.21 (5)
O(2)—Na—O(4)	90.78 (4)	O(4^i)—Na—O(4)	86.52 (4)
O(1)—Na—O(3)	166.22 (5)	O(2)—Na—O(3)	95.16 (5)
O(4^i)—Na—O(3)	83.70 (5)	O(4)—Na—O(3)	81.68 (4)
O(1)—Na—O(1^{ii})	83.75 (4)	O(2)—Na—O(1^{ii})	88.83 (4)
O(4^i)—Na—O(1^{ii})	93.63 (4)	O(4)—Na—O(1^{ii})	167.03 (5)
O(3)—Na—O(1^{ii})	85.45 (4)		

Geometry of the peroxy anion and the water molecules

O—O^{iii}	1.499 (2)	O(1)—H(11)	0.77 (3)
O(1)—H(12)	0.88 (2)	O(2)—H(21)	0.83 (2)
O(2)—H(22)	0.84 (2)	O(3)—H(31)	0.96 (2)
O(3)—H(32)	0.81 (2)	O(4)—H(41)	0.75 (2)
O(4)—H(42)	0.87 (2)		
H(11)—O(1)—H(12)	107 (2)	H(21)—O(2)—H(42)	108 (2)
H(31)—O(3)—H(32)	107 (2)	H(41)—O(4)—H(42)	108 (2)

Hydrogen-bonding geometry

D—H$\cdots A$	H$\cdots A$	D—H$\cdots A$
O(1^{iv})—H(12^{iv})$\cdots$O	1.79 (2)	178 (2)
O(2)—H(21)$\cdots$O	1.80 (2)	177 (2)
O(3^{v})—H(31^{v})$\cdots$O	1.63 (2)	177 (2)
O(3^{vi})—H(32^{vi})$\cdots$O	2.26 (2)	164 (2)
O(4^{vii})—H(41^{vii})$\cdots$O	2.12 (2)	164 (2)
O(4^{viii})—H(42^{viii})$\cdots$O	1.88 (2)	173 (2)

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

All H atoms were found in difference Fourier maps and refined isotropically. All calculations were performed on a PC486 with the program *SHELXL*93 (Sheldrick, 1993). Graphics were produced using the program *SCHAKAL*92 (Keller, 1993).

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Mercury(II) Selenite

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Abstract

The title structure, $HgSeO_3$, is isomorphous with those of a series of perovskite-like $MSeO_3$ compounds and contains corner-sharing HgO_6 octahedra, connecting to form a three-dimensional network, and Se^{4+} ions in the cavities of the structure. The octahedron is substantially distorted with Hg—O bond distances between 2.103 (11) and 2.641 (11) Å. The geometry of the selenite group

deviates significantly from those of the selenites of the isomorphous series.

Comment

Crystal structures of selenite compounds of mercury(II) have not been reported previously. In a study of the solubility of the system $HgO–SeO_2–H_2O$, two phases with compositions $HgSeO_3$ and $3HgSeO_3.H_2SeO_3$ were reported to exist (Gospodinov & Barkov, 1991). The study further confirmed previous findings that $HgSeO_3$ crystallizes in two polymorphic forms of which one is stable at 298 K and the other at 373 K. The two forms are reported to be isomorphous with corresponding polymorphs of $ZnSeO_3$ and $CdSeO_3$ (Markovskii & Sapozhnikov, 1961; Gospodinov & Bogdanov, 1983; Micka, Uchytilova & Ebert, 1984).

Selenite forms an isomorphous series of distorted perovskite-like $MSeO_3$ structures in space group $Pnma$, where M is Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, as reported by Kohn, Inoue, Horie & Akimoto (1976). The metal in compounds of this series is octahedrally coordinated. Recently, Cd^{2+} was also found to form two polymorphous forms of selenite, one of which is isomorphous with the perovskite-like structures, while the other was found to be a monoclinic $CdSeO_3$ structure (Valkonen, 1994). In addition, the crystal structure of another polymorph of $ZnSeO_3$, in space group $Pbca$, has been reported, in which the Zn atom is five-coordinate (Bensch & Gunter, 1986). It seemed interesting to explore the crystallization of $HgSeO_3$ and compare the structure to the above different crystal forms.

$HgSeO_3$ (prepared in this study) crystallizes in space group $Pnma$, isomorphous with the series of perovskite-like $MSeO_3$ structures. The structure can be depicted as composed of HgO_6 octahedra linked together at corners to form a three-dimensional network, with Se^{4+} ions in the cavities of this network. Alternatively, it can be considered as a structure in which the selenite group bridges six Hg^{2+} ions, with all selenite O atoms within bonding distance of two Hg^{2+} ions.

Within the Hg^{2+} coordination octahedron, three unequal pairs of metal–oxygen distances were found [2.103 (11), 2.593 (10) and 2.641 (11) Å] representing a substantial tetragonal flattening of the octahedron. Tetragonal flattening, although notably less marked, was also found in isomorphous $ZnSeO_3$, where the corresponding distances were 2.089, 2.177 and 2.223 Å, whereas in isomorphous $CdSeO_3$, the octahedron about the metal ion was rather regular with corresponding distances of 2.271, 2.348 and 2.357 Å. In isomorphous $CuSeO_3$, the difference between the smallest and largest metal–oxygen distance was even larger than that in the present compound (0.602 Å), but the octahedron was elongated, as is typical of six-coordinate copper (Kohn, Inoue, Horie & Akimoto, 1976; Valkonen, 1994).