

O2—Se1—O3	99.0 (5)	Se1—O3—Se2	117.1 (5)
O3—Se2—O4	100.4 (5)		

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

Data collection and cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN11/82* (Main *et al.*, 1982). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AB1172). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Lithium Perbromate Monohydrate at 296 and 173 K

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Abstract

Lithium tetraoxobromate(1-) monohydrate, $\text{LiBrO}_4 \cdot \text{H}_2\text{O}$, whose perchlorate analog has not yet been de-

scribed, is found to be isomorphic with $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$ and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$. Each of the two inequivalent Li ions is coordinated by six O atoms, thus forming distorted octahedra, each of which has three inequivalent Li—O distances. At room temperature, the average $\text{Li}(1)$ —O and $\text{Li}(2)$ —O distances are 2.150 and 2.164 Å, respectively. The perbromate ion displays very nearly regular tetrahedral geometry, although it is not subject to symmetry constraints. At 296 K the average observed Br—O distance is 1.610 (4) Å and the average O—Br—O angle is 109.5 (6)°, while at 173 K the corresponding values are 1.613 (4) Å and 109.5 (7)°. The perbromate ion shows rigid-body behavior but the lithium coordination polyhedra do not. At 296 K, the average rigid-body corrected Br—O distance in the perbromate ion is 1.624 (3) Å, in excellent agreement with the corresponding value reported for $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$. Refinement of the two inequivalent H atoms allowed detailed analysis of the hydrogen bonding, which is more extensive than in $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$ or in $\text{NaClO}_4 \cdot \text{H}_2\text{O}$. The average observed B values for the H atoms [2.9 (3) Å² at 296 K and 2.8 (3) Å² at 173 K] are sufficiently small to suggest that dynamic disordering of the H atoms (determined by magnetic resonance methods for $\text{NaClO}_4 \cdot \text{H}_2\text{O}$) is not significant in the title salt.

Comment

This study of $\text{LiBrO}_4 \cdot \text{H}_2\text{O}$ is the sequel to an investigation of the structure of $\text{LiBrO}_4 \cdot 3\text{H}_2\text{O}$ (Blackburn, Gallucci, Gerkin & Repart, 1993). It was of particular interest since the perchlorate analog, $\text{LiClO}_4 \cdot \text{H}_2\text{O}$, has not been described. The potentially similar structure of $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$, however, had been determined (Blackburn, Gallucci, Gerkin & Repart, 1992).

A stereoview of the structure is given in Fig. 1; hydrogen bonds have been omitted for clarity. The structure is isomorphic with that of $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$ (Blackburn *et al.*, 1992) and thus, also with that of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Berglund, Thomas & Tellgren, 1975; Berglund, Tellgren & Thomas, 1976).

Each of the two inequivalent Li ions is coordinated by six O atoms at three inequivalent distances. At room temperature, these $\text{Li}(1)$ —O dis-

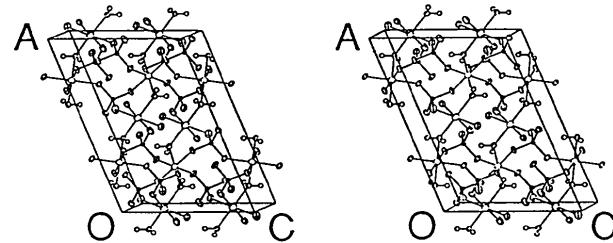


Fig. 1. Stereoview of a unit cell of the lithium perbromate structure at 296 K drawn using *ORTEPII* (Johnson, 1976). Displacement ellipsoids are drawn at 50% probability for all atoms except H, which have been set artificially small. Hydrogen bonds have been omitted for clarity.

tances range from 2.107 to 2.186 Å [average 2.150 Å], while the Li(2)—O distances range from 2.125 to 2.226 Å [average 2.164 Å]. Essentially identical behavior is exhibited by the low-temperature data. Thus, the Li(1)(site symmetry 1)—O distances are as dispersed as the Li(2)(site symmetry 2)—O distances, in contrast to the Na—O distances in both NaBrO₄.H₂O and NaClO₄.H₂O for which the Na(1)—O distances are substantially less dispersed. Overall, the angular departures from regular octahedral geometry (except for angles constrained by symmetry to be 180°) for the title salt at either temperature and for NaBrO₄.H₂O are very similar, if somewhat larger than those for NaClO₄.H₂O.

The perbromate ion in the title compound is subject to no symmetry constraints but, as in NaBrO₄.H₂O, has very nearly regular tetrahedral geometry. The average observed Br—O distances are 1.610(4) (296 K) and 1.613(4) Å (173 K), while the average observed angles are 109.5(6) (296 K) and 109.5(7)° (173 K). These values are in good agreement with those previously reported for perbromate ions (see Blackburn *et al.*, 1992). Corrected for rigid-body motion, the average Br—O distances are 1.624(3) (296 K) and 1.621(3) Å (173 K). Thus, there is excellent agreement with the corresponding value reported for NaBrO₄.H₂O at 296 K of 1.624(3) Å.

The observed H—O—H angles, 96(7) (296 K) and 106(6)° (173 K), fall, within their uncertainties, in the range 101.0–109.8° given by Chiari & Ferraris (1982) for inorganic hydrates of class A (Ferraris & Franchini-Angela, 1972) to which this water belongs. To account for the foreshortening of the water O—H bond distances as determined by X-ray diffraction, the position of each water H atom was adjusted along the corresponding observed O—H bond direction until the O—H bond distance was 0.954 Å, the mean value for class A inorganic hydrates as determined by neutron diffraction (Chiari & Ferraris, 1982). The resulting neutron-adjusted H-atom coordinates were used in the subsequent analysis of hydrogen bonding, the neutron-adjusted H—O(acceptor) distance being taken as the hydrogen-bond length. The hydrogen-bond parameters are given in Table 5.

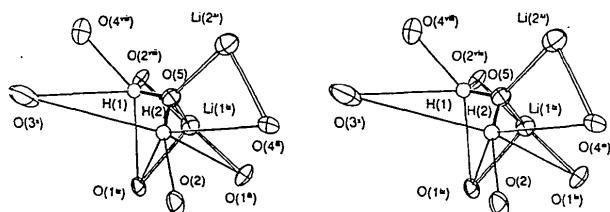


Fig. 2. Stereoview of the hydrogen bonding and cation coordination involving the water molecule in lithium perbromate monohydrate at 296 K drawn using ORTEPII (Johnson, 1976). Displacement ellipsoids are drawn at 50% probability for all atoms except H, which have been set artificially small. [Symmetry code not previously defined: (xi) $\frac{1}{2} + x, y - \frac{1}{2}, z$.]

The water O atom, O(5), constitutes a common corner of the two types of LiO₆ octahedra. The Li(1)—O(5)—Li(2) angle is 125.5(3) (296 K) or 125.8(2)° (173 K), quite similar to the corresponding angle in NaBrO₄.H₂O [117.4 (2)°]. Otherwise, the environment of O(5) is rather different because of a substantially greater number of hydrogen bonds in the present salt, as illustrated in Fig. 2. In addition to single hydrogen bonds involving H(1) and H(2), and a bifurcated bond involving O(3^{vi}) as acceptor, which also occur in NaBrO₄.H₂O (Table 3 and Figs. 2 and 3 in Blackburn *et al.*, 1992), there is a single hydrogen bond involving H(1), two single hydrogen bonds involving H(2), and a second bifurcated bond which involves O(1^{iv}) as an acceptor. Thus, while in NaBrO₄.H₂O each H atom is involved in two-center/bifurcated hydrogen bonding, H(1) in the title compound is involved in four-center/double-bifurcated and H(2) in five-center/double-bifurcated hydrogen bonding.

This extensive hydrogen bonding appears to account for the modest values of the isotropic displacement parameters for H(1) and H(2): average $B = 2.9(3)$ Å² at 296 K and 2.8(3) Å² at 173 K. These values are substantially smaller than the corresponding mean value in NaBrO₄.H₂O [6.0(24) Å² (Blackburn *et al.*, 1992)], and very considerably smaller than that in NaClO₄.H₂O [8.8 (X-ray value) or 9.4 Å² (neutron-diffraction value) (Berglund *et al.*, 1975, 1976)]. Berglund & Tegnfeldt (1977, 1979) concluded from NMR and neutron diffraction studies that in NaClO₄.H₂O the water H atoms 'jump' between two positions associated with a fixed water O-atom position. In NaBrO₄.H₂O, unlike in NaClO₄.H₂O, both H(1) and H(2) are involved simultaneously in moderately short hydrogen bonds and this, together with the smaller B values, suggests that dynamic disordering by hydrogen 'jumping' may be absent in NaBrO₄.H₂O (Blackburn *et al.*, 1992). For LiBrO₄.H₂O, both the increased hydrogen bonding compared with NaBrO₄.H₂O and the great reduction of the isotropic displacement parameters of H(1) and H(2) at both temperatures lead to the surmise that hydrogen 'jumping' is not significant in the title salt.

Experimental

Crystalline LiBrO₄.3H₂O (Blackburn *et al.*, 1993) was heated to constant weight at ~ 400 K, whereupon less than one water of hydration remained per LiBrO₄. This nearly anhydrous material was dissolved in nominally anhydrous methanol and the solution was allowed to evaporate slowly in a chamber purged with dry air until crystals appeared. Analysis showed that these were LiBrO₄.H₂O.

Compound at 296 K

Crystal data

LiBrO₄.H₂O
 $M_r = 168.86$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å

Monoclinic	Cell parameters from 25	Li(1)—O(5 ¹)	2.107 (3)	O(1)—Li(1)—O(2 ⁱⁱⁱ)	96.0 (1)
<i>C</i> 2/ <i>c</i>	reflections	O(1)—O(1 ⁱⁱ)	4.318 (6)	O(1)—Li(1)—O(5 ¹)	88.0 (1)
<i>a</i> = 14.639 (1) Å	$\theta = 18.5\text{--}19.9^\circ$	O(2 ¹)—O(2 ⁱⁱⁱ)	4.373 (6)	O(1)—Li(1)—O(5 ⁱⁱⁱ)	92.0 (1)
<i>b</i> = 5.523 (1) Å	$\mu = 10.02 \text{ mm}^{-1}$	O(5 ¹)—O(5 ⁱⁱⁱ)	4.214 (6)	O(2 ¹)—Li(1)—O(2 ⁱⁱⁱ)	180
<i>c</i> = 10.722 (1) Å	<i>T</i> = 296 K	O(1)—O(2 ¹)	2.909 (4)	O(2 ¹)—Li(1)—O(5 ¹)	83.5 (1)
$\beta = 111.99 (1)^\circ$	Clear chunk	O(1)—O(5 ¹)	2.963 (4)	O(2 ¹)—Li(1)—O(5 ⁱⁱⁱ)	96.5 (1)
<i>V</i> = 803.8 (2) Å ³	0.38 × 0.27 × 0.23 mm	O(2 ¹)—O(5 ¹)	2.860 (4)	O(5 ¹)—Li(1)—O(5 ⁱⁱⁱ)	180
<i>Z</i> = 8	Colorless				
<i>D</i> _x = 2.790 Mg m ⁻³					
<i>Data collection</i>					
Rigaku AFC-5S diffractometer	Part I	Coordination polyhedron (II)			
ω -2θ scans	$h = 0 \rightarrow 18$	Li(2)—O(3)	2.125 (8)	O(3)—Li(2)—O(3 ^v)	100.8 (5)
Absorption correction:	$k = 0 \rightarrow 7$	Li(2)—O(4 ^{iv})	2.226 (8)	O(3)—Li(2)—O(4 ^{iv})	83.2 (1)
empirical (six ψ scans)	$l = -13 \rightarrow 12$	Li(2)—O(5 ⁱⁱⁱ)	2.142 (3)	O(3)—Li(2)—O(4 ^{vi})	175.9 (4)
(North, Phillips & Mathews, 1968)	Part II	Li(2)—O(3 ^v)	2.125 (8)	O(3)—Li(2)—O(5 ⁱⁱⁱ)	98.9 (2)
<i>T</i> _{min} = 0.663, <i>T</i> _{max} = 1.000	$h = 0 \rightarrow 18$	Li(2)—O(4 ^{vi})	2.226 (8)	O(3)—Li(2)—O(5 ^{vii})	87.0 (2)
1920 measured reflections	$k = -7 \rightarrow -1$	Li(2)—O(5 ^{vii})	2.142 (3)	O(3 ^v)—Li(2)—O(4 ^{iv})	175.9 (4)
1021 independent reflections	$l = -13 \rightarrow 12$	O(3)—O(4 ^{iv})	2.889 (5)	O(3 ^v)—Li(2)—O(4 ^{vi})	83.2 (1)
769 observed reflections	6 standard reflections	O(3)—O(4 ^{vi})	4.348 (4)	O(3 ^v)—Li(2)—O(5 ⁱⁱⁱ)	87.0 (2)
$[I > 3\sigma(I)]$	monitored every 150	O(3)—O(3 ^v)	3.274 (6)	O(3 ^v)—Li(2)—O(5 ^{vii})	98.9 (2)
<i>R</i> _{int} = 0.031	reflections	O(3)—O(5 ^{vii})	2.937 (4)	O(4 ^{iv})—Li(2)—O(4 ^{vi})	92.9 (4)
$\theta_{\text{max}} = 27.5^\circ$	intensity variation:	O(3)—O(5 ⁱⁱⁱ)	3.242 (4)	O(4 ^{iv})—Li(2)—O(5 ⁱⁱⁱ)	91.3 (2)
<i>Refinement</i>		O(4 ^{iv})—O(5 ^{vii})	2.876 (4)	O(4 ^{iv})—Li(2)—O(5 ^{vii})	82.3 (2)
Refinement on <i>F</i>	average maximum	O(4 ^{iv})—O(5 ⁱⁱⁱ)	3.124 (4)	O(4 ^{vi})—Li(2)—O(5 ⁱⁱⁱ)	82.3 (2)
<i>R</i> = 0.024	$\pm 2.1\%$	O(4 ^{iv})—O(4 ^{vi})	3.227 (5)	O(4 ^{vi})—Li(2)—O(5 ^{vii})	91.3 (2)
<i>wR</i> = 0.030		O(5 ^{vii})—O(5 ⁱⁱⁱ)	4.270 (6)	O(5 ⁱⁱⁱ)—Li(2)—O(5 ^{vii})	170.8 (6)
<i>S</i> = 1.34					
769 reflections					
76 parameters					
All H-atom parameters					
refined					
$w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(I)/2FLp$, $\sigma^2(I) = \sigma_{\text{cs}}^2(I) + (0.03I)^2$					
$(\Delta/\sigma)_{\text{max}} < 0.01$					
<i>Compound at 173 K</i>					
<i>Crystal data</i>					
LiBrO ₄ ·H ₂ O					
<i>M</i> _r = 168.86					
Monoclinic					
<i>Mo Kα radiation</i>					
$\lambda = 0.71073 \text{ \AA}$					
<i>Cell parameters from 25</i>					
Symmetry codes: (i) $x, -y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$; (iv) $x, 1 + y, z$; (v) $-x, y, \frac{1}{2} - z$; (vi) $-x, 1 + y, \frac{1}{2} - z$; (vii) $x - \frac{1}{2}, \frac{1}{2} + y, z$.					

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) at 296 K*

B_{iso} for H atoms; $B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i.a_j$ for others.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} / <i>B</i> _{eq}	<i>V</i> = 790.5 (2) \AA^3
Li(1)	1/4	1/4	1/2	2.1 (3)	<i>Z</i> = 8
Li(2)	0	0.4347 (19)	1/4	2.2 (4)	<i>D</i> _{<i>x</i>} = 2.838 Mg m^{-3}
Br	0.12981 (2)	-0.04611 (6)	0.20870 (3)	1.12 (2)	
O(1)	0.1730 (2)	-0.0447 (5)	0.3711 (3)	1.8 (1)	
O(2)	0.2188 (2)	-0.0488 (6)	0.1551 (3)	2.2 (1)	<i>Data collection</i>
O(3)	0.0628 (2)	0.1893 (6)	0.1517 (3)	2.7 (1)	<i>Rigaku AFC-5S diff.</i>
O(4)	0.0646 (2)	-0.2876 (6)	0.1567 (3)	2.1 (1)	ter
O(5)	0.3780 (2)	-0.0342 (6)	0.0620 (3)	1.6 (1)	
H(1)	0.378 (4)	-0.034 (11)	0.005 (7)	3.2 (17)	ω - 2θ scans
H(2)	0.356 (4)	0.097 (12)	0.058 (5)	2.6 (13)	Absorption correction

Table 2. Selected bond lengths (Å) and angles (°) for lithium perbromate monohydrate at 296 K

Coordination polyhedron (I)

Li(1)—O(5 ¹)	2.107 (3)	O(1)—Li(1)—O(2 ⁱⁱⁱ)	96.0 (1)	
O(1)—O(1 ⁱⁱ)	4.318 (6)	O(1)—Li(1)—O(5 ¹)	88.0 (1)	
O(2 ¹)—O(2 ⁱⁱⁱ)	4.373 (6)	O(1)—Li(1)—O(5 ⁱⁱⁱ)	92.0 (1)	
O(5 ¹)—O(5 ⁱⁱⁱ)	4.214 (6)	O(2 ¹)—Li(1)—O(2 ⁱⁱⁱ)	180	
O(1)—O(2 ¹)	2.909 (4)	O(2 ¹)—Li(1)—O(5 ¹)	83.5 (1)	
O(1)—O(5 ¹)	2.963 (4)	O(2 ¹)—Li(1)—O(5 ⁱⁱⁱ)	96.5 (1)	
O(2 ¹)—O(5 ¹)	2.860 (4)	O(5 ¹)—Li(1)—O(5 ⁱⁱⁱ)	180	
Coordination polyhedron (II)				
Li(2)—O(3)	2.125 (8)	O(3)—Li(2)—O(3 ^v)	100.8 (5)	
Li(2)—O(4 ^{iv})	2.226 (8)	O(3)—Li(2)—O(4 ^{iv})	83.2 (1)	
Li(2)—O(5 ⁱⁱ)	2.142 (3)	O(3)—Li(2)—O(4 ^{vi})	175.9 (4)	
Li(2)—O(3 ^v)	2.125 (8)	O(3)—Li(2)—O(5 ⁱⁱ)	98.9 (2)	
Li(2)—O(4 ^{vi})	2.226 (8)	O(3)—Li(2)—O(5 ^{vii})	87.0 (2)	
Li(2)—O(5 ^{vii})	2.142 (3)	O(3 ^v)—Li(2)—O(4 ^{iv})	175.9 (4)	
O(3)—O(4 ^{iv})	2.889 (5)	O(3 ^v)—Li(2)—O(4 ^{vi})	83.2 (1)	
O(3)—O(4 ^{vi})	4.348 (4)	O(3 ^v)—Li(2)—O(5 ⁱⁱ)	87.0 (2)	
O(3)—O(3 ^v)	3.274 (6)	O(3 ^v)—Li(2)—O(5 ^{vii})	98.9 (2)	
O(3)—O(5 ⁱⁱ)	2.937 (4)	O(4 ^{iv})—Li(2)—O(4 ^{vi})	92.9 (4)	
O(3)—O(5 ^{vii})	3.242 (4)	O(4 ^{iv})—Li(2)—O(5 ⁱⁱ)	91.3 (2)	
O(4 ^{iv})—O(5 ^{vii})	2.876 (4)	O(4 ^{iv})—Li(2)—O(5 ^{vii})	82.3 (2)	
O(4 ^{iv})—O(5 ⁱⁱ)	3.124 (4)	O(4 ^{vi})—Li(2)—O(5 ⁱⁱ)	82.3 (2)	
O(4 ^{iv})—O(4 ^{vi})	3.227 (5)	O(4 ^{vi})—Li(2)—O(5 ^{vii})	91.3 (2)	
O(5 ^{vii})—O(5 ⁱⁱ)	4.270 (6)	O(5 ⁱⁱ)—Li(2)—O(5 ^{vii})	170.8 (6)	
Water molecule				
O(5)—H(1)	0.62 (7)	H(1)—O(5)—H(2)	96 (7)	
O(5)—H(2)	0.79 (6)			
Perbromate ion: rigid body (I)				
		Rigid-body corrected		
Br—O(1)	1.615 (3)	1.625	O(1)—Br—O(2)	110.0 (1)
Br—O(2)	1.608 (3)	1.623	O(1)—Br—O(3)	110.1 (1)
Br—O(3)	1.606 (3)	1.621	O(1)—Br—O(4)	108.6 (1)
Br—O(4)	1.613 (3)	1.626	O(2)—Br—O(3)	109.4 (2)
			O(2)—Br—O(4)	108.8 (2)
			O(3)—Br—O(4)	109.9 (2)
Symmetry codes: (i) $x, -y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $x, 1 + y, z$; (v) $-x, y, \frac{1}{2} - z$; (vi) $-x, 1 + y, \frac{1}{2} - z$; (vii) $x - \frac{1}{2}, \frac{1}{2} + y, z$.				
Compound at 173 K				
<i>Crystal data</i>				
LiBrO ₄ ·H ₂ O		Mo K α radiation		
$M_r = 168.86$		$\lambda = 0.71073 \text{ \AA}$		
Monoclinic		Cell parameters from 25		
$C2/c$		reflections		
$a = 14.551 (3) \text{ \AA}$		$\theta = 14.0\text{--}15.0^\circ$		
$b = 5.504 (1) \text{ \AA}$		$\mu = 10.18 \text{ mm}^{-1}$		
$c = 10.641 (1) \text{ \AA}$		$T = 173 \text{ K}$		
$\beta = 111.93 (1)^\circ$		Clear chunk		
$V = 790.5 (2) \text{ \AA}^3$		$0.50 \times 0.38 \times 0.35 \text{ mm}$		
$Z = 8$		Colorless		
$D_x = 2.838 \text{ Mg m}^{-3}$				
<i>Data collection</i>				
Rigaku AFC-5S diffractometer		778 observed reflections		
ω -2 θ scans		$[I > 3\sigma(I)]$		
Absorption correction: empirical (six ψ scans)		$R_{\text{int}} = 0.028$		
(North, Phillips & Mathews, 1968)		$\theta_{\text{max}} = 27.5^\circ$		
$T_{\text{min}} = 0.668$, $T_{\text{max}} =$ 1.000		$h = 0 \rightarrow 18$		
1040 measured reflections		$k = 0 \rightarrow 7$		
1000 independent reflections		$l = -13 \rightarrow 12$		
		6 standard reflections		
		monitored every 150		
		reflections		
		intensity variation: $\pm 1.2\%$		

Refinement

Refinement on F $R = 0.022$ $wR = 0.031$ $S = 1.49$

778 reflections

75 parameters

All H-atom parameters

refined

 $w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(I)/2FL_p$, $\sigma^2(I) = \sigma_{cs}^2(I) + (0.03I)^2$ $(\Delta/\sigma)_{\max} < 0.01$

$\Delta\rho_{\max} = 0.89 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.72 \text{ e } \text{\AA}^{-3}$

Extinction correction:

Zachariasen (1963, 1968)

Extinction coefficient:

$1.57(9) \times 10^{-6}$

Atomic scattering factors

from Cromer & Waber

(1974) (non-H) and

Stewart, Davidson &

Simpson (1965) (H)

Perbromate ion: rigid body (I)

	Rigid-body corrected			
Br—O(1)	1.618 (3)	1.624	O(1)—Br—O(2)	110.0 (1)
Br—O(2)	1.615 (3)	1.624	O(1)—Br—O(3)	110.2 (1)
Br—O(3)	1.606 (3)	1.616	O(1)—Br—O(4)	108.3 (1)
Br—O(4)	1.613 (3)	1.621	O(2)—Br—O(3)	109.1 (2)
			O(2)—Br—O(4)	109.4 (1)
			O(3)—Br—O(4)	109.8 (2)

Symmetry codes: (i) $x, -y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $x, 1 + y, z$; (v) $-x, y, \frac{1}{2} - z$; (vi) $-x, 1 + y, \frac{1}{2} - z$; (vii) $x - \frac{1}{2}, \frac{1}{2} + y, z$.Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) at 173 K B_{iso} for H atoms; $B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ for others.

	x	y	z	$B_{\text{iso}}/B_{\text{eq}}$
Li(1)	1/4	1/4	1/2	1.3 (3)
Li(2)	0	0.4340 (18)	1/4	1.2 (3)
Br	0.13044 (2)	-0.04967 (7)	0.21015 (3)	0.59 (2)
O(1)	0.1724 (2)	-0.0485 (5)	0.3740 (2)	1.0 (1)
O(2)	0.2214 (2)	-0.0509 (6)	0.1580 (3)	1.2 (1)
O(3)	0.0633 (2)	0.1867 (6)	0.1516 (3)	1.5 (1)
O(4)	0.0647 (2)	-0.2916 (5)	0.1575 (3)	1.2 (1)
O(5)	0.3781 (2)	-0.0370 (6)	0.0616 (3)	0.9 (1)
H(1)	0.381 (4)	-0.048 (11)	0.005 (7)	2.5 (15)
H(2)	0.350 (4)	0.096 (11)	0.060 (6)	3.1 (14)

Table 4. Selected bond lengths (Å) and angles (°) for lithium perbromate monohydrate at 173 K

Coordination polyhedron (I)

Li(1)—O(1)	2.154 (3)	O(1)—Li(1)—O(1 ⁱⁱ)	180
Li(1)—O(2 ⁱ)	2.173 (3)	O(1)—Li(1)—O(2 ⁱ)	83.7 (1)
Li(1)—O(5 ⁱ)	2.089 (3)	O(1)—Li(1)—O(2 ⁱⁱⁱ)	96.3 (7)
O(1)—O(1 ⁱⁱ)	4.309 (5)	O(1)—Li(1)—O(5 ⁱ)	88.1 (1)
O(2 ⁱ)—O(2 ⁱⁱⁱ)	4.346 (6)	O(1)—Li(1)—O(5 ⁱⁱⁱ)	91.9 (1)
O(5 ⁱ)—O(5 ⁱⁱⁱ)	4.178 (6)	O(2 ⁱ)—Li(1)—O(2 ⁱⁱⁱ)	180
O(1)—O(2 ⁱ)	2.886 (4)	O(2 ⁱ)—Li(1)—O(5 ⁱ)	83.1 (1)
O(1)—O(5 ⁱ)	2.950 (4)	O(2 ⁱ)—Li(1)—O(5 ⁱⁱⁱ)	96.9 (1)
O(2 ⁱ)—O(5 ⁱ)	2.828 (4)	O(5 ⁱ)—Li(1)—O(5 ⁱⁱⁱ)	180

Coordination polyhedron (II)

Li(2)—O(3)	2.126 (7)	O(3)—Li(2)—O(3 ^y)	100.4 (4)
Li(2)—O(4 ^{iv})	2.197 (7)	O(3)—Li(2)—O(4 ^{iv})	83.2 (1)
Li(2)—O(5 ⁱⁱⁱ)	2.129 (3)	O(3)—Li(2)—O(4 ^{vi})	176.2 (4)
Li(2)—O(3 ^{iv})	2.126 (7)	O(3)—Li(2)—O(5 ^{iv})	98.6 (2)
Li(2)—O(4 ^{iv})	2.197 (7)	O(3)—Li(2)—O(5 ^{vi})	86.9 (2)
Li(2)—O(5 ^{vi})	2.129 (3)	O(3 ^y)—Li(2)—O(4 ^{iv})	176.2 (4)
O(3)—O(4 ^{iv})	2.871 (4)	O(3 ^y)—Li(2)—O(4 ^{vi})	83.2 (1)
O(3)—O(4 ^{vi})	4.321 (4)	O(3 ^y)—Li(2)—O(5 ^{iv})	86.9 (2)
O(3)—O(3 ^{iv})	3.267 (6)	O(3 ^y)—Li(2)—O(5 ^{vi})	98.6 (2)
O(3)—O(5 ^{vi})	2.927 (4)	O(4 ^{iv})—Li(2)—O(4 ^{vi})	93.2 (4)
O(3)—O(5 ⁱⁱⁱ)	3.226 (4)	O(4 ^{iv})—Li(2)—O(5 ^{iv})	91.4 (2)
O(4 ^{iv})—O(5 ^{vi})	2.859 (4)	O(4 ^{iv})—Li(2)—O(5 ^{vi})	82.7 (2)
O(4 ^{iv})—O(5 ⁱⁱⁱ)	3.097 (4)	O(4 ^{vi})—Li(2)—O(5 ^{iv})	82.7 (2)
O(4 ^{iv})—O(4 ^{vi})	3.193 (5)	O(4 ^{vi})—Li(2)—O(5 ^{vi})	91.4 (2)
O(5 ^{vi})—O(5 ⁱⁱⁱ)	4.247 (6)	O(5 ⁱⁱⁱ)—Li(2)—O(5 ^{vi})	171.4 (6)

Water molecule

O(5)—H(1)	0.62 (6)	H(1)—O(5)—H(2)	106 (6)
O(5)—H(2)	0.84 (6)		

Table 5. Hydrogen-bond parameters (Å, °) for lithium perbromate monohydrate

$D—H\cdots A$	T	$H\cdots A$ (observed)	$H\cdots A$ (adjusted)*	$D\cdots A$	$D—H\cdots A$
O(5)—H(2)…O(2)	296 173	2.71 (5) 2.59 (6)	2.70 2.58	2.860 (4) 2.829 (4)	93 (4) 98 (5)
O(5)—H(1)…O(4) ^{viii}	296 173	2.40 (7) 2.32 (6)	2.12 2.02	2.941 (4) 2.910 (4)	149 (7) 157 (7)
O(5)—H(2)…O(1) ⁱⁱⁱ	296 173	2.22 (6) 2.14 (6)	2.07 2.03	2.963 (5) 2.934 (4)	158 (5) 158 (5)
O(5)—H(1)…O(1) ^{ix}	296 173	2.83 (6) 2.88 (6)	2.82 2.90	2.963 (4) 2.950 (4)	96 (6) 90 (6)
O(5)—H(2)…O(1) ^x	296 173	2.69 (5) 2.62 (6)	2.66 2.59	2.963 (4) 2.950 (4)	103 (4) 105 (5)
O(5)—H(2)…O(4) ^w	296 173	2.91 (5) 2.86 (6)	2.89 2.84	3.124 (4) 3.097 (4)	98 (4) 99 (4)
O(5)—H(1)…O(2) ^{viii}	296 173	2.90 (6) 2.86 (6)	2.78 2.73	3.203 (4) 3.189 (4)	114 (6) 117 (6)
O(5)—H(1)…O(3) ^x	296 173	2.88 (7) 2.90 (6)	2.65 2.70	3.335 (5) 3.322 (4)	134 (7) 129 (6)
O(5)—H(2)…O(3) ^x	296 173	3.14 (5) 3.19 (6)	3.12 3.19	3.335 (4) 3.322 (4)	97 (6) 92 (6)

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

* See text for details.

Since the monohydrate reacts very readily with moisture in ambient air to form the trihydrate, the crystal for room-temperature study was mounted with epoxy cement and sealed in a capillary tube; for the low-temperature study a crystal was mounted with epoxy cement on a quartz pin and kept in dry air until it was immersed in the cold gas stream produced by a Molecular Structure Corporation low-temperature apparatus. The estimated uncertainty of the crystal temperature is 2 K. The radiation was graphite monochromated.

Unit cells were determined by symmetry-constrained least-squares fits. Scan widths were $(1.35 + 0.35\tan\theta)$ and $(1.40 + 0.35\tan\theta)$ ° in ω for the low-temperature study and the room-temperature study, respectively. The background/scan time ratio was 0.5 for both studies. No correction was required for decay, but both data sets were corrected for Lorentz and polarization effects.

Both sets of intensity data had Laue symmetry and systematic absences consistent with space groups $C2/c$ and Cc . The centrosymmetric alternative ($C2/c$, No. 15) was given initial preference and adopted since refinement proceeded well.

For the low-temperature study, initial coordinates for Br were obtained from a Patterson map. The *TEXSAN* (Molecular Structure Corporation, 1989) package was used to generate a Fourier difference list from which the five O atoms and two Li atoms were located. The two H atoms were also located by Fourier difference methods following anisotropic full-matrix least-squares refinement of all the non-H atoms, and were refined isotropically. For the room-temperature study, initial coordinates were taken from the low-temperature study. An extinction coefficient (Zachariasen, 1963, 1968) was included in the final stages of least-squares refinement in each case: at low temperature the maximum effect was 16.2% of F_o for 002; at room temperature, 18.8% of F_o for 400. The residual electron-density peaks are consistent in magnitude with those of the $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$ study (Blackburn *et al.*, 1992).

Rigid-body analysis of the two Li-O polyhedra and of the perbromate anion was performed using the program *THMA11* (Trueblood, 1986) based on the work of Schomaker & Trueblood (1968). While neither of the lithium coordination polyhedra was found to conform to rigid-body behavior, the average magnitude of the differences in the mean-square displacement amplitudes along the interatomic vectors for the ten unique atom pairs of the perbromate ion was found to be $13(18) \times 10^{-4} \text{ \AA}^2$ for the low-temperature data and $15(20) \times 10^{-4} \text{ \AA}^2$ for the room-temperature data. The Hirshfeld (1976) rigid-bond test, extended as described by Rosenfield, Trueblood & Dunitz (1978), is satisfied and Br—O bond lengths corrected for rigid-body motion are given in Tables 2 and 4.

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Lists of structure factors, anisotropic displacement parameters and data relating to the rigid-body analysis have been deposited with the IUCr (Reference: CR1113). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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