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Structure of Lithium Perbromate Trihydrate

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Abstract

The structure of $LiBrO_4.3H_2O$ consists of stacks, along **z**, of somewhat distorted face-sharing octahedra of water O atoms coordinating Li ions, with each stack surrounded by six stacks of virtually regular tetrahedral perbromate ions. This structure and that of $LiClO_4.3H_2O$ are isomorphic. As in the perchlorate, the Br—O(1) (axial) bonds are oriented in the positive **z** direction. Location and isotropic refinement of the single type of H atom permitted detailed analysis of the hydrogen bonding, which occurs principally with perbromate O atoms and is best described as two-center bifurcated.

Comment

This investigation of the structure of $LiBrO_4.3H_2O$ is one of a continuing series of investigations of the structures of simple salts of perbromic acid. As in previous investigations, elucidation of hydrogen bonding was a matter of particular interest, as was comparison of this structure with that of its perchlorate analog. This is the first reported study of the structure of lithium perbromate trihydrate.

The present data establish that lithium perbromate trihydrate and lithium perchlorate trihydrate (Chomnilpan, Liminga & Tellgren, 1977; Sequeira, Bernal, Brown & Faggiani, 1975) are isomorphic. The single type of lithium ion occupies a site of $3m$ symmetry, which allows two distances for the six coordinated water O atoms. The Li—O distances, 2.148 (16) and 2.135 (16) Å, are not significantly different. Chomnilpan *et al.* (1977) reported the corresponding distances in the perchlorate as 2.127 (5) and 2.121 (5) Å. The two sets of Li—O(water) distances agree within experimental error. Although the two Li—O(water) distances in the title salt are virtually equal, the $Li—O_6$ octahedron has O—Li—O angles deviating substantially from 90°. This result agrees well with the corresponding result for the perchlorate (Chomnilpan *et al.*, 1977). Indeed, the largest difference in corresponding angles in the octahedra in the two salts is only 0.2°. These octahedra share faces with two adjacent octahedra, forming stacks along **z**.

The Br atom is at a site of $3m$ symmetry; it is bonded to an axial O(1) atom (site symmetry $3m$) and a trigonal O(2) atom (site symmetry m). The two crystallographically distinct distances in the perbromate ion are virtually identical and the O—Br—O angles differ by only approximately 0.4° from the values for a regular tetrahedron (Table 2). These Br—O bond distances are the largest we have determined for the perbromate ion, the overall mean observed value for previous salts being near 1.606 Å. Again, the e.s.d.'s for these bond distances are substantially larger than usual in this series of studies. Chomnilpan *et al.* (1977) found values of 1.427 (3) and 1.439 (2) Å for the corresponding Cl—O bonds in the perchlorate. In contrast, Sequeira *et al.* (1975) found equal values for these perchlorate bonds, in agreement with the present results for the perbromate. As in the perchlorate, the Br—O(1) bonds point in the positive **z** direction.

The geometrical parameters of the water molecule found in this study [O(3)—H 0.95 (7) Å, H—O(3)—H 111 (8)°], agree well with the mean values determined by neutron diffraction for water molecules of hydrate class *A*, to which this water molecule belongs [O(water)—H 0.954 Å, H—O(water)—H 105.3° (Ferraris & Franchini-Angela, 1972; Chiari & Ferraris, 1982)]. Each H atom participates in a hydrogen bond with a perbromate trigonal O(2) atom, a bifurcated hydrogen bond with a (common) axial O(1) atom and a very weak hydrogen bond with a water O atom (Table 3). If the very weak bond is included, the system exhibits three-center bifurcated hydrogen bonding (Jeffrey & Maluszynska, 1986). The H—O(2) hydrogen-bond distance, 2.04 (7) Å, and the O(3)—H—O(2) angle, 171 (6)°, are in close agreement with the values determined for the perchlorate by neutron diffraction (Sequeira *et al.*, 1975). In addition to its hydrogen-bonding interactions, each water molecule interacts, through O(3), with two lithium ions.

Considering the hydrogen bonding from the point of view of the perbromate O atoms, we observe that each O(1) atom participates in three bifurcated hydrogen bonds while each O(2) atom participates in two hydrogen bonds. Thus, each perbromate ion participates in nine substantial hydrogen bonds. In agreement with the analysis of Sequeira *et al.* (1975),

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but in disagreement with that of Chomnilpan *et al.* (1977), the three bifurcated hydrogen bonds to perbromate O(1) atoms are regarded as significant interactions. Consistent with this view, lack of hydrogen bonding involving O(1) cannot be properly invoked (Chomnilpan *et al.*, 1977) to rationalize a possible bond-length difference in the perhalate ion.

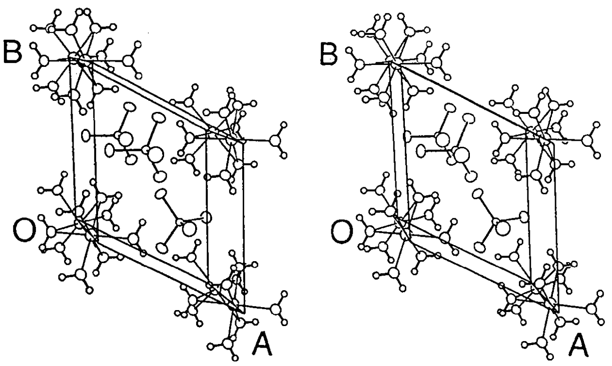

Fig. 1. A stereoview of a unit cell of the lithium perbromate trihydrate structure at 296 K drawn using *ORTEP*II (Johnson, 1976). Displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. Hydrogen bonds have been omitted for clarity.

Experimental

Crystal data

$LiBrO_4.3H_2O$
M_r = 204.89
Hexagonal
$P6_3mc$
a = 7.8723 (5) Å
c = 5.4990 (10) Å
V = 295.13 (6) Å^3
Z = 2
D_x = 2.305 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10.9–13.8°
μ = 6.86 mm^{-1}
T = 296 K
Capped hexagonal column
0.35 × 0.23 × 0.23 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min}$ = 0.864, $T_{\max}$ = 1.000
2291 measured reflections
473 independent reflections
403 observed reflections [$I > \sigma(I)$]

$R_{\rm int}$ = 0.042
$\theta_{\max}$ = 32.5°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = -8 \rightarrow 8$
6 standard reflections
monitored every 150 reflections
intensity variation: ±3%

Refinement

Refinement on F
Final R = 0.037
wR = 0.057
S = 2.55

$\Delta\rho_{\min}$ = −0.88 e Å^{-3}
[0.8 Å from Br and O(1)]
Extinction correction: Zachariasen (1963, 1968)

403 reflections
26 parameters
All H-atom parameters refined
$w = (\sigma_F)^{-2}$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max}$ = 1.14 e Å^{-3}
(0.13 Å from Br)

Extinction coefficient: 2.05 (22) × 10^{-5}
Atomic scattering factors from Cromer & Waber (1974) and Stewart, Davidson & Simpson (1965)

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

H refined isotropically; $B_{\rm eq} = \frac{8\pi^2}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	y	z	$B_{\rm iso}/B_{\rm eq}$
Li	0	0	0.2096 (39)	2.1 (7)
Br	$\frac{1}{3}$	$\frac{2}{3}$	0	1.35 (2)
O(1)	$\frac{1}{3}$	$\frac{2}{3}$	0.2952 (22)	3.1 (3)
O(2)	0.4453 (4)	−0.4453	−0.1000 (12)	2.53 (7)
O(3)	0.1204 (4)	−0.1204	0.4615 (11)	1.9 (1)
H	0.258 (10)	−0.060 (10)	0.445 (13)	2.2 (17)

Table 2. *Bond lengths* (Å) *and angles* (°) *and hydrogen-bond geometry* (Å, °)

LiO_6 polyhedron			
Li—O(3)	2.148 (16)	O(3)—Li—O(3$^{\rm ii}$)	82.9 (7)
Li—O(3$^{\rm i}$)	2.135 (16)	O(3)—Li—O(3$^{\rm i}$)	179.6 (10)
O(3)—O(3$^{\rm ii}$)	2.844 (9)	O(3)—Li—O(3$^{\rm iii}$)	96.8 (1)
O(3)—O(3$^{\rm iii}$)	3.202 (3)	O(3$^{\rm i}$)—Li—O(3$^{\rm iii}$)	83.5 (7)
O(3)—O(3$^{\rm i}$)	4.283 (8)		
Perbromate ion			
Br—O(1)	1.624 (12)	O(1)—Br—O(2$^{\rm iv}$)	109.8 (2)
Br—O(2$^{\rm iv}$)	1.623 (6)	O(2$^{\rm ii}$)—Br—O(2$^{\rm iv}$)	109.1 (2)
Water molecule			
O(3)—H	0.95 (7)	H—O(3)—H$^{\rm v}$	111 (8)
D—H$\cdots A$	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O(3)—H$\cdots$O(2$^{\rm vi}$)	2.04 (7)	2.981 (4)	171 (6)
O(3)—H$^{\rm v}\cdots$O(2$^{\rm vii}$)	2.04 (7)	2.981 (4)	171 (6)
O(3)—H$\cdots$O(1$^{\rm viii}$)	2.63 (7)	3.044 (7)	107 (5)
O(3)—H$^{\rm v}\cdots$O(1$^{\rm viii}$)	2.63 (7)	3.044 (7)	107 (5)
O(3)—H$\cdots$O(3$^{\rm ix}$)	3.05 (7)	3.202 (3)	91 (4)
O(3)—H$^{\rm v}\cdots$O(3$^{\rm iii}$)	3.05 (7)	3.202 (3)	91 (4)

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

An aqueous solution of reagent grade lithium hydroxide (GFS Chemicals) was reacted with a slight excess of approximately 2*M* perbromic acid prepared as described by Appelman (1972). The resulting solution was evaporated at room temperature to produce crystalline lithium perbromate trihydrate. The sample was mounted with epoxy cement and was coated with Apiezon L grease to retard potential loss or gain of water. Unit-cell parameters were obtained from a symmetry-constrained least-squares fit. In the early portion of X-ray exposure of the sample, the intensities of the standards increased. After further exposure, the standard intensities became stable and, subsequently, data were collected using scan widths of (1.05 + 0.35tanθ)° in ω and a background/scan time ratio of 0.5. No decay correction was applied but the data were corrected for Lorentz and polarization effects and for absorption; ψ-scan data were obtained after the standard reflections became stable and just prior to the intensity data collection; the correction method was that of North, Phillips & Mathews (1968). The intensity data have symmetry consistent with Laue group 6/*mmm*. On the basis of systematic absences (*hhl*, *l* = odd), three space groups were allowed, of which two were noncentrosymmetric ($P6_3mc$ and $P\bar{6}2c$) and one was centrosymmetric ($P6_3/mmc$). Since the structure of lithium perchlorate trihydrate had been assigned in $P6_3mc$ (Chomnilpan *et al.*, 1977, and earlier references cited therein), $P6_3mc$ (No. 186) was given initial preference; since refinement proceeded well it was adopted. Subsequent attempts to refine a structure in the potential alternative space groups were not successful. The *TEXSAN* (Molecular Structure Corporation, 1989) structure analysis package was used to generate a Patterson map from which the initial Br position was assigned. Difference Fourier methods were then used to locate the remaining atoms. The non-H atoms, all of which were assigned at special positions, were refined anisotropically, the H atom isotropically, using full-matrix least squares. An extinction coefficient (Zachariasen, 1963, 1968) was included in the least-squares refinement; the maximum effect of extinction was 27.4% of F_o for $00\bar{2}$. Following the extinction correction, 13 reflections had $\Delta F/\sigma_F$ greater than 5.0. The enantiomorphic structure was rejected since its agreement was inferior (R = 0.061 and wR = 0.083).

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Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71005 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1039]

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Structure of Tetraaquacalcium Perbromate

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Abstract

The structure of the title compound consists of columns of Ca ions surrounded by four columns of perbromate ions and four columns of water molecules alternating in pairs. The CaO_8 complex was found to be dimensionally similar to corresponding complexes in other simple tetrahydrated calcium salts. The eight coordinating O atoms form a polyhedron which departs only slightly from a (distorted) square antiprism. Each of the crystallographically inequivalent perbromate ions was found to conform to rigid-body behavior while the CaO_8 complex did not. Although the perbromate ions depart moderately from regular tetrahedral geometry, the mean Br—O bond length agrees well with previously determined values. Hydrogen bonds in this structure involve water-oxygen acceptors as well as perbromate-oxygen acceptors.

Comment

This structural study of $[Ca(H_2O)_4](BrO_4)_2$ is one of a series of such studies of simple salts of perbromic acid. Refinement of the H atoms to permit a detailed description of the hydrogen bonding was a matter of particular interest. This is the first report on the structure of tetraaquacalcium perbromate.

Final atomic coordinates and isotropic and equivalent isotropic displacement parameters and their e.s.d.'s are given in Table 1. A unit cell is shown in Fig. 1.

In this structure, Ca is coordinated by four water O atoms at a mean distance of 2.37 (3) Å and by four anion O atoms at the slightly greater mean distance of 2.57 (4) Å, the overall mean distance being 2.47 (10) Å (Table 2). The same pattern of distances is exhibited by Ca in other simple hydrated salts, for example, in $[Ca(H_2O)_4](NO_3)_2$, for which the corresponding distances are 2.44 (1), 2.52 (3) and 2.48 (5) Å (Leclaire & Monier, 1977), and in $[Ca(H_2O)_4]Cd(NO_2)_4$, for which the corresponding distances are 2.41 (1), 2.58 (1) and 2.49 (9) Å (Aoyama, Ohba & Saito, 1988). In the title salt, the eight coordinating O atoms form a polyhedron which departs only slightly from a (distorted) square