Kobayashi & Sasaki, 1983) and $(Na,K)_8[NiW_6O_{24}].12H_2O$ (Hau, 1970). The Sb atom lies on the C_3 axis in the anion and is positioned at a distance of 0.03 Å from the plane containing six W atoms. In addition, the Sb, O(1), O(2), O(3) and O(4) atoms are located on the mirror plane (Fig. 1). Table 2 lists selected interatomic distances and bond angles. There are three types of O atoms for the anion: three-coordinate bridging atoms, O(1) and $O(2^{ii})$, connected to Sb and two W atoms; two-coordinate bridging atoms, O(3) and $O(4^{ii})$, connected to two adjacent W atoms; terminal O atoms, O(5) and O(6), connected to each W atom. The average W—O distances for [O(1), $O(2^{ii})$], [O(3), $O(4^{ii})$] and [O(5), O(6)] are 2.21, 1.93 and 1.72 Å, respectively. The Sb—O bond length [2.01 (3) Å] is comparable to the values [1.894 (3)–2.102 (3) Å] for $Sb^{V}O_6$ octahedra of Sb_2O_5 (Jansen, 1979). There is little difference in the corresponding bond lengths and angles between crystals of $K_{5.5}H_{1.5}[SbW_6O_{24}].6H_2O$ and $K_5Na_2[SbW_6O_{24}].12H_2O$ (Lee & Sasaki, 1987).

Fig. 2 represents the crystal structure projected onto the (100) plane. K^+—O and O*w*—O distances less than 3.5 Å are also listed in Table 2. The anion is sandwiched between the two layers of K^+ cations: $K(2)$–$K(2^{i})$–$K(2^{ii})$ and $K(3)$–$K(3^{i})$–$K(3^{ii})$ planes (Fig. 2). K(1) achieves sixfold coordination with O*w*(1), $Ow(1^{i})$, $Ow(1^{ii})$, O*w*(2), $Ow(2^{i})$ and $Ow(2^{ii})$ atoms, forming a distorted $K(1)O_6$ octahedron. O*w*(1) and O*w*(2) atoms serve to bind anions together by hydrogen bonding. No atom can be found around the (00*z*) region (Fig. 1), which forms a column-like cavity lying around the *c* axis of the crystal. Such a cavity does not exist in the $K_5Na_2[SbW_6O_{24}].12H_2O$ lattice (Lee & Sasaki, 1987).

The O→W LMCT photoexcitation of $K_{5.5}H_{1.5}[SbW_6O_{24}].6H_2O$ results in a broad luminescence in the range 400–650 nm with a peak at 510 nm. A similar spectrum was reported for $Na_9[Gd(W_5O_{18})_2].18H_2O$ (Blasse, Dirksen & Zonnevijlle, 1981*b*). The relative yield of the luminescence from the O→W LMCT state for $K_{5.5}H_{1.5}[SbW_6O_{24}].6H_2O$ was 2.5 times higher than for $Na_9[Gd(W_5O_{18})_2].18H_2O$, when the samples were exposed to 290 nm light at 77 K.

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Structure of Barium Perrhenate Tetrahydrate

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Abstract. $Ba(ReO_4)_2.4H_2O$, $M_r = 709.80$, monoclinic, $P2_1/n$, $a = 7.376\ (2)$, $b = 12.452\ (2)$, $c = 12.173\ (1)$ Å, $\beta = 90.04\ (1)^\circ$, $V = 1118$ Å^3, $Z = 4$, $D_x = 4.216$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0.70930$ Å, $\mu = 254.3$ cm^{-1}, $F(000) = 1240$, $T = 292$ K, $R = 0.038$ for 2591 observed reflections with $I > 3\sigma(I)$. The metrically pseudo-orthorhombic structure has the approximate space group symmetry *Pmnb* (No. 62). Ba cations constitute a distorted hexagonal close-packed motif with 12 Ba—Ba distances ranging from 7.115 to 7.601 Å. Along with Re atoms they are disposed on the pseudo-mirror plane ($d_{200} = 3.688$ Å). The coordination polyhedron of Ba is a distorted tetradecahedron with Ba—O distances within 2.831 (7)–2.953 (7) Å. Two non-equivalent ReO_4 tetrahedra have irregular geometry, Re—O 1.709 (8)–1.743 (8) Å for Re(1), 1.709 (8)–1.729 (9) Å for Re(2). The structure may be looked upon as composed of buckled ${}^{2}_{\infty}[Ba(ReO_4)_2]$ layers coinciding with the (002) plane ($d_{002} = 6.087$ Å). The layers are

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interlinked by a Ba—O bond and an extensive system of hydrogen bonds with the participation of water molecules.

Introduction. Although all alkaline-earth perrhenates form hydrates (Smith & Maxwell, 1951) only the monoclinic crystal structure of $Ca(ReO_4)_2.2H_2O$ has been investigated so far. Matveeva, Ilyukhin, Varfolomeyev & Belov (1980) have initially solved its structure in the non-centrosymmetric space group *Bb* (*Cc* in the standard setting). Picard, Besse, Chevalier & Gasperin (1987) in an independent investigation ascribed the structure the polar non-centrosymmetric space group *C*2. Soon afterwards they refined it successfully in the centrosymmetric space group *C*2/*c* (Picard, Besse, Chevalier & Gasperin, 1988).

The colourless rectangular tabular crystals of $Ba(ReO_4)_2.4H_2O$ were first studied by Beintema (1937). He determined the lattice geometry [a = 12.19, b = 12.44, c = 7.33 Å, β = 90°] from X-ray rotation photographs and found by optical methods that the inherent symmetry of the crystals was monoclinic. The measured density $D_m = 4.0$ g cm^{-3} corresponded to $Z = 4$. Varfolomeyev, Chupakhin & Plyuschtev (1969) evaluated a different unit cell [a = 7.377 (1), b = 12.158 (1), c = 12.50 (2) Å, β = 90.13 (5)°] and proposed the space group $P2_1/n$ from extinction conditions. Their incomplete powder patterns of $Ba(ReO_4)_2.4H_2O$ stored in the JPCDS Powder Data File as No. 23-831 were recently updated by us (PDF No. 41-328; Macíček, 1990).

The present crystal structure determination of barium perrhenate tetrahydrate was carried out as part of our project on the crystal chemistry of perrhenates of large divalent cations. We were also interested in elucidation of the structural background for the observed orthorhombic pseudosymmetry.

Experimental. Barium perrhenate was prepared according to Smith & Maxwell (1951). Transparent crystals were obtained from aqueous solution by evaporation at room temperature. Well-shaped plate crystals were selected, transferred from the mother liquor into an epoxy glue to prevent dehydration, cut and mounted on the top of a glass capillary. Three of these were examined on an Enraf–Nonius CAD-4 diffractometer (graphite monochromator, Mo $K\alpha$ radiation) and the cell constants were determined from a least-squares fit of 22 carefully centred reflections with $20.0 < \theta < 21.0°$. The significant absorption ($\mu = 254.3$ cm^{-1}) and the crystal shape irregularity troubled the initial determination of the lattice symmetry. The intensity data were collected from the crystal of smallest mosaic structure with approximate dimensions 0.05 × 0.05 × 0.01 mm in ω–2θ scan mode: speed 2–7° min^{-1}, $\Delta\omega = (1.0 + 0.4\tan\theta)°$. 6980 reflections were measured in the range $(\sin\theta)/\lambda < 0.703$ Å^{-1} (h: 0 to 10, k: −17 to 17, l: −17 to 17). Three standard reflections were monitored every 2 h. As the intensity variation was less than 1% no decay correction was applied. The data were corrected for Lorentz and polarization effects. The absorption correction was based on the ψ-scan profiles of nine reflections; the transmission factor varied from 0.6195 to 0.9989. An additional spherical absorption correction ($\mu R = 1.0$, correction factor A^* range 4.12–3.97) did not lead to improvement of the final refinement results and was not applied. The symmetry equivalent reflections were averaged assuming the orthorhombic symmetry (space group *Pmnb*) and 1977 unique reflections with $R_{\rm int} = 0.095$ were used in calculations. The positions of Ba and Re atoms on a mirror plane were found by *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and refined by full-matrix least squares on F to $R = 0.156$. O atoms were approximately localized from $\Delta\rho$ maps and the model was refined. Convergence, however, could not be reached: most of the U values became negative and the ReO_4 tetrahedra became distorted. The symmetry was then lowered to monoclinic (space group $P2_1/n$) and the intensity data reprocessed. 3402 unique reflections with $R_{\rm int} = 0.040$ remained and 811 of these were considered unobserved [$I < 3\sigma(I)$]. The positions of Ba, Re and eight O atoms obtained from the previous calculations were used in the new initial phasing. Subsequent $\Delta\rho$ maps and least-squares refinements revealed all non-H atoms. The positions of H atoms were obtained from $\Delta\rho$ maps; they were added with a fixed $U = 0.05$ Å^2, and refined cautiously with a dampening factor of 0.1. Final $R = 0.038$, wR = 0.048, and $S = 1.423$; weights were defined as $4(F_o)^2/[\sigma(F_o)^2]^2$; maximum $\Delta/\sigma = 0.03$. The residual density varied between $\Delta\rho = 3.07$ and -5.15 e Å^{-3}. Empirical correction for secondary extinction was applied, $F_{c,\rm corr} = F_c/(1 + 6.767 \times 10^{-7}I)$. Atomic scattering factors and anomalous-dispersion coefficients were taken as quoted in the *SDP*/*PDP V*3.0 package (Enraf–Nonius, 1985) operating on a PDP11/44 computer. Final fractional coordinates are given in Table 1.† The relevant geometry parameters and valences are summarized in Table 2. Figs. 1 and 2 show projections of the structure obtained by *STRUPLO*84 (Fischer, 1985), adapted for a PDP11 by one of us (JM).

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† Lists of structure factors, anisotropic displacement parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54667 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0240]

Table 1. *Positional and equivalent isotropic displacement parameters* (Å^2) *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
Ba	0.25211 (6)	0.24842 (4)	0.42911 (4)	0.0124 (1)
Re(1)	0.25295 (4)	0.38750 (3)	0.08899 (3)	0.01343 (7)
Re(2)	0.25038 (4)	0.06995 (3)	−0.04018 (3)	0.01404 (7)
O(11)	0.273 (1)	0.3686 (8)	0.2277 (7)	0.039 (2)
O(12)	0.4144 (9)	0.3147 (6)	0.0206 (7)	0.034 (2)
O(13)	0.284 (1)	0.5225 (6)	0.0561 (7)	0.030 (2)
O(14)	0.0437 (9)	0.3480 (7)	0.0441 (7)	0.036 (2)
O(21)	0.4615 (9)	0.0971 (6)	−0.0929 (7)	0.027 (2)
O(22)	0.0923 (9)	0.1477 (6)	−0.1051 (6)	0.027 (2)
O(23)	0.199 (1)	−0.0640 (6)	−0.0592 (7)	0.029 (2)
O(24)	0.246 (1)	0.0972 (7)	0.0991 (7)	0.034 (2)
O(*W*1)	0.0178 (9)	0.1630 (6)	0.2667 (6)	0.027 (2)
O(*W*2)	0.4750 (9)	0.1369 (7)	0.2740 (6)	0.031 (2)
O(*W*3)	0.2288 (9)	0.2283 (6)	0.6704 (6)	0.028 (2)
O(*W*4)	0.232 (1)	0.0003 (7)	0.6802 (6)	0.035 (2)

Table 2. *Bond distances* (Å) *with valences* (v.u.), *bond angles* (°) *and hydrogen-bond geometry* (Å, °)

BaO$_{10}$ polyhedron

Ba—O(11)	2.877 (9)	0.202	Ba—O(22)	2.854 (7)	0.215
Ba—O(12)	2.840 (7)	0.223	Ba—O(23)	2.845 (8)	0.220
Ba—O(13)	2.831 (8)	0.229	Ba—O(*W*1)	2.832 (8)	0.228
Ba—O(14)	2.833 (8)	0.228	Ba—O(*W*2)	2.863 (7)	0.210
Ba—O(21)	2.892 (8)	0.194	Ba—O(*W*3)	2.953 (8)	0.164

O(11)—Ba—O(12)	121.7 (2)	O(13)—Ba—O(*W*3)	81.3 (2)
O(11)—Ba—O(13)	125.2 (2)	O(14)—Ba—O(21)	152.9 (2)
O(11)—Ba—O(14)	126.9 (2)	O(14)—Ba—O(22)	66.2 (2)
O(11)—Ba—O(21)	67.4 (2)	O(14)—Ba—O(23)	88.7 (2)
O(11)—Ba—O(22)	66.0 (2)	O(14)—Ba—O(*W*1)	130.4 (2)
O(11)—Ba—O(23)	92.3 (2)	O(14)—Ba—O(*W*2)	71.6 (2)
O(11)—Ba—O(*W*1)	68.5 (2)	O(14)—Ba—O(*W*3)	61.1 (3)
O(11)—Ba—O(*W*2)	70.1 (2)	O(21)—Ba—O(22)	109.7 (3)
O(11)—Ba—O(*W*3)	153.5 (2)	O(21)—Ba—O(23)	66.3 (2)
O(12)—Ba—O(13)	67.5 (2)	O(21)—Ba—O(*W*1)	74.5 (2)
O(12)—Ba—O(14)	110.8 (2)	O(21)—Ba—O(*W*2)	133.4 (2)
O(12)—Ba—O(21)	64.5 (2)	O(21)—Ba—O(*W*3)	96.0 (2)
O(12)—Ba—O(22)	162.6 (2)	O(22)—Ba—O(23)	66.3 (2)
O(12)—Ba—O(23)	96.8 (2)	O(22)—Ba—O(*W*1)	127.3 (3)
O(12)—Ba—O(*W*1)	68.6 (2)	O(22)—Ba—O(*W*2)	67.6 (2)
O(12)—Ba—O(*W*2)	128.9 (2)	O(22)—Ba—O(*W*3)	103.6 (3)
O(12)—Ba—O(*W*3)	62.3 (2)	O(23)—Ba—O(*W*1)	140.7 (2)
O(13)—Ba—O(14)	67.6 (2)	O(23)—Ba—O(*W*2)	133.9 (2)
O(13)—Ba—O(21)	126.6 (2)	O(23)—Ba—O(*W*3)	61.5 (2)
O(13)—Ba—O(22)	122.8 (2)	O(*W*1)—Ba—O(*W*2)	73.0 (2)
O(13)—Ba—O(23)	142.4 (2)	O(*W*1)—Ba—O(*W*3)	128.9 (2)
O(13)—Ba—O(*W*1)	67.3 (2)	O(*W*2)—Ba—O(*W*3)	130.4 (3)
O(13)—Ba—O(*W*2)	67.3 (2)		

ReO$_4^-$ anions

Re(1)—O(11)	1.712 (8)	1.800	Re(2)—O(21)	1.718 (7)	1.767
Re(1)—O(12)	1.713 (8)	1.791	Re(2)—O(22)	1.709 (8)	1.813
Re(1)—O(13)	1.743 (8)	1.652	Re(2)—O(23)	1.725 (7)	1.735
Re(1)—O(14)	1.709 (8)	1.811	Re(2)—O(24)	1.729 (9)	1.718

O(11)—Re(1)—O(12)	110.3 (4)	O(21)—Re(2)—O(22)	109.5 (3)
O(11)—Re(1)—O(13)	110.4 (5)	O(21)—Re(2)—O(23)	109.7 (4)
O(11)—Re(1)—O(14)	110.7 (4)	O(21)—Re(2)—O(24)	110.1 (4)
O(12)—Re(1)—O(13)	107.9 (4)	O(22)—Re(2)—O(23)	109.7 (4)
O(12)—Re(1)—O(14)	108.7 (4)	O(22)—Re(2)—O(24)	109.2 (4)
O(13)—Re(1)—O(14)	108.8 (4)	O(23)—Re(2)—O(24)	108.6 (5)

Hydrogen bonds

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(*W*1)—H(11)···O(*W*4^{i})	0.9 (2)	2.3 (2)	2.818 (11)	115 (11)
O(*W*1)—H(12)···O(24)	0.9 (2)	2.0 (2)	2.771 (11)	139 (13)
O(*W*2)—H(21)···O(24)	1.0 (2)	1.8 (2)	2.761 (11)	167 (13)
O(*W*2)—H(22)···O(*W*3^{ii})	1.0 (2)	1.8 (2)	2.814 (10)	158 (15)
O(*W*3)—H(31)···O(*W*1^{iii})	0.8 (2)	2.1 (2)	2.783 (10)	146 (15)
O(*W*3)—H(32)···O(*W*4)	0.8 (2)	2.3 (2)	2.842 (10)	123 (11)
O(*W*4)—H(41)···O(13^{iv})	1.1 (2)	1.9 (2)	2.892 (11)	146 (14)
O(*W*4)—H(42)···O(*W*2^{v})	0.7 (2)	2.1 (2)	2.813 (11)	174 (21)

Symmetry code: (i) $-x, -y, 1-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $-\frac{1}{2}-x, -\frac{3}{2}+y, -\frac{1}{2}-z$; (v) $1-x, -y, 1-z$.

Discussion. Besides the reciprocal-space evidence of the *n*-glide plane (*h*0*l*, $h+l=2n$) and the perpendicular screw axis 2_1 (0*k*0, $k=2n$) the presence of a pseudo *b*-glide plane is manifested in a systematic weakening of *hk*0 reflections with $k=2n+1$. Hence the metrically pseudo-orthorhombic structure obeys the conditions of the space group *Pmnb* (No. 62, full symbol $P2_1/m2_1/n2_1/b$; supergroup of index [2] of the actual monoclinic space group $P2_1/n$). The minuteness of the non-H-atom deviations from the orthorhombic symmetry is illustrated by the magnitudes of splitting the 'equivalent' positions in space group *Pmnb*: 0.031 (Ba), 0.044 (Re), 0.341 O(*W*) and 0.759 Å (O).

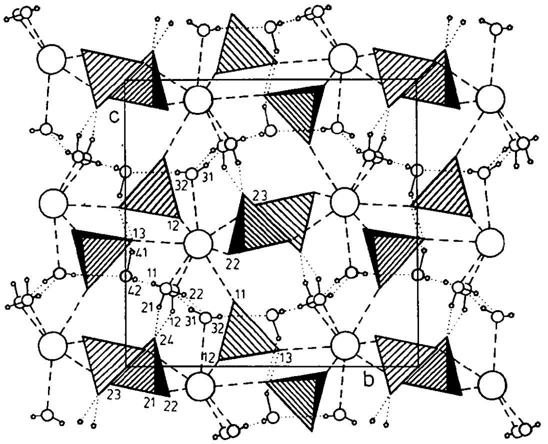

Fig. 1. Projection of the structure onto the *bc* plane. The ReO$_4$ tetrahedra are shaded, dashed lines denote Ba—O coordination bonds, hydrogen bonds are indicated by dotted lines. Large circles represent Ba, medium represent O(*W*) and small represent H atoms. Numbers apply to the respective atom types.

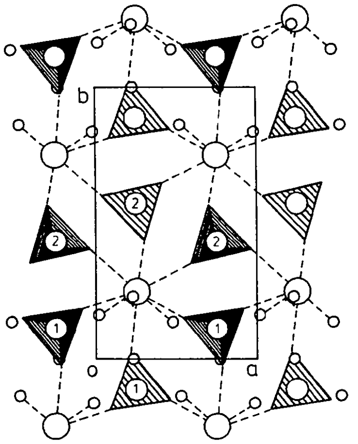

Fig. 2. $^2_\infty$[Ba(ReO$_4$)$_2$] layer defined within $z=\frac{1}{4}$ and $z=\frac{3}{4}$ and projected onto the *ab* plane. Ba and O(*W*) atoms are drawn as circles, H atoms are omitted for clarity. The encircled numbers denote Re(1) and Re(2) tetrahedra.

Ba cations are arranged in a distorted hexagonal close packing with 12 Ba—Ba distances in the anticuboctahedral environment varying from 7.115 to 7.601 Å. The common network of Ba and Re atoms may be sliced into sheets, coincident with the pseudo-mirror plane; these sheets are planar within 0.047 Å and separated by 3.688 Å (d_{200}). Ba is surrounded by seven Re atoms at distances ranging from 4.226 to 4.505 Å. The two non-equivalent Re atoms have nine more scattered neighbours: Re(1)—Ba × 4, Re(1)—Re × 5 (4.255–5.867 Å); and Re(2)—Ba × 3, Re(2)—Re × 6 (4.189–5.994 Å).

The $\mathrm{ReO_4}$ tetrahedra have an irregular geometry; the Re—O bond lengths vary from 1.709 (8) to 1.743 (8) Å [1.709 (8)–1.729 (9) Å] and the O—Re—O angles fall within the range 107.9 (4)–110.7 (4)° [108.6 (5)–110.1 (3)°], for Re(1) [data for Re(2) given in parentheses]. The bond-valence sum around the Re atoms, evaluated employing the parameters $R_o = 1.968$ and $B = 0.35$* (I. D. Brown, 1987; private communication), turned out to be unexpectedly large: 8.15 [8.12] valence units (v.u.) for Re(1) [Re(2)]. With an improved value for $B = 0.37$ and following the recommended procedures (Brown & Altermatt, 1985), we derived from published structural data (36 $\mathrm{Re^{VII}}$–O polyhedra) a new $R_o = 1.929\,(18)$. In this case the recalculated valence sums for Re(1) and Re(2) adopt more realistic values: 7.05 and 7.03 v.u.

All O atoms in the $\mathrm{Re(1)O_4}$ tetrahedron are bonded to Ba cations. The valence sums for O atoms due to contributions from Re—O and Ba—O bonds are 2.00 [O(11)], 2.01 [O(12)], 1.88 [O(13)] and 2.04 v.u. [O(14)]. The valence deficiency at O(13) indicates that this atom should take part in an additional bonding. As may be expected for a hydrate crystal, O(13) plays the acceptor role in a hydrogen bond with a water molecule (*W*4; Table 2). The situation at Re(2) is different. Only three O atoms form bonds with Ba cations and one [O(24)] is uncoordinated. The valence sums for the first three O atoms are similar, *i.e.* 1.96, 2.02 and 1.95 v.u. for O(21), O(22) and O(23) respectively. The bond valence of 1.72 v.u. at O(24) is complemented from the contributions of two O···H—O(*W*) bonds with the water molecules *W*1 and *W*2. From the values of valence sums at O(13) and O(24) it may be concluded that O atoms in $\mathrm{ReO_4^-}$ groups contribute to one O···H bond by approximately 0.13 v.u.

The observed average Re—O distance 1.720 (7) Å corresponds well to the respective value for $\mathrm{ReO_4^-}$ in the following structures: $\mathrm{LiReO_4}$ 1.715 (25) Å (Betz & Hoppe, 1983); $\mathrm{KReO_4}$ 1.719 (6) Å (Krebs & Hasse, 1976), 1.723 (4) Å (Lock & Turner, 1975); $\mathrm{NH_4ReO_4}$ 1.720 (5) Å (Kruger & Reynhardt, 1978); $\mathrm{Ca(ReO_4)_2.2H_2O}$ 1.724 (13) Å (Picard *et al.*, 1988). In other structures containing isolated $\mathrm{ReO_4}$ tetrahedra, the average Re—O distance varies between wider limits: $\mathrm{Yb(ReO_4)_3.4H_2O}$ 1.697 (53) Å (Mashonkin, Ilyukhin & Belov, 1974); $\mathrm{GdNa(ReO_4)_4.4H_2O}$ 1.731 (16) Å (Aït Ali Slimane, Silvestre, Freundlich & Rimsky, 1982); $\mathrm{La(ReO_4)_3.4H_2O}$ 1.732 (32) Å (Mashonkin, Varfolomeyev & Ilyukhin, 1977); $\mathrm{Pb(ReO_4)_2}$ 1.737 (89) Å [Picard, Baud, Besse, Chevalier & Gasperin, 1984); $\mathrm{Dy(ReO_4)_3.4H_2O}$ 1.753 (67) Å (Mashonkin, Ionov, Ilyukhin & Belov, 1975).

The coordination polyhedron of Ba is a distorted tetradecahedron (*cis*-bicapped cube; Favas & Kepert, 1981) of ten O atoms (Fig. 3). Seven Ba—O bonds radiate to corners of seven $\mathrm{ReO_4^-}$ tetrahedra and the other three to water molecules. The distances range from 2.831 (7) to 2.953 (7) Å, the longest one being that of Ba—O(*W*3). Nine Ba—O bond valences ($R_o = 2.285$; Brown & Altermatt, 1985) adopt values 0.22 (1) v.u. and only one, Ba—O(*W*3), constitutes 0.16 v.u., giving together the valence sum of 2.11 v.u. for Ba.

The structure may be alternatively considered as built up of buckled layers with the composition $^{2}_{\infty}[\mathrm{Ba(ReO_4)_2}]$ and coinciding with the (002) plane ($d_{002} = 6.087$ Å). Ba and Re atoms form a slab 2.168 Å thick, the centre of mass of which is displaced −0.002 Å from the unit-cell origin (unpublished program *DENSE*; J. Macíček, 1991). Each $\mathrm{ReO_4^-}$ group within the layer is linked to three Ba cations and is in the neighbourhood of three other $\mathrm{ReO_4}$ tetrahedra. Every two adjacent Ba atoms are bridged *via* two $\mathrm{ReO_4}$ tetrahedra, which are oriented in two different ways (Fig. 2). The bridges running down the [100] direction have identical *syn*-oriented tetrahedra (*s*-type bridges) and those in the [110] and [1$\bar{1}$0] directions are formed from *anti*-disposed ones (*a*-type bridges). The six neighbours of a Ba atom are connected *via* four *a*-type and two *s*-type bridges. A different arrangement of the tetrahedra occurs in the

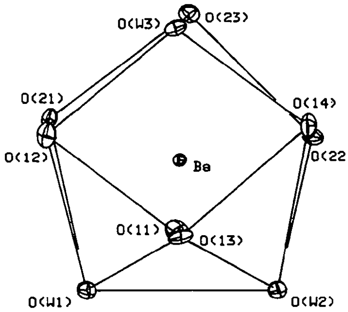

Fig. 3. $\mathrm{BaO_{10}}$ tetradecahedron (*cis*-bicapped cube) with O(*W*1) and O(*W*2) at the caps.

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* The exponential formula used was $s_i = \exp[(R_o - R_i)/B]$, s_i = bond valence, R_i = experimental bond length.

trigonal structure of $Pb(ReO_4)_2$ (Picard *et al.*, 1984), where all six bridges are of the *a*-type.

The layers form a three-dimensional structure *via* Ba—O(11) bonds and an extensive system of O···H—O bonds with the participation of the water molecules (*W*1–*W*4). *W*1, *W*2 and *W*3 are coordinated to Ba and, besides donating two protons each, they also accept one: *W*1 from *W*3, *W*2 from *W*4, and *W*3 from *W*2. The molecule *W*4 represents an interstitial water and is completely involved in hydrogen bonding both as donor and acceptor. The non-H tetrahedral neighbourhood of the water O atoms includes either Ba and three O atoms (*W*1, *W*2, *W*3) or four O atoms (*W*4), the O···O/Ba—O distances extending from 2.771 (11) [O(*W*1)···O(24)] to 2.953 (8) Å [Ba—O(*W*3)].

The presence of *W*4 in the structure together with the non-uniformity of the Ba—O bond valences which, according to the valence-matching principle (Brown, 1981), is a source of internal strength in the structure, may explain the observed instability of $Ba(ReO_4)_2.4H_2O$ crystals in air and their slow decomposition into a lower hydrate (Macíček, 1990). Our attempts to obtain crystals of the latter hydrate, suitable for X-ray analysis, gave promising results which would make it possible to examine their structure containing no 'redundant' water molecules.

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Structure of $Rb_3D(SeO_4)_2$ at 25, 110 and 297 K

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Abstract. Trirubidium deuteriumbiselenate, $Rb_3D(SeO_4)_2$, $M_r = 544.3$, $A2/a$, $Z = 4$, $\lambda(\mathrm{Mo}\ K\alpha) = 0.71073$ Å, $\mu = 22.4\ \mathrm{mm}^{-1}$, $F(000) = 976$. At $T = 297$ K, $a = 10.4775\ (6)$, $b = 6.086\ (1)$, $c = 15.421\ (1)$ Å, $\beta = 102.919\ (9)°$, $V = 958.1\ (3)$ Å^3, $D_x = 3.773\ \mathrm{Mg\ m^{-3}}$; at $T = 110$ K, $a = 10.4019\ (7)$, $b = 6.049\ (1)$, $c = 15.321\ (1)$ Å, $\beta = 102.827\ (8)°$, $V = 939.9\ (2)$ Å^3, $D_x = 3.846\ \mathrm{Mg\ m^{-3}}$; at $T = 25$ K, $a =$