Data collection

Enraf–Nonius CAD-4 diffractometer	1857 observed reflections $[I > 3\sigma(I)]$
$\theta/2\theta$ scans	$R_{int} = 0.081$
Absorption correction:	$\theta_{max} = 30°$
ψ scan (North, Philips & Mathews, 1968)	$h = 0 \rightarrow 19$
	$k = 0 \rightarrow 19$
$T_{min} = 0.5299$, $T_{max} = 0.9549$	$l = 0 \rightarrow 19$
	2 standard reflections
4064 measured reflections	frequency: 60 min
2910 independent reflections	intensity decay: 2.2%

Refinement

Refinement on F	Extinction correction: Stout
$R = 0.044$	& Jensen (1968)
$wR = 0.055$	Extinction coefficient:
$S = 1.25$	6.8×10^{-8}
1857 reflections	Atomic scattering factors
65 parameters	from *International Tables*
$w = 1/\sigma^2(F)$	*for X-ray Crystallography*
$(\Delta/\sigma)_{max} < 0.01$	(1974, Vol. IV)
$\Delta\rho_{max} = 1.6$ e Å^{-3}	
$\Delta\rho_{min} = -0.5$ e Å^{-3}	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ce	0.54899 (3)	x	x	1.472 (2)
K	3/8	0.1875 (1)	$\bar{y} + 3/4$	3.05 (3)
N1	0.3995 (5)	0.4124 (5)	0.6397 (5)	2.5 (1)
O11	0.4440 (4)	0.3900 (3)	0.5610 (4)	2.47 (9)
O12	0.4170 (4)	0.4964 (4)	0.6753 (4)	2.7 (1)
O13	0.3419 (5)	0.3555 (5)	0.6778 (4)	4.2 (1)
N2	5/8	0.5127 (4)	$y + 1/4$	1.57 (9)
O21	0.5934 (4)	0.5952 (4)	0.7418 (4)	2.36 (9)
O22	5/8	0.4463 (3)	$y + 1/4$	1.92 (8)

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

Ce—O11	2.596 (5)	K—O13	2.807 (7)
Ce—O12	2.585 (5)	K—O13^{iv,v}	2.931 (6)
Ce—O21	2.763 (5)	K—O13^{iii}	2.807 (7)
Ce—O22	2.652 (4)	K—O21^{vi,vii}	2.973 (6)
Ce—O11^{i,ii}	2.596 (5)	N1—O11	1.266 (8)
Ce—O12^{i,ii}	2.585 (5)	N1—O12	1.264 (8)
Ce—O21^{i,ii}	2.763 (5)	N1—O13	1.217 (8)
Ce—O22^{i,ii}	2.652 (4)	N2—O21	1.234 (7)
K—O11	2.909 (5)	N2—O21^{viii}	1.234 (7)
K—O11^{iii}	2.909 (5)	N2—O22	1.275 (5)
K—O12^{iv,v}	3.168 (6)		
O11—N1—O12	116.9 (6)	O21—N2—O21^{viii}	122.6 (6)
O11—N1—O13	120.9 (7)	O21—N2—O22	118.7 (5)
O12—N1—O13	122.2 (7)	O21^{viii}—N2—O22	118.7 (5)

Symmetry codes: (i) z, x, y; (ii) y, z, x; (iii) $\frac{3}{4} - x, \frac{3}{4} - z, \frac{3}{4} - y$; (iv) $z - \frac{1}{4}, \frac{1}{4} - x, 1 - y$; (v) $\frac{5}{4} - z, y - \frac{1}{4}, \frac{1}{4} + x$; (vi) $1 - x, y - \frac{1}{4}, \frac{1}{4} - z$; (vii) $x - \frac{1}{4}, z - \frac{3}{4}, \frac{5}{4} - y$; (viii) $\frac{5}{4} - x, z - \frac{1}{4}, \frac{1}{4} + y$.

Data were corrected for Lorentz–polarization effects. The unit-cell dimensions were found by indexing the powder diffraction pattern with the program *DICVOL91* (Boultif & Louër, 1991). The final parameters were refined by the program *NBS*AIDS83* (Mighell, Hubbard & Stalick, 1981). The structure was solved in the $P4_132$ space group. The position of the Ce atom was determined by direct methods (*MUL-TAN80*; Main *et al.*, 1980) and confirmed by interpretation

of a Patterson map. The remaining atoms were located by one subsequent difference Fourier synthesis. Calculations were performed with the *MolEN* (Fair, 1990) package on a MicroVAX 3100 computer. Diagrams were prepared using *OR-TEPII* (Johnson, 1976).

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Barium Perrhenate Monohydrate

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Abstract

The triclinic lattice of barium perrhenate monohydrate, $Ba(ReO_4)_2.H_2O$, is metrically pseudomonoclinic. The

structural motif resembles the *P2/c* space group pattern with one Ba(ReO$_4$)$_2$.H$_2$O formula in the pseudo-asymmetric unit. Ba atoms are tenfold coordinated by corners of different ReO$_4$ tetrahedra and two water O atoms. The BaO$_{10}$ polyhedra are associated in pairs through a triangular face which includes the twofold pseudo-axis. The large Ba cations and ReO$_4$ anions are ordered in infinite columns of face-sharing Ba$_2$Re$_4$ octahedra running along [100] in a quadratic mesh. The intercolumnar space is occupied by the water molecules.

Comment

In the early work of Noddack & Noddack (1929), the crystals formed by the evaporation of an aqueous solution of barium perrhenate at ambient temperature were assigned the composition Ba(ReO$_4$)$_2$. Later, Wilke-Dorfurt & Gunzert (1933) reported the formation under similar conditions of Ba(ReO$_4$)$_2$.2H$_2$O; this dihydrate was also assumed by Ghosh & Nag (1987). However, Beintema (1937) indicated that the crystallohydrate contains four molecules of water. This finding was further supported by Smith & Maxwell (1951) and Varfolomeyev, Chupakhin & Plyuschtev (1969), and confirmed by X-ray structure analysis (Macíček & Todorov, 1992).

In the course of an investigation of the Ba(ReO$_4$)$_2$–H$_2$O system, we observed that the initially transparent colourless Ba(ReO$_4$)$_2$.4H$_2$O crystals turned slowly to snow white in open air at room temperature. This phenomenon was associated with the formation of a lower hydrate (Macíček & Todorov, 1992), unknown previously. An X-ray powder pattern of the volatilized crystalline mass indicated the coexistence of at least three phases: Ba(ReO$_4$)$_2$.4H$_2$O (PDF 41-328; ICDD, 1993), δ-Ba(ReO$_4$)$_2$ (PDF 42-681) and the presumed intermediate hydrate. A carefully designed thermal analysis (DTA, TG) of freshly prepared Ba(ReO$_4$)$_2$.4H$_2$O clearly showed that in the temperature range 293–383 K the dehydration process passes through two stages. This observation enabled us to select appropriate conditions to prepare the lower hydrate in a pure form, evaluate its powder pattern (PDF 43-31) and to obtain single crystals suitable for X-ray investigation. Preliminary results of this work have been presented elsewhere (Todorov & Macíček, 1992)

The triclinic lattice is metrically pseudomonoclinic with angles α and γ deviating from 90° by only 0.08 (1) and 0.45 (1)°, respectively. The asymmetric unit encompasses two Ba(ReO$_4$)$_2$.H$_2$O formula units which are related by a twofold-axis pseudosymmetry operation $1 - x, y, \frac{1}{2} - z$ (Table 1; the second atomic set is marked by primes). The procedure of Diamond (1988) reveals that the two sets (without H atoms) are geometrically similar ($S = 0.139$; Tchernikova, Lavut & Zorkii, 1979) with a maximum misfit of 0.242 Å between O24 and O24'. Hence the structure may be looked upon as a

pattern of the space group $P12/c1$ (Fig. 1) and, in the following, the primed atoms are related to the unprimed atoms by the pseudosymmetry of the monoclinic space group.

The structure description is facilitated by the planar concentration of Ba and Re atoms (*DENSE*; Macíček, 1993) in two sheets parallel to [100] related by a centre of symmetry (Fig. 1). The mean planes of the sheets are localized at 1.819 and 5.431 Å from the origin. Within the translation period of 7.250 Å (d_{100}), this implies that the mean planes are evenly separated by 3.612 and 3.637 Å. The Ba–Re sheets are buckled within 0.598 Å and are significantly flatter than the similar layers in Ba(ReO$_4$)$_2$.4H$_2$O (Macíček & Todorov, 1992). In the sheet, the Ba atom has a distorted hexagonal environment formed by four close [4.101 (1)–4.392 (1) Å] and two more distant [5.847 (1) and 6.185 (1) Å] Re atoms (Fig. 2, left). The Re atoms are in a geometrically comparable environment of three Ba [4.101 (1)–6.185 (1) Å] atoms alternating with three Re [4.105 (1)–5.510 (1) Å] atoms. The three-dimensional network of Ba and Re atoms is composed of Ba$_2$Re$_4$ octahedra stacked into infinite face-sharing columns along [100] (Fig. 2, right). The columns are arranged in a square net with the connections between the columns taking the form of highly distorted octahedral (along **b**) and tetrahedral (along **c**) cages.

The Ba atom is tenfold coordinated by eight O atoms, pertaining to eight ReO$_4$ tetrahedra and two O atoms from the water molecules. The Ba—O distances vary between 2.67 (1) and 3.12 (5) Å (Table 2). As in the structure of Ba(ReO$_4$)$_2$.4H$_2$O (Macíček & Todorov, 1992), this polyhedron may be described as a distorted
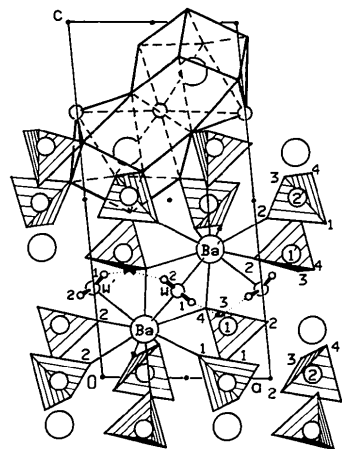
Fig. 1. Ba(ReO$_4$).H$_2$O projected down the *b* axis. A pair of the BaO$_{10}$ polyhedra are highlighted. The large circles denote Ba atoms, the intermediate ones within the tetrahedra represent Re atoms, and the dots correspond to the centres of symmetry. The encircled Re atom number followed by the tetrahedron corner number gives a two-digit label of an O atom. Hydrogen bonds are marked by dotted lines.
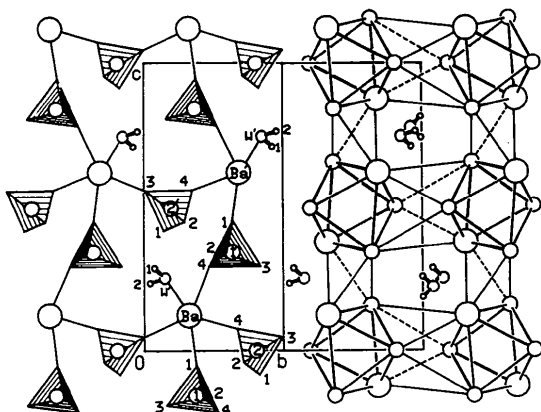
Fig. 2. Features of the Ba and Re cationic motifs. Projection is down the *a* axis. Left: one $Ba(ReO_4)_2.H_2O$ sheet showing the distorted hexagonal surroundings of the Ba and Re atoms. The ReO_4 tetrahedra, water molecules and the Ba—O bonds are depicted for clarity. Right: Ba_2Re_4 octahedral columns and additional metal-metal links. The channels are occupied by water molecules.

tetradecahedron (*cis*-bicapped cube; Favas & Kepert, 1981), a decatetrahedron (Robertson, 1977), or a 2242 (C_{2v}) stack (King, 1970). The BaO_{10} polyhedra share a triangular face formed by the O*W* atom and two O14 atoms; this peanut-like bipolyhedron is oriented along [102]. The bipolyhedra of pseudo-C_2 symmetry share one O atom of the second water molecule along [100].

A similar facial coupling of CaO_9 polyhedra has been observed in the structure of $Ca(ReO_4)_2.2H_2O$ (Matveeva, Ilyukhin, Varfolomeyev & Belov, 1980; Picard, Besse, Chevalier & Gasperin, 1987). In this case, however, the bipolyhedra possess C_i symmetry and are isolated.

The ReO_4 tetrahedra have irregular geometry with Re—O distances within the range 1.66 (2)–1.76 (1) Å and O—Re—O angles varing from 104.9 (8) to 114.5 (9)°. The average Re—O distance of 1.717 (32) Å is virtually equal to that of 1.720 (7) Å found for $Ba(ReO_4)_2.4H_2O$ (Macíček & Todorov, 1992). The different range of the individual Re—O distances in the two hydrates indicates that the loss of the water molecules during the dehydration of the tetrahydrate causes appreciable distortion of the ReO_4 tetrahedra. Each $Re2O_4$ tetrahedron is linked with the closest four Ba atoms by all O apices while each $Re1O_4$ tetrahedron shares only three O apices with Ba atoms (Table 4). The O14 atom forms non-equivalent bonds to two Ba atoms and O13 is an acceptor of H atoms from the neighbouring two water molecules. The O13···O*W* distances of 2.85 (2)–3.10 (2) Å indicate that only weak hydrogen bonds are realised in this structure. The water molecule is classified as type *B* (Ferraris & Franchini-Angela, 1972; Chiari & Ferraris, 1982) with two Ba atoms coordinated along two lone-pair orbitals of each of the water O atoms.

Experimental

Crystals of $Ba(ReO_4)_2.H_2O$ were obtained by evaporating an aqueous solution of barium perrhenate at 363 K.

Crystal data

$Ba(ReO_4)_2.H_2O$	Mo $K\alpha$ radiation
$M_r = 655.75$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 22
$P\bar{1}$	reflections
$a = 7.288$ (1) Å	$\theta = 20.27$–$21.04°$
$b = 7.514$ (1) Å	$\mu = 33.76$ mm^{-1}
$c = 15.441$ (1) Å	$T = 292$ K
$\alpha = 90.08$ (1)°	Prismatic
$\beta = 95.90$ (1)°	$0.24 \times 0.23 \times 0.21$ mm
$\gamma = 90.45$ (1)°	Colourless
$V = 841.1$ (3) Å^3	
$Z = 4$	
$D_x = 5.177$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	8248 measured reflections
Continuous profiles	4046 independent reflections
Absorption corrections:	3301 observed reflections
(1) ψ scan (North, Phillips & Mathews, 1968)	$[I > 3.0\sigma(I)]$
	$R_{int} = 0.030$
$T_{min} = 0.742$, $T_{max} = 0.995$	$\theta_{max} = 28.0°$
(2) spherical	$h = -9 \rightarrow 9$
$T_{min} = 0.013$, $T_{max} = 0.031$	$k = -9 \rightarrow 9$
	$l = -20 \rightarrow 20$
(3) refined from ΔF (*DIFABS*; Walker & Stuart, 1983)	3 standard reflections frequency: 120 min intensity decay: 3.9%
$T_{min} = 0.662$, $T_{max} = 0.994$	

Refinement

Refinement on F	$\Delta\rho_{max} = 4.588$ e Å^{-3}
$R = 0.053$	$\Delta\rho_{min} = -4.257$ e Å^{-3}
$wR = 0.062$	Extinction correction: Stout
$S = 2.678$	& Jensen (1968) formula
3301 reflections	17.16
218 parameters	Extinction coefficient:
All H-atom parameters refined	4.938×10^{-7}
$w = 1/[\sigma^2(F) + (0.001F)^2]$	Atomic scattering factors from *SDP/PDP* (Enraf–
$(\Delta/\sigma)_{max} = 0.025$	Nonius, 1985)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba	0.2796 (2)	0.3245 (1)	0.13667 (7)	0.0155 (2)
Ba'	0.7173 (2)	0.3143 (1)	0.36359 (7)	0.0155 (2)
Re1	0.7818 (1)	0.6307 (1)	0.14660 (5)	0.0155 (2)
Re1'	0.2002 (1)	0.6392 (1)	0.35146 (5)	0.0176 (2)
Re2	0.2612 (1)	0.8079 (1)	0.01323 (5)	0.0165 (2)
Re2'	0.7368 (1)	0.8029 (1)	0.49074 (5)	0.0172 (2)
O11	0.721 (2)	0.623 (2)	0.039 (1)	0.031 (4)
O12	1.018 (2)	0.582 (2)	0.159 (1)	0.027 (4)
O13	0.744 (2)	0.838 (2)	0.179 (1)	0.034 (4)

O14	0.658 (2)	0.470 (2)	0.198 (1)	0.030 (4)
O11'	0.267 (2)	0.643 (2)	0.464 (1)	0.031 (4)
O12'	−0.024 (2)	0.594 (2)	0.339 (1)	0.027 (4)
O13'	0.233 (2)	0.842 (2)	0.304 (1)	0.039 (4)
O14'	0.325 (2)	0.470 (2)	0.308 (1)	0.031 (4)
O21	0.415 (2)	0.830 (2)	−0.064 (1)	0.035 (4)
O22	0.062 (2)	0.713 (2)	−0.038 (1)	0.026 (4)
O23	0.202 (3)	1.000 (2)	0.058 (1)	0.049 (5)
O24	0.359 (2)	0.671 (2)	0.094 (1)	0.030 (4)
O21'	0.580 (2)	0.856 (2)	0.563 (1)	0.034 (4)
O22'	0.930 (2)	0.706 (2)	0.548 (1)	0.036 (4)
O23'	0.802 (2)	0.987 (2)	0.432 (1)	0.031 (4)
O24'	0.638 (2)	0.648 (2)	0.421 (1)	0.039 (5)
OW	0.497 (2)	0.082 (2)	0.2456 (9)	0.022 (3)
OW'	−0.005 (3)	0.150 (2)	0.252 (1)	0.047 (5)

Table 2. Selected geometric parameters (Å)

Ba—O11^i	2.74 (2)	Ba'—OW	2.88 (1)
Ba—O12^{ii}	2.78 (2)	Ba'—OW'^{vi}	3.06 (2)
Ba—O14	3.02 (1)	Re1—O11	1.68 (2)
Ba—O14'	2.85 (2)	Re1—O12	1.75 (1)
Ba—O21^i	2.85 (2)	Re1—O13	1.67 (2)
Ba—O22^{iii}	2.79 (1)	Re1—O14	1.74 (2)
Ba—O23^{iv}	2.75 (2)	Re1'—O11'	1.76 (1)
Ba—O24	2.76 (2)	Re1'—O12'	1.66 (2)
Ba—OW	2.86 (1)	Re1'—O13'	1.72 (2)
Ba—OW'	3.15 (2)	Re1'—O14'	1.74 (2)
Ba'—O14	2.81 (2)	Re2—O21	1.72 (2)
Ba'—O11'^{v}	2.67 (1)	Re2—O22	1.73 (1)
Ba'—O12'^{vi}	2.86 (1)	Re2—O23	1.68 (2)
Ba'—O14'	3.13 (2)	Re2—O24	1.72 (1)
Ba'—O21'^{v}	2.85 (2)	Re2'—O21'	1.72 (2)
Ba'—O22'^{vii}	2.79 (1)	Re2'—O22'	1.75 (2)
Ba'—O23'^{iv}	2.73 (2)	Re2'—O23'	1.75 (2)
Ba'—O24'	2.74 (2)	Re2'—O24'	1.69 (2)

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

Table 3. Hydrogen-bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
OW—H1···O13^i	0.95	1.92	2.85 (2)	164
OW—H2···O13'^{i}	0.95	1.92	2.84 (2)	162
OW'—H1'···O13'^{ii}	0.94	2.13	2.97 (2)	147
OW'—H2'···O13^{ii}	1.01	2.09	3.10 (2)	175

Symmetry codes: (i) $x, y - 1, z$; (ii) $x - 1, y - 1, z$.

Table 4. Distribution of bond valences

The bond-valence parameter, r_o, in formula (2) of Brown & Altermatt (1985) was 2.285 Å for Ba—O and 1.929 Å for Re—O; $B = 0.37$.

	Ba	Ba'	Re1	Re1'	Re2	Re2'	$\Sigma(-)$
O11	0.293	–	1.975	–	–	–	2.268
O11'	–	0.355	–	1.585	–	–	1.940
O12	0.264	–	1.620	–	–	–	1.884*
O12'	–	0.209	–	2.071	–	–	2.280
O13	–	–	2.026	–	–	–	2.031
O13'	–	–	–	1.783	–	–	1.779*
O14	0.138	0.242	1.663	–	–	–	2.043
O14'	0.215	0.101	–	1.667	–	–	1.983
O21	0.217	–	–	–	1.740	–	1.957
O21'	–	0.219	–	–	–	1.766	1.985
O22	0.254	–	–	–	1.702	–	1.956
O22'	–	0.258	–	–	–	1.619	1.877*
O23	0.285	–	–	–	1.965	–	2.250
O23'	–	0.301	–	–	–	1.644	1.945
O24	0.280	–	–	–	1.742	–	2.022
O24'	–	0.291	–	–	–	1.916	2.207
OW	0.213	0.200	–	–	–	–	0.413
OW'	0.098	0.123	–	–	–	–	0.221
$\Sigma(+)$	2.257	2.299	7.284	7.106	7.149	6.945	–

* Hydrogen-bond contribution has been disregarded for these sums.

Several transparent and well shaped crystals were examined on a CAD-4 diffractometer. All of them exhibited a triclinic lattice with pseudomonoclinic symmetry. The cell geometry was verified by the d-spacings of the powder pattern of $Ba(ReO_4)_2.H_2O$ (PDF 43-31; ICDD, 1993). The intensities collected in the full sphere from a crystal with $\mu R = 3.9$ were corrected for absorption in three subsequent steps: (1) empirical correction (North, Phillips & Mathews, 1968) based on ψ curves of nine reflections; (2) angular θ correction for a spherical crystal of 0.23 mm diameter; and, after refinement of the whole structure motif with U_{iso}, (3) applying the DIFABS procedure (Walker & Stuart, 1983). Thus treated intensities were used in the final stage of the structure refinement, which converged at $R = 0.053$. Further support for the plausibility of such absorption corrections is found in the values of the most absorption-sensitive structural parameters, the displacement parameters; the ellipsoids, which although not uniform, in general have regular shapes.

The triclinic structure exhibiting the atomic pattern of the space group $P2/c$ was checked for an overlooked monoclinic symmetry despite the deviation of 0.45 (1)° of γ from 90°. A symmetrized monoclinic lattice with $\alpha = \gamma = 90°$ was adopted. Initially, despite the fact that several reflections of the type $h0l$, l = odd, and $I > 15\sigma(I)$ were present in the data set, the space group $P2/c$ was considered. 7924 of 8248 collected reflections were consistent with the $P2/c$ extinction conditions and averaged to 2796 with $R_{int}(F) = 0.122$. The refinement of positional and isotropic atomic displacement parameters of all non-H atoms with 1939 3σ-reflections after DIFABS gave $R = 0.137$ and $wR = 0.152$. The U-tensors of eight O atoms became non-positive. Secondly, the raw data were averaged in the $P2$ space group to 3002 reflections with $R_{int}(F) = 0.119$. Because of the closeness of the merging factors in $P2/c$ and $P2$, it did not make sense to prefer the non-centrosymmetric group, and because $P2$ is of the same order (2) as $P\bar{1}$, for which $R_{int}(F) = 0.030$, the space group $P2$ was rejected as an appropriate alternative. No attempts to refine the structure in Pc were made for the above reasons.

The reliability of assessment of the structural model was additionally checked using the weak reflections. The experimental data were corrected for the effect of absorption (empirical and spherical correction) and those with $I < 0$ and $I > 3\sigma(I)$ were rejected. These 'weak' reflections were averaged ($P2/c$) and assigned unit weights. The refinement of the scale factor in $P2/c$ with 489 reflections including the systematically absent $h0l$ gave $R = 0.540$ and $wR = 0.562$. At the same time, in $P\bar{1}$ the scale-factor refinement with 608 observations resulted in $R = 0.380$ and $wR = 0.441$. Although the R factors are rather high (the intensities of the 'weak' reflections were not treated by DIFABS), the latter results are in favour of the correct choice of space group, $P\bar{1}$.

The H-atom positions were deciphered from $\Delta\rho$ maps and refined as riding on OW with fixed U_{iso}.

Data collection: CAD-4 (Enraf–Nonius, 1988). Cell refinement: CAD-4. Data reduction: SDP/PDP (Enraf–Nonius, 1985). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SDP/PDP. Software used to prepare material for publication: KAPPA (Macíček, 1992; unpublished).

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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Na$_2$O$_2$.8H$_2$O†

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Abstract

The structure of sodium peroxide octahydrate has been determined from single-crystal X-ray data and contains Na(H$_2$O)$_6^+$ 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$_2$O$_2$, we obtained colourless crystals. The composition Na$_2$O$_2$.8H$_2$O 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$_2$O$_2$.8H$_2$O contains slightly distorted Na(H$_2$O)$_6^+$ 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$_2$O)$_6^+$ octahedra is 3.637 (1) Å. This

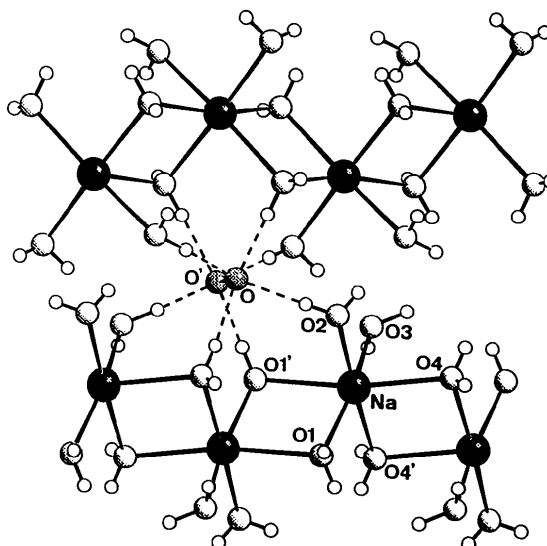† Dedicated to Mr R. M. Schulze on the occasion of his 65th birthday.

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