Table 3. *The* N···F *and* N···O *contacts* (Å) *with e.s.d.'s in parentheses*

N(1)···F(21^{i})	2·816 (8)	N(2)···F(31^{iv})	2·850 (8)
F(22^{ii})	2·884 (8)	F(32^{v})	2·922 (9)
O(14^{ii})	2·883 (8)	F(42^{x})	2·973 (8)
O(31^{vii})	2·939 (9)	O(24^{xi})	2·979 (9)
N(3)···F(21^{viii})	2·803 (8)	N(4)···F(41^{xii})	2·850 (8)
O(13^{vi})	2·978 (8)	F(42^{xiii})	2·812 (8)
O(21^{v})	2·801 (8)	O(32^{xii})	2·962 (8)
O(12^{ix})	3·037 (9)	O(11^{xiv})	2·986 (9)
N(5)···F(3)	2·986 (9)	N(6)···F(23^{xv})	2·872 (8)
F(41^{xvii})	2·902 (9)	F(31^{iv})	2·855 (8)
F(43^{xvi})	2·859 (9)	F(33^{iii})	2·963 (9)
O(31)	2·889 (9)	O(21^{v})	2·955 (9)

Symmetry code: none x, y, z; (i) $x+1, y, z+1$; (ii) $x+1, y, z$; (iii) $x, y, z+1$; (iv) $y-x, 1-x, z+1$; (v) $y-x, 1-x, z$; (vi) $1+x, 1+y, z+1$; (vii) $1-x+y, 1-x, z$; (viii) $1-y, 1+y-x, z+1$; (ix) $x-1, y-1, z$; (x) $1-y, y-x, z$; (xi) $1-y, 1+y-x, z$; (xii) $x-1, y, z-1$; (xiii) $x-1, y, z$; (xiv) $y-x, -x, z$; (xv) $x+1, y+1, z$; (xvi) $1-y, y-x, z-1$; (xvii) $x, y, z-1$.

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Structure of Nickel(II) Perbromate Hexahydrate at 169 K

By Judith C. Gallucci, Roger E. Gerkin* and William J. Reppart†

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, *USA*

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Abstract. $Ni(BrO_4)_2.6H_2O$, $M_r = 454·61$, trigonal, $P\bar{3}$, $a = 7·817\ (2)$, $c = 5·235\ (1)$ Å, $V = 277·03\ (14)$ Å^3, $Z = 1$, $D_x = 2·725$ g cm^{-3}, $\lambda(\text{Mo}\ K\bar{\alpha}) = 0·71069$ Å, $\mu = 89·7$ cm^{-1}, $F(000) = 222$, $T = 169$ K, $R = 0·029$ for 417 unique reflections with $I > 0$. The structure consists of stacks of hydrated nickel ions and stacks of perbromate groups with hydrogen bonds from a given water molecule involving three stacks of perbromate groups. The water O atoms form a very slightly distorted octahedron about nickel while the perbromate geometry is virtually ideally tetrahedral. This structure and that of mercury(II) perchlorate hexahydrate, though assigned in different space groups, are very similar and are interestingly related as described in the text.

Introduction. Interest has arisen in this laboratory concerning detailed similarities and differences in the structures of corresponding simple salts containing perbromate or perchlorate anions. Since at the inception of these investigations very little structural information was available for perbromates, it appeared worthwhile to determine the structures of a number of simple perbromate salts. We have previously reported on the structure of barium perbromate trihydrate (Gerkin, Reppart & Appelman, 1988).

Experimental. Nickel perbromate was prepared by the aqueous reaction of suspended nickel(II) hydroxide with a slight excess of ~2*M* perbromic acid.‡ [The

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* To whom correspondence should be addressed.

† Present address: Shell Development Company, Houston, Texas 77001, USA.

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nickel hydroxide was prepared by treating nickel(II) sulfate with dilute potassium hydroxide, followed by repeated washing of the precipitate with distilled water.]

Despite the effort to remove the counterions (K^+ and SO_4^{2-}), and due to the relatively very high solubility of nickel perbromate, slow evaporation of the slightly acidic solution at room temperature yielded monoclinic nickel sulfate hexahydrate as the first crystalline nickel salt. Upon removal of the crystalline nickel sulfate and further evaporation, nickel perbromate hexahydrate crystallized, predominantly in platy forms.

The crystal selected for this study was cut from a hexagonal plate; it had 11 bounding faces (100, $\bar{1}00$, $\bar{1}10$, $1\bar{1}0$, $\bar{1}51$, $0\bar{1}0$, 001, $00\bar{1}$, $\bar{1}11$, $0\bar{1}1$, 101) and principal dimensions 0·46 × 0·64 × 0·15 mm.

Intensity data were measured at 169 K (estimated uncertainty ±2K) using a Syntex $P\bar{1}$ automated four-circle diffractometer equipped with an LT1 low-temperature attachment. Temperature measurements were made at the cold-stream exit nozzle during data collection and at the crystal site after data collection with a Fluke 2100 A digital thermometer (type K thermocouple). Graphite-monochromated Mo $K\bar{\alpha}$ radiation was used throughout.

Unit-cell parameters were determined from a least-squares fit of the setting angles for 25 well centered reflections ($22 < 2\theta < 30°$). Intensities were measured using the ω–2θ scan technique, with scan widths from 2θ(Mo $K\alpha_1$)$-1{\cdot}0°$ to 2θ(Mo $K\alpha_2$) $+1{\cdot}2°$ and a background/scan time ratio of 0·5. Uncertainties were assigned to each reflection using the formula $\sigma_I^2 = R^2(C+4B) + (0{\cdot}02I)^2$, where R is the variable scan rate, C is the total number of counts, B is the total number of background counts, and I is the integrated intensity [$I = R(C-2B)$]. Six standard reflections ($5\bar{2}1$, $40\bar{2}$, 312, $\bar{2}32$, $\bar{4}1\bar{2}$, 023) were measured after every 94 reflections. The intensity variations of the standards were less than 4·8% of the respective average intensities. 1418 reflections were measured in the range $4 \leq 2\theta \leq 55°$; index ranges were: $\pm h$, $+k$, $\pm l$; $h_{\max} = 10$, $k_{\max} = 10$, $l_{\max} = 6$. Transmission factors ranged from 0·11 to 0·27. The data were corrected for Lorentz and polarization effects, and an analytical absorption correction was applied using the program of de Meulenaer & Tompa (1965) and Alcock (1970).

Analysis and refinement

Preliminary analysis indicated a trigonal or hexagonal Laue group; reflection intensities permitted only $\bar{3}$ Laue symmetry. Of the six space groups consistent with $\bar{3}$ Laue symmetry, four could be rejected since no reflection-limiting conditions were observed. $P3$ (No. 143) and $P\bar{3}$ (No. 147) were thus the only allowed space groups; the centrosymmetric choice was given preference, and since subsequent refinement proceeded well we retained $P\bar{3}$ as the appropriate space-group assignment.

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$), *calculated using the relation* $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33} - U_{12})$

Standard deviations are given within parentheses.

	x	y	z	U_{eq}
Ni	0	0	$\frac{1}{2}$	9 (<1)
Br	$\frac{1}{3}$	$\frac{2}{3}$	0·17821 (8)	9 (<1)
O(1)	$\frac{1}{3}$	$\frac{2}{3}$	0·8718 (6)	14 (1)
O(2)	0·2393 (3)	0·0872 (3)	0·2659 (4)	16 (1)
O(3)	0·3982 (3)	0·5146 (3)	0·2822 (4)	18 (1)
H(1)	0·286 (6)	0·198 (5)	0·218 (6)	40 (13)
H(2)	0·328 (7)	0·086 (7)	0·314 (8)	56 (17)

Following placement of the single Ni atom ($Z = 1$) at $00\frac{1}{2}$, one of the two positions allowed for it in $P\bar{3}$ (the other is 000; this choice results merely in shifting all z coordinates reported here by 0·5), a series of Fourier difference maps was generated from which atom locations were assigned and least-squares-refined one at a time. Full-matrix least-squares refinement was performed using the *SHELX*76 program (Sheldrick, 1976) which minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma_F^{-2}$. Initially all 425 unique reflections with $I > 0$, for which $R_{\text{int}} = 0{\cdot}021$, were included in the calculations; in the later stages, eight reflections ($\bar{1}11$, 021, 002, 010, 122, 020, $\bar{2}21$, $\bar{1}31$) for which the calculated deviation of F_c from F_o was greater than five times the standard deviation were rejected. The H atoms were also located from Fourier difference maps and the coordinates and isotropic thermal parameters were refined by least-squares methods.

Final least-squares refinement cycle details are as follows: 35 parameters; $R = 0{\cdot}029$; $wR = 0{\cdot}034$; $S = 2{\cdot}8$; 417 observations; $(\Delta/\sigma)_{\max} = 0{\cdot}02$; $\Delta\rho_{\max} = 0{\cdot}5$, $\Delta\rho_{\min} = -1{\cdot}1$ e Å^{-3}. The final atomic coordinates and equivalent isotropic thermal parameters for the nickel perbromate hexahydrate structure are given in Table 1.*

Atomic scattering factors for Ni and Br were taken from Cromer & Waber (1965), for O from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965). Correction factors for anomalous dispersion for Ni and Br were taken from Cromer & Liberman (1970).

Important interatomic distances and angles and their uncertainties were calculated using the *XRAY* system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and are listed in Table 2.

Discussion. As illustrated in Fig. 1, this structure consists of stacks of nickel ions coordinated virtually

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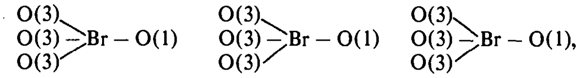
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44942 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *for nickel*(II) *perbromate hexahydrate at* 169 K

Coordination polyhedron			
Ni–O(2)	2·047 (2)		
$O(2)–O(2^{i})$	4·094 (4)	$O(2)–Ni–O(2^{i})$	180
$O(2)–O(2^{ii})$	2·840 (2)	$O(2)–Ni–O(2^{ii})$	87·9 (1)
$O(2)–O(2^{iii})$	2·948 (3)	$O(2)–Ni–O(2^{iii})$	92·1 (1)
Water molecule			
O(2)–H(1)	0·79 (4)	H(1)–O(2)–H(2)	102 (5)
O(2)–H(2)	0·74 (6)		
Perbromate ion			
Ni–Br	4·817 (4)		
$Br–O(1^{iv})$	1·603 (3)	$O(1^{iv})–Br–O(3)$	109·8 (1)
Br–O(3)	1·603 (3)	$O(3)–Br–O(3^{v})$	109·1 (1)
Hydrogen bonds			
O(2)–O(3)	2·926 (4)	O(2)–H(1)–O(3)	153 (3)
$O(2)–O(1^{iii})$	2·992 (3)	$O(2)–H(1)–O(1^{iii})$	108 (4)
		$O(2)–H(2)–O(1^{iii})$	118 (4)
$O(2)–O(3^{vi})$	3·050 (4)	$O(2)–H(2)–O(3^{vi})$	139 (4)
$O(2)–O(3^{iii})$	3·128 (3)	$O(2)–H(2)–O(3^{iii})$	142 (5)
$O(2)–O(2)^{vii})$	2·840 (2)	$O(2)–H(1)–O(2^{vii})$	87 (3)
$O(2)–O(2^{viii})$	2·948 (3)	$O(2)–H(1)–O(2^{viii})$	81 (3)
$O(2)–O(2^{ix})$	3·231 (4)	$O(2)–H(1)–O(2^{ix})$	114 (3)
$O(2)–O(2^{iii})$	2·948 (3)	$O(2)–H(2)–O(2^{iii})$	88 (3)

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*; (vi) 1*−y, x−y, z*; (vii) *−y, x−y, z*; (viii) *x−y, x,* 1*−z*; (ix) *x−y, x, −z*.

octahedrally by six water molecules and stacks of virtually regular tetrahedral perbromate ions, with hydrogen bonding occurring between these two types of stacks. In the perbromate stacks the arrangement is



$$O(3)_3{>}Br-O(1) \quad O(3)_3{>}Br-O(1) \quad O(3)_3{>}Br-O(1),$$

the Br—O(1) (axial) vectors pointing up or down in alternate stacks.

As the data from Table 2 make apparent, the perbromate-ion geometry is very nearly ideally tetrahedral. Two Br—O distances are allowed within the perbromate group in this structure, yet they differ by less than 0·001 Å, much less than the uncertainties of the measurements; the angles, too, differ from the ideal values, but by only 0·3 and 0·4°, approximately four times the uncertainty of these angles.

While all six of the Ni—O(water) distances are required to be equal in this structure, we find a slightly distorted octahedron of water O atoms, the angles differing from those of the ideal geometry by 2·1°.

It appears from our analysis that H(1) is involved in hydrogen bonding with a trigonal oxygen, O(3), of one perbromate stack and an axial oxygen, O(1), of a second perbromate stack and that H(2) is involved in hydrogen bonding with both a trigonal and an axial oxygen of the second perbromate stack just mentioned and a trigonal oxygen of a third perbromate stack. Both H(1) and H(2) are also involved in some hydrogen bonding within the hydrated nickel stacks, as delineated in Table 2.

Space-group assignments for perchlorate salts of hexahydrated divalent transition metals whose structures have been reported have not included $P\bar{3}$, reported here for an analogous perbromate. However, the closely related space group $P\bar{3}m1$ has been assigned in the analysis of the structure of mercury(II) perchlorate hexahydrate (Johansson & Sandström, 1978) and, aside from some additional symmetry relations among coordinates dictated by $P\bar{3}m1$ and some expected slight changes of distances, the two structures are describable in very similar terms.

In both of these structures, a stack of octahedra of water O atoms is formed along the *z* axis, every second one of which contains a metal ion. Those alternate octahedral centers which are occupied by metal ions in the mercury salt are the centers which are vacant in the nickel salt, and *vice versa*. Further, whereas the 'unoccupied' octahedra are compressed along *z* (relative to the 'occupied' octahedra) and are more nearly

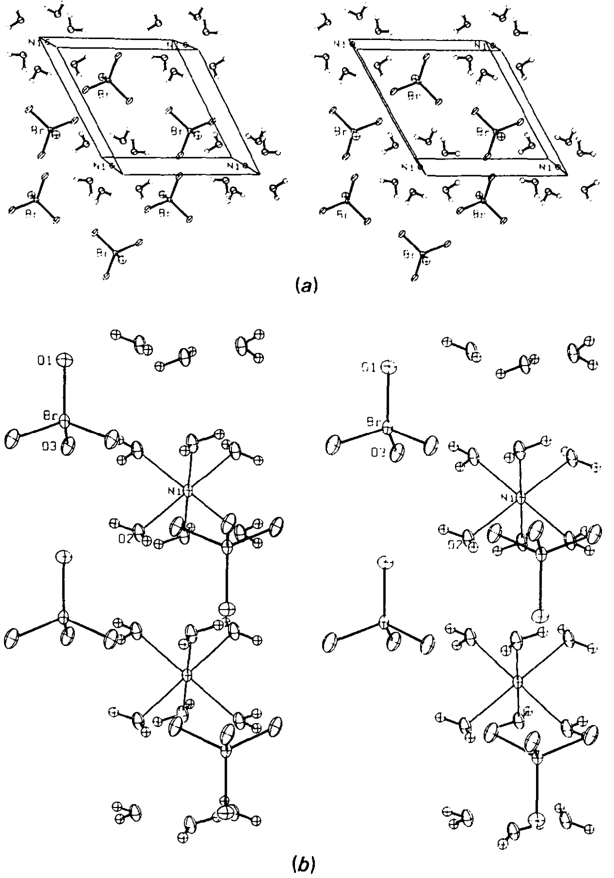


Fig. 1. (*a*) Stereoview of a portion of the nickel perbromate hexahydrate structure including a unit cell, from an orientation nearly parallel to the *z* axis. (*b*) Stereoview of a portion of the structure from an orientation perpendicular to the *z* axis, showing the stacking of water octahedra along the *z* axis (vertical in the illustration). Drawn using *ORTEP*II (Johnson, 1971). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

regular than the 'occupied' octahedra in the mercury salt, the converse is true in the nickel salt: the 'occupied' octahedra are compressed along z and are more nearly regular than the 'unoccupied' octahedra (O—O octahedral distances are as follows: nickel salt: occupied: 2·840 and 2·948 Å, unoccupied: 2·840 and 3·231 Å; mercury salt: occupied: 3·188 and 3·430 Å, unoccupied: 3·188 and 3·059 Å).

As the numerical values make clear, the 'occupied' nickel salt octahedra depart substantially less from regularity than do the 'occupied' mercury salt octahedra.

The anion stacks are essentially geometrically identical in the two structures within the qualifications given above.

The Ni—O(water) distance in the present salt, 2·047 (2) Å, accords well with values from other recent determinations of Ni^{II}—O(water) distances, *e.g.* 2·06 Å (average) in room-temperature nickel(II) nitrate hexahydrate (Bigoli, Braibanti, Tiripicchio & Camellini, 1971) and 2·064 Å in room-temperature nickel(II) iodide hexahydrate (Louër, Grandjean & Weigel, 1973).

Finally, the Br—O distance in the perbromate ion in the present salt, 1·603 (3) Å, is found to be in very good agreement, *e.g.*, with the room-temperature value, 1·608 (3) Å, found for barium perbromate trihydrate (Gerkin *et al.*, 1988). The difference between these best values, though of little statistical significance, is consistent with an average linear thermal expansion coefficient of the order 20×10^{-6} deg^{-1}, a quite plausible value.

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Structure of Tripotassium Monohydroxo(pentahydroxoundecaoxoheptaborato)platinate(IV) Trihydrate

BY HELMUT BEHM

Crystallography Laboratory, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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Abstract. $K_3[Pt\{B_7O_{11}(OH)_5\}(OH)].3H_2O$, $M_r = 720·13$, orthorhombic, *Pnma*, $a = 19·283$ (3), $b = 11·480$ (2), $c = 8·106$ (2) Å, $V = 1794·4$ (4) Å^3, $Z = 4$, $D_x = 2·66$ Mg m^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1·54184$ Å, $\mu(\text{Cu}\,K\alpha) = 22·12$ mm^{-1}, $F(000) = 1368$, $T = 293$ K, final conventional $R = 0·027$ for 1458 observed reflections. The structure contains isolated mononuclear $[Pt\{B_7O_{11}(OH)_5\}(OH)]$ complexes, which are held together by potassium ions and water molecules. The borate complex, with seven boron atoms, acts as a pentadentate ligand which encloses the Pt nucleus on one side. The coordination sphere of the Pt atom is an almost regular octahedron, built up by five oxygen atoms of the borate complex and one additional OH group. The structure reported here is the first platinum borate. It is the first instance of a true heptaborate which forms a novel type of molecular structure. The proton distribution in the structure cannot be described by the borate rules given by Christ & Clark [*Phys. Chem. Miner.* (1977), **2**, 59–87].

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