in particular garnet compositions rather than others. In what follows, the bond-strength sums for the X cation are related to the occupations of the X and Y sites and x as defined by the hydrogarnet formula: 2.12 ($X = \mathrm{Sr}$, $Y = \mathrm{Al}$, $x = 3$); 3.07 ($X = \mathrm{Sr}$, $Y = \mathrm{Al}$, $x = 0$); 1.93 ($X = \mathrm{Ca}$, $Y = \mathrm{Al}$, $x = 3$); 2.52 ($X = \mathrm{Ca}$, $Y = \mathrm{Al}$, $x = 0$); 2.31 ($X = \mathrm{Ca}$, $Y = \mathrm{Fe}$, $x = 0$); 1.72 ($X = \mathrm{Mg}$, $Y = \mathrm{Al}$, $x = 0$). For $Sr_3Al_2(SiO_4)_3$ ($X = \mathrm{Sr}$, $Y = \mathrm{Al}$, $x = 0$) bond-strength sums were calculated from the Sr—O distances predicted by Novak & Gibbs (1971). The bond-strength sums to Ca in grossular and andradite indicate a significant amount of overbonding, *i.e.* Ca is too large for the dodecahedral cavity based on a comparison of the mean Ca—O distances (2.405 and 2.433 Å for grossular and andradite, respectively) and the sum of the ionic radii for $^{[8]}$Ca and $^{[4]}$O (2.50 Å) (Shannon, 1976). Underbonding of the X site in pyrope also reflects a size misfit, but in this case, Mg is too small for the cavity. As the substitution $(O_4H_4) \leftrightarrow (SiO_4)$ causes an expansion of the dodecahedron (Lager *et al.*, 1989), overbonded sites will be stabilized and underbonded sites destabilized as the OH content increases (Zabinski, 1966). This line of reasoning is consistent with experimental data for grossular, andradite and pyrope (see above). The extreme overbonding at the X site in $Sr_3Al_2(SiO_4)_3$ may be the reason that this garnet has not been synthesized. Based on these simple arguments, a limited $(O_4H_4) \leftrightarrow (SiO_4)$ substitution should exist for Sr garnets; however, the stability field will be displaced, relative to the Ca analogs, toward the hydrogarnet end member.

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Structure of Sodium Perbromate Monohydrate

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Abstract. $NaBrO_4.H_2O$, $M_r = 184.90$, monoclinic, $C2/c$, $a = 15.7575\,(19)$, $b = 5.7373\,(15)$, $c = 11.3390\,(19)$ Å, $\beta = 111.193\,(10)°$, $V = 955.8\,(3)$ Å^3, $Z = 8$, $D_x = 2.570\ \mathrm{g\,cm^{-3}}$, $\lambda(\mathrm{Mo}\ K\bar{\alpha}) = 0.71073$ Å, $\mu = 85.2\ \mathrm{cm^{-1}}$, $F(000) = 704$, $T = 296$ K, $R = 0.039$ for 1137 unique reflections having $I > \sigma_I$. In this structure, there are two inequivalent Na ions, each coordinated by six O atoms. In each of the two types

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of distorted octahedra, there are three inequivalent Na—O distances; the average Na(1)—O and Na(2)—O distances are 2.379 (10) and 2.405 (23) Å, respectively. The perbromate ion in this structure displays very nearly regular tetrahedral geometry, although it is subject to no symmetry constraints; the average observed Br—O distance is 1.601 (4) Å, while the average observed O—Br—O angle is 109.5 (9)°. These values agree well with previously reported values. The perbromate ion, but neither of the sodium coordination polyhedra, shows rigid-body behavior. The average rigid-body corrected Br—O distance in the perbromate ion is 1.624 (3) Å. Refinement of the two inequivalent H atoms permitted detailed analysis of the hydrogen bonding, which is slightly different from that reported for the isomorphic sodium perchlorate monohydrate. Dynamic disordering of the H atoms as detailed by magnetic resonance methods for sodium perchlorate monohydrate is not clearly indicated in our X-ray study of sodium perbromate monohydrate.

Introduction. The structures of simple perbromate salts are under investigation in our laboratory, in part to permit comparisons of their structures with those of the corresponding perchlorates. This report presents the structure of sodium perbromate monohydrate, which has not previously been described.

Experimental. Sodium perbromate was obtained in a mixture of sodium salts by elemental fluorine oxidation of an aqueous sodium bromate–sodium hydroxide solution as described by Appelman (1972). The dried salt mixture was extracted with acetone, and the extract was evaporated to dryness at room temperature. The resulting solid, which was principally sodium perbromate, was dissolved in water. This solution was slowly evaporated at room temperature to produce clear crystals of $NaBrO_4.H_2O$. While many crystals were plate-like, the experimental sample was a chunk with approximate principal dimensions 0.23 × 0.27 × 0.32 mm. The sample was coated with Apiezon L grease to retard potential loss or gain of water and was analyzed at 296 K with a Rigaku AFC5S diffractometer utilizing graphite-monochromated Mo $K\bar{\alpha}$ radiation.

Unit-cell parameters were obtained from a symmetry-constrained least-squares fit of the setting angles for 25 centered reflections with $23 < 2\theta < 30°$. Intensity data were measured for 1944 reflections (exclusive of standards) with $+h$, $+k$, $\pm l$ indices ($h_{\max} = 23$, $k_{\max} = 8$, l: -17 to $+17$) and 2θ values in the range $4 \leq 2\theta \leq 65°$. The ω–2θ-scan technique was employed with scan widths $(1.25 + 0.35 \tan\theta)°$ in ω, and a background/scan time-ratio of 0.5. The variance assigned to each reflection was $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$, in which σ_{cs} is based on counting statistics and I is the integrated intensity. Six standard reflections (110, 31$\bar{2}$, 020, 531, 62$\bar{4}$ and 226) were measured after every 150 reflections. The first three standards, which can be categorized as low-angle standards ($2\theta < 15°$), exhibited a systematic increase in intensity until the later stages of the first data collection, when they became constant. A second data set was then collected on this same crystal in the same manner as the first. During this second data collection, the same standard reflections exhibited, on average, a maximum non-systematic relative intensity variation of ±3.1%. Thus, no decay corrections were required for the second data set and the structure was analyzed using these data; except where explicitly stated otherwise, all values cited in the present work are based upon this second set of data. The data were corrected for Lorentz and polarization effects. A ψ-scan absorption correction was applied based on ψ-scan data obtained near the end of the first data collection, after the standards were no longer changing systematically; the range of normalized transmission factors was 0.627–1.000, with an average value 0.818.

The intensities were found to be consistent with Laue group $2/m$. The systematic absences were consistent with two C-centered monoclinic space groups: Cc and $C2/c$. The centrosymmetric alternative, $C2/c$ (No.15), was given initial preference and, since refinement proceeded well, it was adopted. Initial coordinates for Br in a general position were obtained using a Patterson map. Fourier difference methods were then used to assign Na(1) and Na(2) in special positions with site symmetries $\bar{1}$ and 2, respectively, O(1) through O(5), and H(1) and H(2) in general positions. Full-matrix least-squares refinement was performed using the *TEXSAN* (Molecular Structure Corporation, 1989) structure analysis package to minimize the function $\sum\sigma_F^{-2}(|F_o| - |F_c|)^2$ in which $\sigma_F = \sigma_I/2F\text{Lp}$. Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for Br, Na, and O; the scattering factor for H was taken from Stewart, Davidson & Simpson (1965). Following anisotropic refinement of all non-H atoms, the ψ-scan absorption correction was applied and the data were averaged ($R_{\text{int}} = 0.032$ for 60 pairs of reflections). Then refinement, using all unique reflections with $I > \sigma_I$ and treating the secondary-extinction coefficient as an adjustable parameter, proceeded with all atoms but H anisotropic and with H isotropic.

The results for the final refinement cycle were: 1137 independent observations having $I > \sigma_I$, 75 variables, $R = 0.039$, $wR = 0.037$, $w = \sigma_F^{-2}$, $S = 1.15$, $(\Delta/\sigma)_{\max} < 0.01$. The final refined value of the secondary-extinction coefficient (Zachariasen, 1963, 1968) was $2.87\ (54) \times 10^{-7}$. Maximum and minimum peaks in the final electron density difference map were 0.92 e Å^{-3} near (0.08, 0.06, 0.17), approximately 0.8 Å from O(3) and Br, and −0.76 e Å^{-3} near (0.38, −0.04, 0.09), approximately 0.5 Å from O(5), respectively. While the magnitudes of these residual peaks are larger than is commonly expected, they are basically consistent with the corresponding magnitudes for other perbromate structures (Gerkin, Reppart & Appelman, 1988; Gallucci, Gerkin & Reppart, 1989, 1990). [For the final refinement cycle for 1034 independent observations having $I > 3\sigma_I$, $R = 0.033$, $wR = 0.035$, $S = 1.13$. Similarly, for the 1466 independent observations having $I > 0$, $R = 0.065$, $wR = 0.040$, $S = 1.08$. These latter two refinements were performed for comparison purposes only.]

The final atomic coordinates, isotropic and equivalent isotropic displacement parameters and their e.s.d's are given in Table 1.* Selected interatomic distances and angles in the cation coordination polyhedra, in the perbromate anion and in the water molecule are given in Table 2 together with their e.s.d.'s. A stereoview of the structure is given in Fig. 1; hydrogen bonds have been omitted for clarity.

Rigid-body analysis of the two sodium–oxygen polyhedra and of the perbromate anion was performed using the program *THMA*11 (Trueblood, 1986) based on the work of Schomaker & Trueblood (1968). While neither of the sodium 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 25(29) × 10^{-4} Å^2. We concluded that the Hirshfeld (1976) rigid-bond test, extended as described by Rosenfield, Trueblood & Dunitz (1978), is satisfied, and have applied corrections for the rigid-body motion. The corrected Br—O bond lengths are given in Table 2.

[In our first data collection, as noted above, the low-angle standards showed intensity growth during the data collection; similar behavior was documented for sodium perchlorate monohydrate by Berglund, Thomas & Tellgren (1975). However, no growth was evident until after collection of the subset of data containing the low-angle standards. Thus, it was judged that the optimum procedure, using the first set of data, was to make no correction for growth or decay of intensities; the least-squares best-fit coordinates for all atoms except H so obtained agreed,

Table 1. *Final positional parameters and equivalent isotropic and isotropic displacement parameters, $B_{\rm eq}/B$ (Å^2), for sodium perbromate monohydrate at* 296 K

E.s.d.'s are given in parentheses.

The form of the equivalent isotropic displacement parameter is $B_{\rm eq} = \frac{8}{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}/B$
Na(1)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	2.43 (7)
Na(2)	0	0.4505 (5)	$\frac{1}{4}$	2.72 (7)
Br	0.12735 (3)	−0.03816 (7)	0.19885 (4)	2.017 (11)
O(1)	0.1650 (3)	−0.0303 (6)	0.3508 (3)	3.33 (10)
O(2)	0.2103 (3)	−0.0248 (7)	0.1497 (4)	4.25 (13)
O(3)	0.0618 (3)	0.1806 (7)	0.1443 (4)	4.71 (14)
O(4)	0.0734 (2)	−0.2779 (6)	0.1538 (3)	3.40 (11)
O(5)	0.3754 (3)	0.0112 (9)	0.0513 (4)	3.07 (11)
H(1)	0.392 (4)	0.008 (11)	−0.001 (7)	4.7 (18)†
H(2)	0.362 (5)	0.122 (14)	0.042 (7)	7.3 (29)†

† Refined isotropically.

Table 2. *Selected bond distances* (Å) *and angles* (°) *for sodium perbromate monohydrate*

E.s.d.'s are given in parentheses.

Coordination polyhedron I			
Na(1)—O(1)	2.367 (3)	O(1)—Na(1)—O(1$^{\rm ix}$)	180
Na(1)—O(2$^{\rm iv}$)	2.390 (3)	O(1)—Na(1)—O(2$^{\rm iv}$)	85.1 (1)
Na(1)—O(5$^{\rm iv}$)	2.379 (4)	O(1)—Na(1)—O(2$^{\rm vi}$)	94.9 (1)
O(1)—O(1$^{\rm ix}$)	4.735 (6)	O(1)—Na(1)—O(5$^{\rm iv}$)	87.2 (1)
O(2$^{\rm iv}$)—O(2$^{\rm vi}$)	4.780 (6)	O(1)—Na(1)—O(5$^{\rm vi}$)	92.8 (1)
O(5$^{\rm iv}$)—O(5$^{\rm vi}$)	4.758 (8)	O(2$^{\rm iv}$)—Na(1)—O(2$^{\rm vi}$)	180
O(1)—O(2$^{\rm iv}$)	3.217 (5)	O(2$^{\rm iv}$)—Na(1)—O(5$^{\rm iv}$)	83.9 (2)
O(1)—O(5$^{\rm iv}$)	3.274 (6)	O(2$^{\rm iv}$)—Na(1)—O(5$^{\rm vi}$)	96.1 (2)
O(2$^{\rm iv}$)—O(5$^{\rm iv}$)	3.187 (6)	O(5$^{\rm iv}$)—Na(1)—O(5$^{\rm vi}$)	180
Coordination polyhedron II			
Na(2)—O(3)	2.372 (4)	O(3)—Na(2)—O(3$^{\rm ii}$)	98.5 (2)
Na(2)—O(4$^{\rm i}$)	2.423 (4)	O(3)—Na(2)—O(4$^{\rm i}$)	80.9 (1)
Na(2)—O(5$^{\rm vi}$)	2.420 (4)	O(3)—Na(2)—O(4$^{\rm iii}$)	176.0 (1)
Na(2)—O(3$^{\rm ii}$)	2.372 (4)	O(3)—Na(2)—O(5$^{\rm vi}$)	102.8 (2)
Na(2)—O(4$^{\rm iii}$)	2.423 (4)	O(3)—Na(2)—O(5$^{\rm v}$)	88.1 (2)
Na(2)—O(5$^{\rm v}$)	2.420 (4)	O(3$^{\rm ii}$)—Na(2)—O(4$^{\rm i}$)	176.0 (1)
O(3)—O(4$^{\rm i}$)	3.112 (5)	O(3$^{\rm ii}$)—Na(2)—O(4$^{\rm iii}$)	80.9 (2)
O(3)—O(4$^{\rm iii}$)	4.792 (5)	O(3$^{\rm ii}$)—Na(2)—O(5$^{\rm vi}$)	88.1 (2)
O(3)—O(3$^{\rm ii}$)	3.594 (8)	O(3$^{\rm ii}$)—Na(2)—O(5$^{\rm v}$)	102.8 (2)
O(3)—O(5$^{\rm v}$)	3.331 (6)	O(4$^{\rm i}$)—Na(2)—O(4$^{\rm iii}$)	99.9 (2)
O(3)—O(5$^{\rm vi}$)	3.744 (6)	O(4$^{\rm i}$)—Na(2)—O(5$^{\rm vi}$)	88.2 (2)
O(4$^{\rm i}$)—O(5$^{\rm v}$)	3.151 (5)	O(4$^{\rm i}$)—Na(2)—O(5$^{\rm v}$)	81.2 (1)
O(4$^{\rm i}$)—O(5$^{\rm vi}$)	3.368 (6)	O(4$^{\rm iii}$)—Na(2)—O(5$^{\rm vi}$)	81.2 (1)
O(4$^{\rm i}$)—O(4$^{\rm iii}$)	3.710 (7)	O(4$^{\rm iii}$)—Na(2)—O(5$^{\rm v}$)	88.2 (2)
O(5$^{\rm v}$)—O(5$^{\rm vi}$)	4.788 (8)	O(5$^{\rm vi}$)—Na(2)—O(5$^{\rm v}$)	163.4 (3)
Water molecule			
O(5)—H(1)	0.73 (6)	H(1)—O(5)—H(2)	94 (7)
O(5)—H(2)	0.67 (8)		

Perbromate ion: rigid-body I

	Observed distance	Rigid-body corrected distance		
Br—O(1)	1.607 (3)	1.626	O(1)—Br—O(2)	109.9 (2)
Br—O(2)	1.598 (3)	1.622	O(1)—Br—O(3)	109.2 (2)
Br—O(3)	1.601 (4)	1.627	O(1)—Br—O(4)	108.3 (2)
Br—O(4)	1.600 (3)	1.621	O(2)—Br—O(3)	108.8 (2)
			O(2)—Br—O(4)	109.7 (2)
			O(3)—Br—O(4)	110.9 (2)

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

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* Lists of structure factors and anisotropic displacement parameters and supplementary material relating to the rigid-body analysis have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54591 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0334]

on average, with the corresponding coordinates obtained using the second set of data to within 0.5 of the combined e.s.d.'s. The H—O—H angle determined from the first data set was 108 (6)° whereas from the second data set it was 94 (7)°. This difference is virtually equal to the combined e.s.d.'s and might be regarded as simply insignificant except that very similar results were obtained by Berglund *et al.* (1975) and Berglund, Tellgren & Thomas (1976) for $NaClO_4.H_2O$: from their neutron diffraction data, which showed no growth of standards, the H—O—H angle was observed to be 105.7 (8)°, whereas from their X-ray diffraction data, collected after standards had stopped growing, a value of 95° was obtained. Thus, it appears that extinction effects may be implicated, at least in part, in the occurrence of the observed angular differences.]

Discussion. Each of the two inequivalent Na ions is octahedrally coordinated by O atoms: Na(1) is located at a site having symmetry $\bar{1}$, and there are therefore three inequivalent Na—O distances associated with it; Na(2) is located at a site having symmetry 2, and the O atoms of this polyhedron are so arranged that it too has three inequivalent Na—O distances. The average observed Na(1)—O and Na(2)—O distances are 2.379 (10) and 2.405 (23) Å, respectively. Corresponding distances in the isomorphic sodium perchlorate monohydrate structure are 2.371 (5) and 2.391 (25) Å, respectively, based on X-ray data (Berglund *et al.*, 1975); 2.375 (5) and 2.395 (28) Å, respectively, based on neutron diffraction data (Berglund *et al.*, 1976). Although corresponding distances and angles in the cation coordination polyhedra of these two isomorphs are generally very similar, in the present case there is greater angular deviation from regular octahedral geometry for each angle not constrained by symmetry to be 180°.

The perbromate ion in this structure has virtually regular tetrahedral geometry although it is subject to no symmetry constraints. The average observed Br—O distance is 1.601 (4) Å. The average observed O—Br—O angle is 109.5 (9)°. These values are in good agreement with those previously reported for perbromate ions: from $Ba(BrO_4)_2.3H_2O$, $TlBrO_4$, and $[Ni(H_2O)_6](BrO_4)_2$ at room temperature the mean Br—O distances and O—Br—O angles were found to be 1.608 Å and 109.4°, 1.604 Å and 109.4°, and 1.606 Å and 109.5°, respectively (Gerkin *et al.*, 1988; Gallucci *et al.*, 1989, 1990). The average Br—O bond distance corrected for rigid-body motion is 1.624 (3) Å. This value may be compared with the corresponding value from Gallucci *et al.* (1990), 1.629 (3) Å.

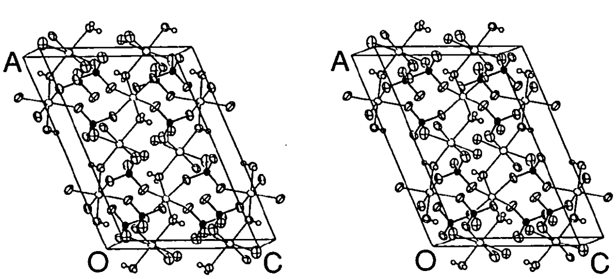

Fig. 1. Stereoview of a unit cell of the sodium perbromate monohydrate structure drawn using *ORTEP*II (Johnson, 1976). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. Hydrogen bonds have been omitted for clarity in this view.

The observed H—O—H angle 94 (7)° falls, within its uncertainty, 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 and, as discussed above, agrees well with the value for the corresponding angle in sodium perchlorate monohydrate as determined by an X-ray study (Berglund *et al.*, 1975).

Our analysis of hydrogen bonding is based partially upon treatments of hydrogen bonding by Jeffrey (1987) and Chiari & Ferraris (1982). To account for the foreshortening of the water O—H bond distance as determined by X-ray diffraction, the position of each water H atom was adjusted along the corresponding O—H bond direction until the O—H bond distance was 0.954 Å, the mean value for the O—H bond distance for class *A* inorganic hydrates as determined by neutron diffraction (Chiari & Ferraris, 1982). The resulting neutron-adjusted H coordinates were then used in analyzing the hydrogen-bonding situation. [In the present case, the value adopted for the O—H distance, 0.954 Å, may be compared with the mean value determined by neutron diffraction for the O—H distance in $NaClO_4.H_2O$, 0.920 Å, which is, however, described by the investigators (Berglund *et al.*, 1976) as anomalously severely shortened due to the exceptionally large orientational freedom of (the H atoms of) the water molecule.] Hydrogen-bond parameters are given in Table 3: observed and neutron-adjusted H—O(acceptor) distances are given, but since neutron-adjusted O—H—O(acceptor) angles typically differed from observed angles by no more than their e.s.d.'s, adjusted angles are not tabulated. In the following material, the neutron-adjusted H—O(acceptor) distance is taken to be the hydrogen-bond length.

The water oxygen, O(5), makes up a common corner of the two types of NaO_6 octahedra. The Na(1)—O(5)—Na(2) angle is 117.4 (2)°; the corresponding angle for $NaClO_4.H_2O$ is 117.80 (5)° (Berglund *et al.*, 1975). The water molecule donates weak hydrogen bonds to three perbromate O atoms in what can be called two-center/bifurcated hydrogen

Table 3. *Hydrogen-bond parameters for sodium perbromate monohydrate*

E.s.d.'s are given in parentheses.

Water oxygn—acceptor atom	Distance (Å)	Proton—acceptor atom	Observed distance (Å)	Neutron-adjusted distance (Å)*	Observed O—H—acceptor angle (°)
O(5)—O(1^{vi})	3.012 (6)	H(2)—O(1^{vi})	2.45 (7)	2.23	143 (8)
O(5)—O(4^{viii})	3.034 (6)	H(1)—O(4^{viii})	2.40 (6)	2.21	148 (6)
O(5)—O(3^{vii})	3.257 (6)	H(1)—O(3^{vii})	2.69 (7)	2.53	137 (6)
		H(2)—O(3^{vii})	3.00 (8)	2.93	107 (8)

Symmetry code: (vi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (viii) $\frac{1}{2}-x, -\frac{1}{2}-y, -z$.

* See text for details.

bonding (see Figs. 2 and 3). Although this type of hydrogen bonding was not reported for $NaClO_4.H_2O$ by Berglund *et al.* (1975), closer inspection makes apparent only slight differences in these hydrogen-bonding situations, which are illustrated in Fig. 3. As shown in Fig. 3(*b*), H(2)···O(2) is not reported as a hydrogen bond; similarly, there is an H(1)···O(4) separation of 3.02 Å which is not reported as a hydrogen bond even though the corresponding O(5)···O(4) distance, 3.151 (5) Å, falls into the accepted range for O(donor)—O(acceptor) distances. If these two weak interactions were to be included as hydrogen bonds, the structure would display three-center/bifurcated hydrogen bonding. We judge that the hydrogen bonding is best described as two-center/bifurcated.

Subsequent to the X-ray and neutron diffraction studies of the structure of sodium perchlorate monohydrate cited above, Berglund & Tegenfeldt (1977, 1979) further investigated, by nuclear magnetic resonance methods, the behavior of the H atoms in an attempt to determine whether disorder is responsible for the larger-than-expected mean values of the H displacement parameters observed both in the X-ray diffraction study ($B = 8.8$ Å^2) and in the neutron diffraction study ($B = 9.4$ Å^2). In their 1979 study Berglund & Tegenfeldt concluded that the water H atoms are 'jumping' between two positions associated with a fixed water-oxygen position. In one of these positions, H(1) is involved in a single 'short' (2.19 Å) hydrogen bond while H(2) is involved in two 'long' (2.44 and 2.40 Å) hydrogen bonds; in the other position, after 'jumping', the roles are interchanged: H(1) is then involved in two 'long' (2.51 and 2.37 Å) hydrogen bonds and H(2) in a single 'short' (2.10 Å) hydrogen bond. This situation is illustrated in Fig. 3 of that study.

We note that the mean value of the isotropic displacement parameters determined in the present research for the H atoms in sodium perbromate monohydrate is 6.0 (2.4) Å^2, only approximately two-thirds as large as the values reported for the perchlorate monohydrate. Moreover, as shown in our Fig. 3, the H positions as determined for the present salt (Fig. 3*b*) are such that, unlike the neutron diffraction positions 'as determined' (Fig. 3*a*), each H is simultaneously involved in a moderately short hydrogen bond. Thus, dynamic disordering by hydrogen 'jumping' may be absent in the present structure, but definitive assessment of this question would be implemented by neutron diffraction and nuclear magnetic resonance studies.

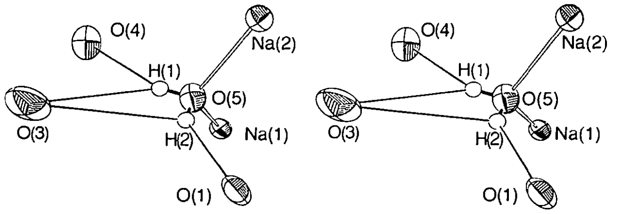

Fig. 2. Stereoview of hydrogen bonding and cation coordination involving the water molecule in sodium perbromate monohydrate drawn using *ORTEP*II (Johnson, 1976). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

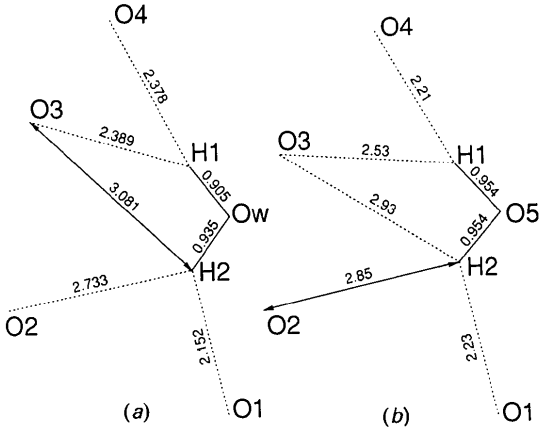

Fig. 3. Oxygen coordination of water H atoms in (*a*) $NaClO_4.H_2O$ (Berglund *et al.*, 1976) and (*b*) $NaBrO_4.H_2O$ (this research). The water O atom is designated O*w* in (*a*); O(5) in (*b*). Dotted lines represent hydrogen bonds. Solid arrows depict potential hydrogen-bonding interactions which fail to satisfy commonly accepted criteria for hydrogen bonds: in (*a*), the H(2)—O(3) distance was regarded as too great, although the O(*w*)—O(3) distance is acceptable; in (*b*), the O(2)—O(5) distance (3.671 Å) is too great. If the two rejected interactions are allowed, the differences in the descriptions of these two cases are slight.

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Structure of Zinc(II), Magnesium(II) and Manganese(II) Bis(phosphoenolpyruvate) Dihydrate

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Abstract. $Zn^{2+}.2(C_3H_4O_6P)^-.2H_2O$, $M_r = 435.47$, triclinic, $P\bar{1}$, $a = 5.184\,(3)$, $b = 5.341\,(5)$, $c = 12.124\,(9)$ Å, $\alpha = 84.69\,(7)$, $\beta = 86.72\,(6)$, $\gamma = 86.36\,(7)^\circ$, $V = 333.1\,(5)$ Å^3, $Z = 1$, $D_m = 2.17$, $D_x = 2.171\,(4)$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 22.2$ cm^{-1}, $F(000) = 220$, $T = 294\,(1)$ K, final $R = 0.0236$ for 1486 non-zero reflections. $Mg^{2+}.2(C_3H_4O_6P)^-.2H_2O$, $M_r = 394.41$, triclinic, $P\bar{1}$, $a = 5.172\,(3)$, $b = 5.333\,(3)$, $c = 12.184\,(6)$ Å, $\alpha = 85.30\,(4)$, $\beta = 86.90\,(4)$, $\gamma = 86.56\,(4)^\circ$, $V = 333.9\,(4)$ Å^3, $Z = 1$, $D_m = 1.91$, $D_x = 1.961\,(3)$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 42.0$ cm^{-1}, $F(000) = 202$, $T = 293\,(1)$ K, final $R = 0.0294$ for 1170 non-zero reflections. $Mn^{2+}.2(C_3H_4O_6P)^-.2H_2O$, $M_r = 425.04$, triclinic, $P\bar{1}$, $a = 5.277\,(3)$, $b = 5.443\,(3)$, $c = 12.090\,(6)$ Å, $\alpha = 83.74\,(4)$, $\beta = 86.35\,(4)$, $\gamma = 85.96\,(4)^\circ$, $V = 343.8\,(4)$ Å^3, $Z = 1$, $D_m = 2.04$, $D_x = 2.053\,(3)$ g cm^{-3}, μ(Cu $K\alpha$) = 111.9 cm^{-1}, $F(000) = 215$, $T = 295\,(1)$ K, final $R = 0.0296$ for 1268 non-zero reflections. All three salts are isomorphous with calcium bis(phosphoenolpyruvate) dihydrate. The M^{2+} ions occupy centers of symmetry and are six coordinate (by two water and four phosphate O atoms). Two terminal O atoms of each phosphate group bridge pairs of M atoms, thereby forming linear chains along **b**. The carboxylic hydroxyl is *trans* planar to the ester O atom in the Mn and Ca crystals but is *syn* planar in the Zn and Mg salts.

Introduction. We are currently investigating the crystal structures of phosphoenolpyruvate (PEP) salts and complexes (Weichsel & Lis, 1990; Lis & Kuczek, 1991) to see how PEP geometries depend on the cations present, on the solvent used during crystallization and on the protonation.

Experimental. Almost colorless crystals of the title compounds were grown from aqueous solutions containing a 1:1 molar ratio mixture of MCl_2 (where M