

Table 1. Fractional coordinates and thermal parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
U	0.0250 (0)	0.250 (0)	0.250 (0)	0.38 (5)	Be(1)	0.000 (0)	0.000 (0)	0.000 (0)	0.6 (5)
Be(2)	0.000 (0)	0.1151(9)	0.1765 (9)	0.8 (3)	U_{11}	0.0 (0)	0.0 (0)	0.0 (0)	U_{23}
				1.2 (3)	U_{33}				-0.3 (3)
					U_{12}				
					U_{13}				
					U_{23}				

The anisotropic temperature factor is $\exp[-2\pi^2(U'_{11}h^2 + U'_{22}k^2 + U'_{33}l^2 + U'_{12}hk + U'_{13}hl + U'_{23}kl)]$, where $U'_{ij} = U_{ij}a_i^*a_j^*$ and U_{ij} is multiplied by 100.

Table 2. Nearest-neighbor distances in UBe_{13}

Bond to atom	Number of bonds	<i>d</i> (\AA)
Bonds involving U		
Be(2) (0, <i>y</i> , <i>z</i>)	24	3.013 (5)
Bonds involving Be(1)		
Be(2) (0, <i>y</i> , <i>z</i>)	12	2.163 (9)
Bonds involving Be(2)		
U ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	2	3.013 (5)
Be(1) (0,0,0)	1	2.163 (9)
Be(2) (0, <i>z</i> , $\frac{1}{2} - y$)	2	2.231 (9)
Be(2) (<i>z</i> ,0, <i>y</i>)	4	2.25 (1)
Be(2) (0, - <i>y</i> , <i>z</i>)	1	2.3635 (7)
Be(2) (<i>y</i> ,0, $\frac{1}{2} - z$)	2	2.25 (1)

phase, which are different from the cell constants obtained for polycrystalline-phase material (Smith *et al.*, 1985). The material consisting of multiple phases was prepared by arc melting which exposes the material to an extreme rate of cooling, while the single-phase material is prepared to slow cooling of the constituents in an Al flux. It is possible that the multiple-phase material actually has a non-equilibrium (defect) structure. This study shows the standard deviations of the *y* and *z* parameters for Be(2) are sufficiently small to allow their measure-

ment as a function of pressure. Such a pressure-dependent structural investigation should provide a better understanding of the nature of the 30 kbar transition observed in electrical-resistivity measurements on UBe_{13} (McElfresh, Maple, Willis, Fisk, Thompson & Smith, 1989).

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Structure of Nickel(II) Perbromate Hexahydrate at 296 K

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Abstract. $\text{Ni}(\text{BrO}_4)_2 \cdot 6\text{H}_2\text{O}$, $M_r = 454.61$, trigonal, $P\bar{3}$, $a = 7.874$ (1), $c = 5.423$ (2) \AA , $V = 291.2$ (1) \AA^3 , $Z = 1$, $D_x = 2.59$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71069$ \AA , $\mu = 85.36$ cm^{-1} , $F(000) = 222$, $T = 296$ K, $R = 0.029$ for 457 unique reflections having $I > 0$. The room-temperature structure is very similar to that reported

previously for a sample at 169 K. The water O atoms form a very slightly distorted octahedron about nickel while the perbromate-ion geometry is virtually regular tetrahedral. Both the coordination polyhedron and the perbromate ion were tested and found to behave as rigid bodies. Corrected for rigid-body motion, the Ni—O(2) distance is 2.064 (2) \AA and the mean Br—O distance in the perbromate ion is 1.629 (3) \AA . A detailed account of the hydrogen bonding is presented. The structure previously

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determined at 169 K is most probably not the stable structure at that temperature.

Introduction. We have previously reported on the structure of nickel(II) perbromate hexahydrate at 169 K (Gallucci, Gerkin & Reppart, 1988). In view of the known phase transitions in nickel(II) perchlorate hexahydrate at 311 K and at a lower temperature variously reported from 224 to 250 K (Svare & Fimland, 1981), it was of interest to determine the room-temperature structure of nickel(II) perbromate hexahydrate.

Experimental. The sample preparation was as described by Gallucci, Gerkin & Reppart (1988). The experimental crystal was cut from a hexagonal plate and had principal dimensions approximately $0.35 \times 0.23 \times 0.46$ mm. It was coated with a thin layer of epoxy cement to prevent gain or loss of water. The sample was analyzed at 296 K with a Rigaku AFC5S diffractometer utilizing graphite-monochromated Mo $K\alpha$ radiation.

Unit-cell parameters were obtained from a symmetry-restricted least-squares fit of the setting angles for 25 well centered reflections with $25 \leq 2\theta \leq 30^\circ$. Intensity data were measured for 1452 reflections (exclusive of standards) with $\pm h$, $+k$, $\pm l$ indices ($h_{\max} = 10$, $k_{\max} = 10$, $l_{\max} = 7$), and 2θ values in the range $4 \leq 2\theta \leq 55^\circ$. The ω - 2θ scan technique was employed with scan widths $(1.68 + 0.35 \tan \theta)^\circ$ in ω , and a background/scan time ratio of 0.5. Uncertainties were assigned to each reflection using the formula $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$, where σ_{cs} is based on counting statistics and I is the integrated intensity. Six standard reflections ($\bar{2}01$, $\bar{1}20$, 021 , 033 , 321 and 410) were measured after every 150 reflections; while $\bar{1}20$ showed a substantial monotonic increase in intensity, the remaining five standards showed, on average, a maximum nonsystematic relative intensity variation of 1.8%. Accordingly no decay correction was applied. The data were corrected for Lorentz and polarization effects. A ψ -scan absorption correction was applied based on ψ -scan data obtained at the conclusion of intensity data collection; the range of transmission factors was 0.566–1.000, with an average value 0.837.

Consistent with the observed $\bar{3}$ Laue symmetry and the observed lack of reflection-limiting conditions, two space groups were allowed by the data: $P3$ (No. 143) and $P\bar{3}$ (No. 147). The centrosymmetric choice was given initial preference and since refinement proceeded well we concluded that $P\bar{3}$ is the appropriate space-group assignment of the room-temperature structure. Coordinate assignments were obtained using Patterson and Fourier methods. Full-matrix least-squares refinement was performed using the *TEXSAN* structure analysis package (Molecular

Structure Corporation, 1988) to minimize the function $\sum \sigma_F^{-2}(|F_o| - |F_c|)^2$, in which $\sigma_F = \sigma_I/2FLp$. Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for Ni, Br and O; the scattering factor for H was taken from Stewart, Davidson & Simpson (1965).

Following refinement to the isotropic stage for all atoms except hydrogen using the data having $I > 3\sigma_I$, the ψ -scan absorption correction was applied and the data were averaged ($R_{\text{int}} = 0.024$ for 92 quadruples and 355 triples of reflections). Then, using all the unique reflections with $I > 0$ and treating the secondary-extinction coefficient as an adjustable parameter, least-squares refinement proceeded to the anisotropic stage for all atoms except hydrogen and to the isotropic stage for the hydrogens.

The results for the final refinement cycle were: 457 independent observations having $I > 0$; 36 variables; $R = 0.029$; $wR = 0.026$; $w = \sigma_F^{-2}$; $S = 1.11$; $(\Delta/\sigma)_{\max} < 0.01$. Maximum and minimum peaks on the final electron density difference map had values $+0.45$ and $-0.56 \text{ e } \text{\AA}^{-3}$, respectively. The maximum peak was located at $x = 0.00$, $y = 0.01$, $z = 0.39$, $\sim 0.6 \text{ \AA}$ from Ni; the minimum peak was located at $x = 0.67$, $y = 0.33$, $z = 0.75$, $\sim 0.4 \text{ \AA}$ from Br. [For the final refinement cycle for 394 independent observations having $I > \sigma_I$: $R = 0.020$; $wR = 0.025$; $S = 1.19$. Similarly, for the 345 independent observations having $I > 3\sigma_I$: $R = 0.017$; $wR = 0.024$; $S = 1.20$. These latter two refinements were performed for comparative purposes only; all structural information presented is based on the final refinement described above.]

The final atomic coordinates and equivalent isotropic displacement parameters and their uncertainties are given in Table 1.* Selected interatomic distances and angles in the coordination polyhedron about nickel, in the perbromate ion, and in the water molecule are given in Table 2 together with their uncertainties. Hydrogen bonds involving the water-molecule oxygen and its two protons are delineated in Table 3, as discussed in detail below.

Rigid-body analysis of the Ni–O complex and the perbromate ion was performed using the program *THMA11* (Schomaker & Trueblood, 1968; Trueblood, 1986). The average magnitude of the differences in the mean-square displacement amplitudes (m.s.d.a.'s) along the interatomic vectors for the four unique atom pairs of the perbromate ion

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52832 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters and displacement parameters ($\text{\AA}^2 \times 10^3$) for nickel(II) perbromate hexahydrate at 296 K with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33} - U_{12}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}$
Ni	0	0	1/2	18 (<1)
Br	1/2	1/2	0-17900 (6)	20 (<1)
O(1)	1/2	1/2	0-88353 (48)	34 (1)
O(2)	0-24091 (24)	0-09702 (28)	0-27594 (34)	35 (1)
O(3)	0-41429 (25)	0-52839 (26)	0-28054 (33)	41 (1)
H(1)	0-2897 (47)	0-2113 (44)	0-2430 (51)	82 (13)
H(2)	0-3295 (50)	0-0681 (51)	0-2934 (52)	93 (12)

Table 2. Bond lengths (\AA) and angles ($^\circ$) for nickel(II) perbromate hexahydrate at 296 K

Observed		Rigid-body corrected	Observed	Rigid-body corrected
Coordination polyhedron: rigid body 1				
Ni—O(2)	2.052 (2)	2.064		
O(2)—O(2 ⁱ)	4.104 (4)	4.128	O(2)—Ni—O(2 ⁱ)	180
O(2)—O(2 ⁱⁱ)	2.863 (3)	2.877	O(2)—Ni—O(2 ⁱⁱ)	88.50 (8)
O(2)—O(2 ⁱⁱⁱ)	2.939 (3)	2.960	O(2)—Ni—O(2 ⁱⁱⁱ)	91.50 (8)
Water molecule				
O(2)—H(1)	0.80 (3)		H(1)—O(2)—H(2)	109 (3)
O(2)—H(2)	0.84 (3)			
Perbromate ion: rigid body 2				
Br—O(1 ^v)	1.602 (3)	1.625	O(1 ^v)—Br—O(3)	110.01 (7)
Br—O(3)	1.609 (2)	1.630	O(3)—Br—O(3 ^v)	108.92 (7)

Code for symmetry-related atoms: none *x*, *y*, *z*; (i) $-x$, $-y$, $1-z$; (ii) $y-x$, $-x$, *z*; (iii) y , $y-x$, $1-z$; (iv) x , *y*, $z-1$; (v) $1-y$, $1+x-y$, *z*.

was found to be $11(13) \times 10^{-4} \text{\AA}^2$. The average magnitude of the differences in the m.s.d.a.'s along the interatomic vectors for the four unique atom pairs of the Ni—O complex was found to be $34(15) \times 10^{-4} \text{\AA}^2$. On the basis of these values, we concluded that Hirshfeld's rigid-bond test, as described by Dunitz, Schomaker & Trueblood (1988), is satisfied for the Ni—O complex and for the perbromate ion, and have applied corrections for the rigid-body motion. The corrected bond lengths and angles are given in Table 2.

Discussion. This structure is quite similar to that determined at 169 K (Gallucci, Gerkin & Reppart, 1988) and the general structural description given there is fully applicable.

The single type of nickel coordination polyhedron has, by symmetry [the site symmetry at nickel is $\bar{3}$], a single Ni—O(2) distance [observed value 2.052 (2) \AA] and thus departs only in an angular sense, by 1.5° , from regular octahedral geometry, as documented in Table 2. (The corresponding angular departure at 169 K was found to be 2.1° .) Corrected for rigid-body motion, the single Ni—O(2) distance becomes 2.064 \AA , in excellent agreement with the rigid-body-motion-corrected Ni—O(2) distance recently reported for $\text{Ni}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.060 (1) \AA (Gallucci & Gerkin, 1990).

For the single type of perbromate ion, two Br—O distances are allowed by symmetry (the site symmetry at bromine is 3): Br—O(1) [observed value 1.602 (3) \AA] and Br—O(3) [observed value 1.609 (2) \AA]; corrected for rigid-body motion these become 1.625 and 1.630 \AA , respectively, differing by approximately their combined uncertainties.

The 169 K data have also been analyzed with respect to rigid-body motion of the Ni—O complex and the perbromate ion. The average magnitude of the difference in the m.s.d.a.'s along the interatomic vectors for the four unique atom pairs of the perbromate ion was found to be $9(16) \times 10^{-14} \text{\AA}^2$, while for the four unique atom pairs of the Ni—O complex it was found to be $16(16) \times 10^{-4} \text{\AA}^2$. Thus Hirshfeld's rigid-bond test was satisfied for both the Ni—O complex and for the perbromate ion at 169 K. The observed Ni—O(2) distance at 169 K, 2.047 (2) \AA , becomes 2.052 \AA when corrected for rigid-body motion; the observed Br—O(1) and Br—O(3) distances, 1.603 (3) and 1.603 (3) \AA , became 1.612 and 1.612 \AA , respectively, when corrected for rigid-body motion. Comparing these results from the 169 K study with the results from the present study at room temperature, we observe that since the room-temperature values for the Ni—O(2) and Br—O(1) and Br—O(3) distances are as large or larger than the corresponding values at low temperature, application of rigid-body corrections lessens the degree of agreement of the two sets of values. This indicates that at least one factor in addition to harmonic vibrations is involved in determining the differences between the room-temperature and low-temperature results.

For the water molecule the observed H—O—H angle (Table 2) is 109 (3) $^\circ$. This value agrees well with the value for water-molecule H—O—H angles determined by neutron diffraction and tabulated by Chiari & Ferraris (1982): for inorganic hydrates of class *L* (Chiari & Ferraris, 1982; Ferraris & Franchini-Angela, 1972), to which this salt belongs, the tabulated value is 107.6° .

The occurrence of a single type of nearly regular octahedra of water O atoms and a single type of nearly regular tetrahedral perbromate ions leads to a rather simple hydrogen-bonding situation, which has been described in some detail previously (Gallucci, Gerkin & Reppart, 1988). Our further analysis of the bond geometries here 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 proton was adjusted along the corresponding O—H bond direction (as determined by the X-ray data) until the O—H bond distance was 0.963 \AA , the mean value for the O—H

Table 3. *Hydrogen-bond parameters for nickel(II) perbromate hexahydrate at 296 K with e.s.d.'s in parentheses*

Water oxygen-acceptor oxygen	Distance (Å)	Proton-acceptor oxygen	Observed distance (Å)	Neutron-adjusted distance (Å)	Observed O—H—O angle (°)	Neutron-adjusted O—H—O angle (°)
O(2)—O(2 ⁱⁱⁱ)	2.863 (3)	H(1)—O(2 ⁱⁱⁱ)	2.82 (3)	2.84	85 (2)	82
O(2)—O(2 ^{vi})	2.939 (3)	H(2)—O(2 ^{vi})	2.92 (3)	2.94	83 (2)	81
O(2)—O(2 ^{vii})	2.939 (3)	H(1)—O(2 ^{vii})	2.91 (3)	2.93	84 (2)	81
O(2)—O(3)	2.960 (2)	H(1)—O(3)	2.19 (3)	2.04	162 (3)	160
O(2)—O(3 ⁱⁱⁱ)	3.014 (2)	H(2)—O(3 ⁱⁱⁱ)	2.22 (3)	2.10	158 (3)	157
O(2)—O(1 ⁱⁱⁱ)	3.035 (2)	H(1)—O(1 ⁱⁱⁱ)	2.71 (3)	2.67	106 (3)	103
		H(2)—O(1 ⁱⁱⁱ)	2.60 (3)	2.56	113 (2)	111
O(2)—O(3 ⁱⁱⁱ)	3.259 (3)	H(2)—O(3 ⁱⁱⁱ)	2.71 (3)	2.64	124 (2)	122

Code for symmetry-related atoms: none x, y, z ; (iii) $y, y-x, 1-z$; (vi) $1-y, x-y, z$; (vii) $-y, x-y, z$; (viii) $x-y, x, 1-z$.

bond distance as determined by neutron diffraction in inorganic hydrated crystals of class *L* (Chiari & Ferraris, 1982). The resulting adjusted proton coordinates were then used to calculate adjusted distances and angles involving potential hydrogen-bond-acceptor O atoms. The observed angles (calculated directly from the X-ray-determined coordinates) and the adjusted angles are tabulated together with observed O(water)—O(acceptor) distances and observed and neutron-adjusted H—O(acceptor) distances in Table 3. In the following material, the neutron-adjusted H—O(acceptor) distance is taken to be the hydrogen-bond length.

As shown in Table 3, each of the two nonequivalent H atoms is involved in a hydrogen bond in the H—O(acceptor) distance range 2.04–2.10 Å in which the acceptor is a trigonal perbromate oxygen, O(3); each of the two associated O(water)—H—O(acceptor) angles has a value near 160°. While these distances are somewhat larger than the value 1.80 Å given for class *L* by Ferraris & Franchini-Angela (1972), they lie below the maximum value (2.258 Å) given for this distance in inorganic hydrates by Chiari & Ferraris (1982). In the H—O(acceptor) distance range 2.56–2.67 Å we find a bifurcated hydrogen bond (see Jeffrey, 1987) involving the axial perbromate oxygen, O(1), as the acceptor which is the only substantial hydrogen-bonding interaction involving O(1); in addition there is a single weaker hydrogen bond between H(2) and O(3) of length 2.64 Å. These hydrogen bonds are delineated in Fig. 1, which depicts all these bonds in a view centered on one perbromate ion.

No substantial hydrogen-bonding interactions involving water oxygens, O(2), as both donor and acceptor are present. [The minimum H—O(2)(acceptor) distance is 2.84 Å, as given in Table 3.] Nonetheless, the three tabulated interactions involving water O atoms as both donors and acceptors are characterized by O(2)—O(acceptor) distances appropriate for hydrogen bonds and by proton—O(acceptor) distances less than the corresponding O(2)—O(acceptor) distances. On these bases they have been included as (weak) hydrogen bonds.

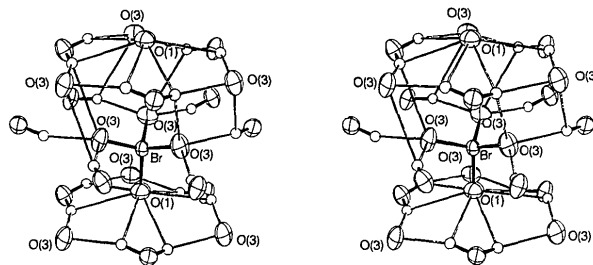


Fig. 1. Stereoview of the near environment of a central perbromate ion in the nickel(II) perbromate hexahydrate structure from an orientation with the z axis almost vertical. All hydrogen bonds to the single O(1) and to the three O(3) atoms of this perbromate ion are shown. Drawn using *ORTEPII* (Johnson, 1971). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

By comparison of the room-temperature structure with the 169 K structure it can be noted that whereas the difference in the Ni—O(2) distances in the nickel coordination polyhedron is 0.005 Å (observed; 0.012 Å upon rigid-body correction) and the average difference in the Br—O distances in the perbromate ion is 0.005 Å (observed; 0.017 Å upon rigid-body correction), the average difference in the O(2)—O(1)(acceptor) or O(2)—O(3)(acceptor) hydrogen-bonded distances is 0.043 Å, roughly eight times as large (three times as large upon rigid-body correction). Thus, as is physically plausible, thermal expansion of the structure is observably nonuniform with the weaker bonds changing in length more than the stronger bonds.

On the basis of the known phase behavior of nickel(II) perchlorate hexahydrate as tabulated, for example, by Svare & Fimland (1981), and the apparent similarities in the structural behavior of perchlorates and perbromates as suggested by our structural studies of perbromates, we must tentatively conclude that the structure previously determined at 169 K for nickel(II) perbromate hexahydrate is not the stable structure at that temperature. We are therefore exploring the matter of the equilibrium phases of this substance over a temperature range down to 150 K.

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Structure of the Sodium Ion Conductor $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$

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Abstract. Heptasodium triiron tetrakis(diarsenate), $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$, $M_r = 1375.83$, monoclinic, $C2/c$, $a = 9.940$ (1), $b = 8.5483$ (7), $c = 28.762$ (2) Å, $\beta = 93.683$ (8)°, $V = 2438.9$ (4) Å³, $Z = 4$, $D_x = 3.747$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 12.81$ mm⁻¹, $F(000) = 2572$, $T = 294$ (1) K, $R = 0.033$ for 2440 independent reflections. The structure consists of a three-dimensional framework of FeO_6 octahedra sharing corners with As_2O_7 groups and an interstitial space in which the Na ions are located. The framework can be described as a succession of layers of $\text{Fe}(\text{As}_2\text{O}_7)_2$ (*A*) and $\text{Fe}_2(\text{As}_2\text{O}_7)_2$ (*B*), parallel to (001). The presence of wide windows between the Na sites as well as the delocalization of some of the Na ions account for the fast cation-transport properties exhibited by the solid. The diffusion of Na ions seems to be easy parallel to (001) through the *A* layer while crossing the *B* layer requires passage through a rather narrow bottleneck.

Introduction. A new sodium iron diphosphate, $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$, and the isotopic diarsenate, $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$, have recently been synthesized. Both exhibit good cation-exchange properties and a rather high ionic conductivity (d'Yvoire, Masquelier, Bretey, Peytour & Berthet, 1990). The crystal structure of the arsenate is reported here.

Experimental. Crystals of $\text{Na}_7\text{Fe}_3(\text{As}_2\text{O}_7)_4$ were prepared in a flux of sodium arsenates. A mixture of composition $\text{Fe}_2\text{O}_3 + 3.7\text{As}_2\text{O}_5 + 5.1\text{Na}_4\text{As}_2\text{O}_7$ was melted at 1073 K, cooled at a rate of 100 K h⁻¹ down to room temperature and then washed with water in order to eliminate the excess of sodium arsenates. Small single crystals delimited by $\{\bar{1}11\}$ and $\{001\}$ were obtained. The selected crystal was elongated along [101] (0.16 × 0.11 × 0.09 mm). The unit-cell constants, measured from 25 independent reflections with $6.91 \leq \theta \leq 25.55^\circ$, are $a = 9.926$ (2), b