

Fig. 2. The construction of the $\text{Re}_{14}\text{Al}_{57-x}$ structure with inverted WAl_4 -type slabs. The domain boundaries have been indicated with solid lines. The outlines of the WAl_4 unit cells within the slab are dashed and those of $\text{Re}_{14}\text{Al}_{57-x}$ are dotted in correspondence with the chosen outlines of the unit cells presented in Figs. 1(b) and 1(a). The shaded segment corresponds to the shaded segment of Fig. 1(a).

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Structures of Holmium Bromate Enneahydrate at 168 and 294 K and their Implications for the Isomorphic Series of Rare-Earth Bromate Enneahydrates

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Abstract. $\text{Ho}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$, $M_r = 710.77$, orthorhombic, $Cmcm$, $Z = 4$, $F(000) = 1336$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $T = 168 \text{ K}$: $a = 11.670 (1)$, $b = \sqrt{3}a = 20.213 (2)$, $c = 6.611 (1) \text{ \AA}$, $V = 1559.4 (3) \text{ \AA}^3$, D_x

the partially occupied Al sites near the interface [Al(2)–Al(3) 2.39; Al(18)–Al(21) 2.53 Å].

In connection with the interpretation of the $\text{Re}_{14}\text{Al}_{57-x}$ structure as a periodic domain structure one should mention the defect structure of Al-rich Mo–Al alloys studied by Van Tendeloo, Van Landuyt & Amelinckx (1975), who found by electron diffraction a pattern characteristic of inversion domains for MoAl_4 .

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$= 3.03 \text{ g cm}^{-3}$, $\mu = 128.32 \text{ cm}^{-1}$, $R = 0.041$ for 1565 unique reflections with $I > 0$; $T = 294 \text{ K}$: $a = 11.699 (1)$, $b = \sqrt{3}a = 20.263 (2)$, $c = 6.671 (1) \text{ \AA}$, $V = 1581.4 \text{ \AA}^3$, $D_x = 2.98 \text{ g cm}^{-3}$, $\mu = 126.53 \text{ cm}^{-1}$, $R = 0.041$ for 1304 unique reflections with $I > 0$. Examination of crystals of twelve (La, Pr, Nd, Sm–Lu) rare-earth bromate enneahydrates revealed that these

crystals are optically biaxial, and that they frequently manifest twinning such that six triangular sections combine to form hexagonal columns. Diffraction intensity data for holmium bromate enneahydrate at 168 and 294 K were inadequate to establish the space group definitively even though they were obtained from a crystal cut from a single triangular section. Analysis of the data is presented in terms of the orthorhombic space group $Cmcm$, the higher-symmetry group of the two space groups allowed by the diffraction data and by all known properties of these crystals. On the basis of the magnitudes of certain thermal parameters it is suggested that the water molecules and bromate ions are statically disordered in these structures.

Introduction. The first rare-earth bromate crystal structure was reported by Helmholtz (1939), who found that neodymium bromate enneahydrate was hexagonal, with Laue symmetry D_{6h} . The systematic absences indicated three possible space groups: $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$, but the positive results of a pyroelectric experiment indicated the space group to be $P6_3mc$. Helmholtz found that the nine-coordinated neodymium ion had approximate $\bar{6}m$ (D_{3h}) symmetry, although the space group required only C_{3v} symmetry at the rare-earth-ion site. One of the O atoms in the bromate group was found to be disordered, occupying each of two positions one-third or two-thirds of the time.

The visible absorption spectra of single-crystal praseodymium and neodymium bromate enneahydrates in the temperature range 55–85 K were reported by Hellwege & Hellwege (1950). These authors were able to detect a phase change at ~ 65 K in each type of crystal from an increase in the number of lines in the absorption spectra. The occurrence of the additional lines results from (a) the lowering of the symmetry at the site of the rare-earth ion from $\bar{6}m$ (from Helmholtz) to at most monoclinic symmetry, and (b) the appearance of several inequivalent rare-earth ions in the crystal. Further work reported the next year by Hellwege & Kahle (1951), using single-crystal europium bromate enneahydrate, established that at room temperature, the symmetry at the site of the rare-earth ion is only pseudo-hexagonal. Employing a polarized excitation source, quantum-mechanical selection rules, and the Zeeman effect, the authors determined that above the phase-transition temperature of 67 K, the site symmetry at the rare-earth is only $\bar{2}$, with the mirror plane being parallel with the pseudo sixfold axis. Below 67 K, it was found that the symmetry of the rare-earth-ion site is triclinic.

The optical properties of nine rare-earth bromate enneahydrate salts (La, Pr, Nd, Sm, Eu, Gd, Er, Tb and Dy) were reported by Schumann (1952), who found that crystals of each salt were biaxial. The acute bisectrix for each crystal was found to be parallel to the pseudo-hexagonal axis, with the $2V$ angles (the acute

angles between the optic axes) ranging from 1° for terbium bromate to 8° for gadolinium and samarium bromates. The interference figures for neodymium, samarium, dysprosium and erbium bromates displayed inclined dispersion, whereas the interference figure for europium bromate displayed horizontal dispersion, indicating monoclinic symmetry for the unit cell of each of these salts. As all of the rare-earth bromate enneahydrates are isomorphic, this implies therefore that all of them have a monoclinic unit cell. The deviation from hexagonal symmetry was sufficiently small, however, that two of the three indices of refraction were equal within the experimental error. Schumann found also that although the rare-earth bromate enneahydrate crystals grew as regular hexagonal columns ($\{10\bar{1}0\}$), some crystals of neodymium, europium, samarium and erbium bromate were composed of six triangular sections, twinned in such a manner as to give the appearance of a hexagonal column (Fig. 1a). This type of twinning is somewhat similar to that found in the aragonite form of calcium carbonate (Fig. 1b), although the twinning occurs across a different plane in the rare-earth bromates. Conoscopic illumination of a thin section of a hexagonal column produced a uniaxial interference figure, whereas the interference figure obtained from a single triangular section was clearly biaxial.

The room-temperature fluorescence and absorption spectra of single-crystal terbium bromate enneahydrate were reported by Geisler & Hellwege (1953). The resolution of their spectrograph was insufficient to enable the observation of splitting due to the lower symmetry, however, and the spectrum was analyzed assuming $\bar{6}m$ symmetry at the rare-earth site. Additionally, these authors obtained an interesting result by decomposing some of the bromate groups in the crystal. Following irradiation of the bromate crystal with sufficient ultraviolet radiation to turn the crystal color

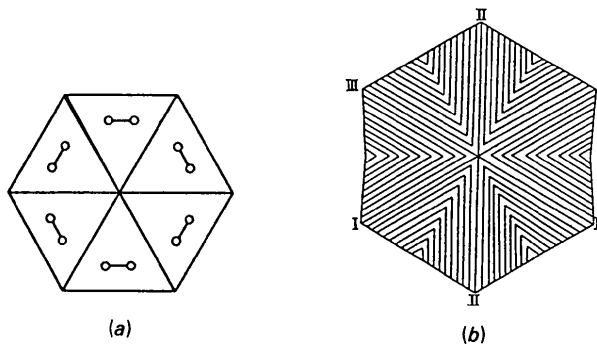


Fig. 1. (a) Twinning found in rare-earth bromate enneahydrate crystals. The symbol in each sector represents the optical plane for that sector. (Reproduced by permission from Hellwege & Kahle, 1951.) (b) Aragonite crystal twinned on (110). (Reproduced by permission from Bragg, 1924.)

visually from colorless to brown, the optical absorption spectrum showed no perceptible change from that of an undamaged crystal. Geisler & Hellwege concluded on this basis that the bromate groups contribute in only a small way to the crystal field at the rare-earth-ion site.

The absorption spectrum of neodymium bromate enneahydrate at room temperature and liquid-nitrogen temperature was reported by Satten (1953), while the absorption spectrum and Zeeman effect for this salt at liquid-helium temperature was reported by Dieke & Heroux (1956). In both papers, the authors report the appearance of absorption bands which result from the breakdown of the electric dipole selection rules. Since the presence of these 'extra' lines cannot be ascribed to the local symmetry of the rare-earth ion [as was the case with Hellwege & Hellwege (1950)], Satten (1957) postulated that vibrational-electronic interactions between the rare-earth ion and the surrounding water molecules are responsible.

The optical absorption spectrum of a single section of a hexagonal europium bromate enneahydrate crystal was reported by Kahle (1959*a,b*) over the temperature range 68–290 K. The results of this study confirmed the results of the earlier work by Hellwege & Kahle (1951), namely that the point symmetry at the rare-earth-ion site is C_3 , with the $\bar{2}$ axis perpendicular to the pseudo-hexagonal axis and parallel to the outer prism face. It was also noted that the deviation from pseudo-hexagonal symmetry became more pronounced as the temperature was lowered.

The room-temperature crystal structure of samarium bromate enneahydrate was determined by Sikka (1969) using neutron diffraction. Sikka, apparently unaware of the previous spectroscopic work on the rare-earth bromates, initially assumed the space group to be $P6_3mc$ as found by Helmholz (1939). Later, after no Bijvoet differences were observed, the space-group assignment was changed to the centrosymmetric $P6_3/mmc$, in which a successful structural refinement was carried out. The crystals used for the structure determination were hexagonal columns, bounded by $\{100\}$ and $\{101\}$ faces. Since samarium bromate enneahydrate was one of the compounds found by Schumann (1952) to display triple-twinning, it is probable that the crystal used for this structure determination was not single.

The infrared absorption spectra of a number of rare-earth bromate enneahydrates (Pr, Nd, Sm, Dy, Ho, Er and Yb) were reported by Yakunina, Kharzeeva & Serebrennikov (1969), who found that the presence of the rare-earth ions had no observable effect on the absorption bands of the bromate ion, indicating very little interaction between the rare-earth and bromate ions. This is in complete agreement with the earlier results of Geisler & Hellwege (1953).

Poulet, Mathieu, Vergnat, Vergnat, Hadni & Gerbaux (1975) reported single-crystal studies of neo-

dymium and gadolinium bromate enneahydrates determining the infrared and Raman spectra, as well as the pyroelectric signal as a function of temperature. The heat capacity at constant pressure for gadolinium bromate enneahydrate in the temperature range 20–110 K was also reported, which showed a λ -type transition at 66 K, very close to the temperatures found for the phase transitions in praseodymium and neodymium (Hellwege & Hellwege, 1950), as well as europium (Hellwege & Kahle, 1951; Kahle, 1959*a,b*) bromate enneahydrates. It was also found that pyroelectric signals of gadolinium and neodymium bromates show maxima near the temperature of the phase transition. At temperatures above the phase transition, the pyroelectric signal rapidly decreases, so that for neodymium bromate, there is no pyroelectricity above 74 K (Mangin & Hadni, 1978). Poulet *et al.* (1975) also studied neodymium and gadolinium bromate enneahydrate crystals using a polarizing microscope, and found both that these crystals were biaxial and that some samples showed triple-twinning. They make no mention, however, of the earlier discovery of these results by Schumann (1952). As the interference pattern does not exhibit any appreciable change between 30 and 300 K, they concluded that the phase change occurs without a change in the crystal system, a conclusion which is untenable in light of the results of Hellwege & Kahle (1951) and Kahle (1959*a,b*), work of which Poulet *et al.* were also apparently unaware. Finally, these authors assumed the space group to be $Cmc2_1$ for the rare-earth bromates. This conclusion was apparently reached (although no clear line of reasoning was given) from (a) the biaxial nature of the crystals, (b) the similarity of the twinning to that of aragonite (which is orthorhombic), and (c) the need to accommodate in the unit cell the type of 1/3, 2/3 disorder of the bromate group found by Helmholz. Surprisingly, these authors were apparently unaware of the work on the samarium bromate structure by Sikka (1969), which would have removed the need to satisfy (c). It was pointed out earlier that the twinning in the lanthanide bromates occurs across a different plane than in aragonite, and as the biaxial nature of the crystals does not dictate that the unit cell be orthorhombic, this space-group assignment is questionable.

The crystal structures of praseodymium and ytterbium bromate enneahydrates were reported by Albertsson & Elding (1977), who assumed the space group to be $P6_3/mmc$ (based on Sikka). Although it was not clearly stated, these authors apparently used hexagonal-shaped crystals, so again it is possible that triply twinned crystals were used for the structure determination.

The vibrational spectra of lanthanum and neodymium bromate enneahydrates were reported by Kato, Okada, Fukuzaku & Tanenaka (1978), who analyzed their spectra in terms of C_{3v} symmetry (from

Helmholz). They make no mention of any of the other reported structures, optical spectra, or even the study of the vibrational spectrum of neodymium by Poulet *et al.*, stating, 'To our knowledge there has been no previous investigation of the vibrational structure of these crystals.'

The crystal structure of terbium bromate enneahydrate was reported by Gallucci, Gerkin & Reppart (1982), who assumed the space group $P6_3/mmc$, consistent with the best-determined published structures. The crystal used for this structure determination was cut from a large hexagonal column, but since these authors were unaware of the work by Schumann, no effort was made to obtain the crystal fragment from a single section. It is not certain therefore whether the crystal used was actually single.

Electron paramagnetic resonance (EPR) spectra of gadolinium as a dilute substitutional guest in crystals of the lanthanide bromate enneahydrates were studied by Washington (1982). All of the crystals used in these experiments were hexagonal columns, and the EPR spectra were measured with the applied magnetic field parallel to the pseudo-hexagonal axis. A typical spectrum obtained for this orientation is shown in Fig. 2. As expected on the basis of previous studies of Gd^{3+} ($^8S_{7/2}$) in similar hydrated crystals, seven lines appear in the spectrum. However, for a hexagonal crystal field with the magnetic field aligned along the hexagonal axis, one expects a spectrum which shows mirror symmetry across the central peak, which is clearly not seen in the spectrum shown in Fig. 2. None of the gadolinium/lanthanide bromate spectra had the expected line pattern, showing instead an increasing compression of the high-field side of the spectrum with increasing atomic number of the host rare-earth ion. Indeed, for the host materials terbium through lutetium bromate, the highest field lines began to fold back and overlap with other lines in the spectrum. Washington was unable to analyze the gadolinium spectra in terms of a spin-Hamiltonian with hexagonal symmetry, and was unable to fit the observed spectra. The failure of the

hexagonal spin-Hamiltonian appears obvious in light of the results of Hellwege, Kahle & Schumann described above; Washington, however, was unaware of these results. Results described in the next section show that the crystals used for the EPR studies were biaxial, with some of them displaying twinning of the sort shown in Fig. 1(a). It should be pointed out though, that with the external magnetic field parallel to the pseudo-hexagonal axis, all six sections of the hexagonal column have equivalent orientations with respect to the magnetic field. Thus, EPR spectra measured along this direction are the same as those which would be observed from a single crystal section similarly oriented.

The magnetic susceptibility of single-crystal neodymium bromate in the temperature range 90–300 K was reported by Neogy, Chatterji & Purohit (1984). These authors reference the work of Satten (1953), but (by their own admission) were unaware of most of the other work on the absorption spectra of the rare-earth bromates. These authors stated that the hexagonal neodymium bromate crystals used in their research were tested under a polarizing microscope for twinning, but no mention was made as to whether uniaxial or biaxial interference figures were observed. No magnetic anisotropy was observed perpendicular to the pseudo-hexagonal axis, but if the crystals used were triply-twinned, such anisotropy would not be expected. It is unfortunate that the lower limit of the temperature range was not below the phase transition temperature, ~65 K. Low-temperature susceptibilities have been determined for a number of rare-earth bromate enneahydrates (Simizu, Bellesis & Friedberg, 1984), but these measurements cover a temperature range from only ~0.06 to 4 K.

To summarize the results of the previous work, crystals of the isomorphous rare-earth bromate enneahydrates are biaxial, but display pseudo-hexagonal symmetry. Crystals of some of the salts are composed of six triangular sections, twinned in such a manner that the external form of the crystal is a hexagonal column. The pseudo-hexagonal character of the crystals decreases with temperature down to ~65 K, at which temperature a phase transition occurs. Below ~65 K, the symmetry at the site of the rare-earth ion is triclinic, and there are several inequivalent rare-earth ions in the unit cell. Above the phase transition temperature, there is $\bar{2}$ ($=m$) symmetry at the rare-earth-ion site. The mirror plane contains the pseudo-hexagonal axis, and is parallel with the prism face of the triangular section. The crystal field at the rare-earth-ion site is predominantly determined by the water molecules surrounding the rare-earth ion, with the bromate ions having only a small influence. The symmetry of the crystal field will therefore be determined predominantly by the symmetry of the hydrated ion.

The present investigation of the holmium bromate crystal structure was undertaken in order to establish



Fig. 2. EPR X-band spectrum of Gd^{3+} in europium bromate enneahydrate.

by crystallographic methods the appropriate space group and rare-earth-ion site symmetry for the isomorphous lanthanide bromate enneahydrate series.

Experimental. Gadolinium bromate was prepared by the aqueous reaction of gadolinium sulfate with barium bromate, the precipitated barium sulfate being removed by filtration. Crystals in the shape of hexagonal columns were obtained by slow evaporation using a sand bath at ~ 313 K. The remaining crystals used in this research (La, Pr, Nd, Sm, Eu, Tb–Lu bromates) were prepared by Dr N. M. Washington using the same method.

Crystals of all the lanthanide bromate enneahydrates examined in the present study produced biaxial interference figures in convergent polarized light (Fig. 3). The optical plane was found to be parallel to the external hexagonal face, as shown in Fig. 1(a). In addition, some hexagonal columnar crystals of lanthanum, dysprosium and holmium bromates were observed to be triply twinned (Fig. 1a). These observations, combined with the observations of Schumann (1952), bring to seven the number of lanthanide bromate salts reported to show this type of twinning. It therefore seems likely that such twinning occurs for every salt in the isomorphous series. In contrast to the results of Schumann, however, no dispersion of the bisectrices was observed in any of the interference figures.

A triply twinned holmium bromate crystal was sufficiently large that a crystal for diffraction studies was cut from a single triangular section of the twin. The resulting crystal had six bounding faces $[001, 00\bar{1}, \bar{2}10,$

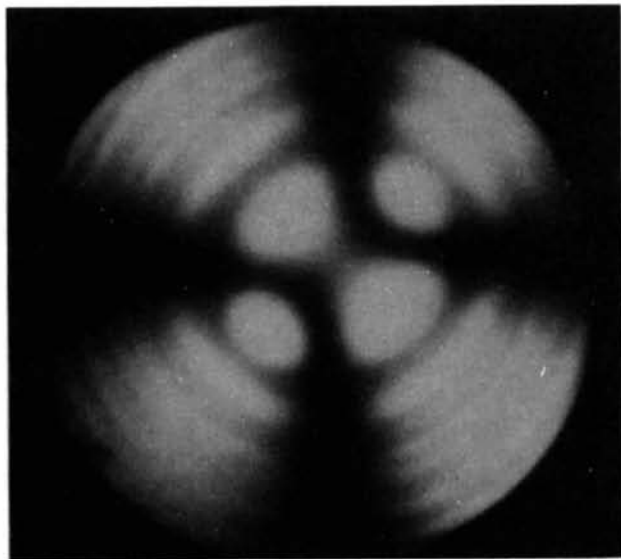


Fig. 3. Biaxial interference figure observed for holmium bromate enneahydrate parallel to the pseudo-hexagonal axis.

Table 1. *Experimental details*

Temperature (K)	294	168
Reflections measured	5152	5873
2θ range ($^\circ$)	4–60	4–65
Index range*	$\pm h, -k, \pm l$ $h_{\max} = 14; k_{\max} = 16;$ $l_{\max} = 9$	$\pm h, +k, \pm l$ $h_{\max} = 15; k_{\max} = 17;$ $l_{\max} = 10$
Transmission factors	0.04–0.11	0.02–0.13
Unique reflections	1307	1565
R_{int}	0.032	0.033
R	0.041	0.041
wR	0.039	0.037
S	2.9	2.8
No. of parameters	73	73
$(\Delta/\sigma)_{\max}$	0.02	0.3
$\Delta\rho_{\max}$ ($e \text{ \AA}^{-3}$)	1.3	2.1
$\Delta\rho_{\min}$ ($e \text{ \AA}^{-3}$)	–1.9	–1.8

* Indices in terms of a hexagonal unit cell.

$2\bar{1}0, 010$ and $0\bar{1}0$ (hexagonal description)] and dimensions $0.26 \times 0.29 \times 0.31$ mm. Precession photographs taken parallel to and normal to the pseudo-hexagonal axis showed no deviation from Laue symmetry $6/mmm$, however.

Intensity data were measured at 168 and 294 K 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 2100A digital thermometer (type K thermocouple). Graphite-monochromated Mo $K\alpha$ radiation was used throughout.

Unit-cell parameters were determined from a least-squares fit of the setting angles for 25 well-centered reflections ($20^\circ < 2\theta < 30^\circ$). Data collection details are given in Table 1. Intensities were measured using the ω – 2θ scan technique, with scan widths from $2\theta(\text{Mo } K\alpha_1) - 1.0^\circ$ to $2\theta(\text{Mo } K\alpha_2) + 1.1^\circ$ and a background/scan time ratio of 0.5. Uncertainties were assigned to each reflection using the formula $\sigma_I^2 = R^2(C + 4B) + (0.02I)^2$, 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. Six standard reflections [231, 151, 203, 421, 301 and 222 (hexagonal description)] were measured after every 94 reflections. The intensity variations of the standard reflections were less than 6.5% of the average intensity. 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).

Space-group selection and least-squares refinement

Although it was known from the biaxial nature of the crystal that the space group must be triclinic, monoclinic or orthorhombic, the unit-cell constants and systematic absences observed in the precession photographs as well as the two sets of diffractometer intensity data (hhl , l odd, and $00l$, l odd) were

entirely consistent with three hexagonal space groups: $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$. Intensity data collected for an equivalent C -centered orthorhombic cell showed that all of the reflections expected to be systematically absent due to the lattice centering were indeed not present.

For the three possible hexagonal space groups, the non-isomorphic subgroups which retain a side-centered lattice and a glide plane perpendicular to the b axis are shown in Fig. 4. Each of these subgroups corresponds to a hexagonal space group with some of the symmetry elements removed. The systematic absences for each of the sub-hexagonal space groups account for most of the absences found in the diffraction pattern, with the exception of some reflections which are systematically absent due to the pseudohexagonal symmetry. Each of these five subgroups is therefore a possible choice for the space group of the rare-earth bromates. Although the pseudohexagonal character of the unit cell theoretically allows three possible orientations for the unit cell in each subgroup, the orientation of the optical indicatrix determines the appropriate choice uniquely.

Since both holmium and bromine have relatively large anomalous-scattering coefficients, it should be possible to determine whether or not the space group is centrosymmetric on the basis of the Bijvoet differences. However, no such differences were observed in the hexagonal, orthorhombic, or monoclinic settings. In addition, later attempts at least-squares refinement in each of the non-centrosymmetric space groups shown in Fig. 4 resulted in non-positive-definite thermal parameters for some atoms. Hence, there remained only two possible choices for the space group: $Cmcm$ or $C2/c$.

Refinement of the holmium bromate structure at low temperature was carried out for each of these two space groups. Full-matrix least-squares refinement was per-

formed using the *SHELX76* program (Sheldrick, 1976), which minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma_F^{-2}$. All unique, non-systematically absent reflections with $I > 0$ were included in the calculations. A refinement in the hexagonal space group $P6_3/mmc$ was also performed for comparison, and the results are listed in Table 2. The small differences between these parameters for the orthorhombic and monoclinic space groups, combined with the lack of any observable dispersion of the bisectrices (orthorhombic, horizontal, crossed, or inclined dispersion) led to the selection of $Cmcm$ as the space group. Clearly, this choice is somewhat arbitrary, but it was thought preferable to err in the direction of higher symmetry.

Table 2. Results for the least-squares refinement of the low-temperature holmium bromate enneahydrate structure in three space groups

	$P6_3/mmc$	$Cmcm$	$C2/c$
R	0.036	0.041	0.044
wR	0.033	0.037	0.041
S	4.1	2.8	2.4
Max. $\Delta\rho$ peak ($e \text{ \AA}^{-3}$)	2.1	2.1	2.1

Table 3. Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for holmium bromate enneahydrate at 168 K

The equivalent isotropic temperature factor was calculated using the relation: $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} - U_{12})$.

	x	y	z	U_{eq}
Ho	0.5	0.16671 (2)	0.25	10
Br(1)	0.5	0.37008 (4)	0.75	23
Br(2)	0.19479 (6)	0.06487 (3)	0.75	23
O(1A)	0.5	0.0799 (2)	0.4926 (7)	16
O(1B)	0.3699 (3)	0.2101 (1)	0.4929 (4)	16
O(2A)	0.5	0.2878 (3)	0.25	24
O(2B)	0.3187 (4)	0.1066 (2)	0.25	20
O(3A)	0.3873 (4)	0.3195 (2)	0.75	16
O(3B)	0.2144 (4)	0.1463 (2)	0.75	16
O(3C)	0.3267 (4)	0.0341 (2)	0.75	15
O(4A)	0.5	0.4052 (7)	0.545 (3)	61
O(4B)	0.1409 (8)	0.0481 (4)	0.548 (2)	52

Table 4. Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for holmium bromate enneahydrate at 294 K

The equivalent isotropic temperature factor was calculated using the relation: $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} - U_{12})$.

	x	y	z	U_{eq}
Ho	0.5	0.16670 (2)	0.25	16
Br(1)	0.5	0.36954 (5)	0.75	32
Br(2)	0.19541 (7)	0.06506 (4)	0.75	31
O(1A)	0.5	0.0801 (3)	0.4930 (8)	27
O(1B)	0.3699 (3)	0.2100 (2)	0.4918 (6)	29
O(2A)	0.5	0.2878 (4)	0.25	33
O(2B)	0.3188 (4)	0.1065 (3)	0.25	32
O(3A)	0.3885 (4)	0.3187 (3)	0.75	30
O(3B)	0.2156 (5)	0.1463 (3)	0.75	30
O(3C)	0.3270 (5)	0.0348 (3)	0.75	26
O(4A)	0.5	0.4052 (8)	0.547 (3)	81
O(4B)	0.141 (1)	0.0487 (5)	0.549 (2)	73

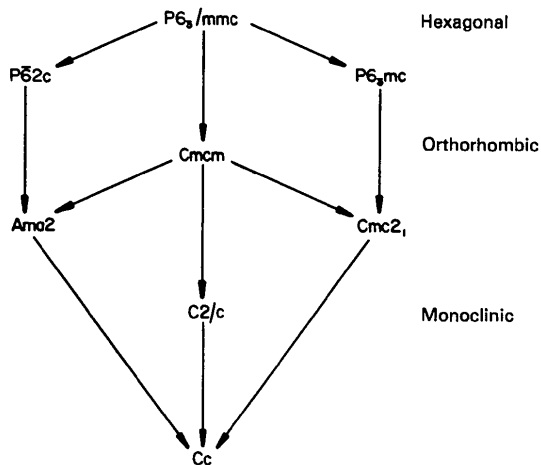


Fig. 4. Non-isomorphic subgroups of the space group $P6_3/mmc$. Maximal non-isomorphic subgroups are connected with arrows.

The final atomic coordinates and thermal parameters for the holmium bromate structures at the two temperatures are listed in Tables 3 and 4. Final least-squares refinement details are given in Table 1.* Since not all of the H atoms were found in the density difference maps, no H atoms were included in the least-squares refinement.

Atomic scattering factors for holmium and bromine were taken from Cromer & Waber (1965), while that for oxygen was from Cromer & Mann (1968). Correction factors for anomalous dispersion were taken from Cromer & Liberman (1970).

Discussion.

Description of the structures

The structure consists of columns of bromate groups centered on the 2_1 axis located at the origin, and columns of hydrated rare-earth ions located at the position $x = 0$, $y = \frac{1}{3}$. The bromate ions are linked by hydrogen bonds to water molecules coordinating the metal ion.

Each holmium ion is coordinated to nine water molecules: two O(1A) and four O(1B) atoms are situated at the vertices of a trigonal prism, and one O(2A) and two O(2B) atoms lie in the mirror plane containing the metal ion. The O(2) atoms cap the faces of the trigonal prism, and are at a slightly greater distance from the metal ion than are the O(1) atoms (Table 5). The symmetry of the coordinated rare-earth ion is, to within the experimental uncertainty, D_{3h} . The geometries of the coordinated ion at 168 and 294 K are very similar, with most of the differences in bond lengths and angles being within the combined uncertainties of the corresponding values. The environments of the holmium ion at 168 and 294 K are shown in Fig. 5. It is of interest to note that the average Ho—O distances found in holmium bromate (2.408 Å at 294 K and 2.400 Å at 168 K) are nearly equal to the average metal—O distance (2.412 Å) found in holmium ethyl sulfate enneahydrate at 171 K (Gerkin & Reppart, 1984).

The Br and O(3) atoms of the bromate groups lie on the mirror planes through $z = \pm \frac{1}{4}$. The O(4) atoms are evenly distributed above and below these planes, giving rise to disorder in the structure. As expected, the shape of the bromate group is pyramidal, but the Br—O(3) and Br—O(4) bond lengths were not found to be equal. The explanation for this undoubtedly lies in the apparently large thermal motion of the O(4) atoms, which is discussed in the next section. Hydrogen bonds occur between O(3) and O(1) atoms and O(3) and O(2)

Table 5. Bond lengths (Å) and angles (°) for holmium bromate enneahydrate at 168 and 294 K

	294 K	168 K
Coordination polyhedron		
Ho—O(1A)	2.389 (5)	2.378 (4)
Ho—O(1B)	2.386 (4)	2.378 (3)
Ho—O(2A)	2.454 (7)	2.449 (6)
Ho—O(2B)	2.447 (5)	2.440 (4)
O(1A)—O(2B)	2.722 (5)	2.709 (4)
O(1B)—O(2A)	2.721 (6)	2.711 (5)
O(1B)—O(2B)	2.713 (5)	2.706 (4)
Bromate ions		
Br(1)—O(3A)	1.663 (5)	1.666 (4)
Br(1)—O(4A)	1.533 (17)	1.530 (13)
Br(2)—O(3B)	1.663 (5)	1.662 (4)
Br(2)—O(3C)	1.657 (5)	1.660 (4)
Br(2)—O(4B)	1.520 (11)	1.515 (8)
O(3A)—Br(1)—O(3A')	103.4 (4)	104.2 (3)
O(3A)—Br(1)—O(4A)	107.0 (5)	106.6 (4)
O(3B)—Br(2)—O(3C)	103.6 (3)	104.1 (2)
O(3B)—Br(2)—O(4B)	106.0 (5)	106.2 (4)
O(3C)—Br(2)—O(4B)	107.9 (5)	107.5 (4)
Hydrogen bonds		
O(1A)—O(3C)	2.807 (6)	2.800 (4)
O(1B)—O(3A)	2.805 (5)	2.797 (4)
O(1B)—O(3B)	2.810 (6)	2.801 (5)
O(2A)—O(3B)	2.855 (6)	2.834 (4)
O(2B)—O(3A)	2.860 (6)	2.831 (5)
O(2B)—O(3C)	2.864 (7)	2.845 (4)
O(2A)—O(4A)	3.10 (2)	3.07 (2)
O(2B)—O(4B)	3.11 (2)	3.10 (1)

Symmetry code: (i) $1-x, y, z$.

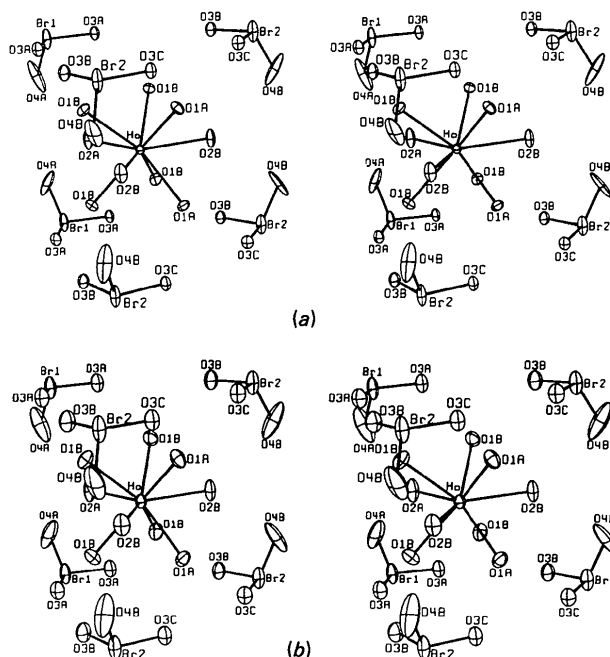


Fig. 5. ORTEPII (Johnson, 1971) stereoviews showing the environment of the metal ion in holmium bromate enneahydrate: (a) at 168 K, and (b) at 294 K. (Only one of the positions for each disordered oxygen is shown in these drawings.)

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atoms, with O—O distances in the range 2.80–2.87 Å. There also appears to be possible hydrogen bonding between the O(4) and O(2) atoms, which are separated by ~3.1 Å. The calculation of the O(4)—O(2) distances is affected by the apparently shortened Br—O(4) bond, so that the actual hydrogen-bond distance is probably somewhat smaller than 3.1 Å.

The highest peaks ($2.1 \text{ e } \text{Å}^{-3}$) found on the final electron density difference map for the holmium bromate structure at low temperature are at a distance of ~0.5 Å from the Br atoms. A number of smaller peaks ($\sim 1 \text{ e } \text{Å}^{-3}$) are found near the O(2) and O(4) atoms. Peaks at nearly the same locations but having smaller heights are also found in the difference map for the room-temperature holmium bromate structure. Since none of these peaks is located along bonding directions, they cannot be attributed to bonding electron density. Helmholz found similar peaks near the Br atoms in neodymium bromate, but attributed these to the incompleteness of his data. Neither Sikka, nor Albertsson & Elding, mentions the location or height of any peaks in their final electron density difference maps.

As seen from Table 5, the Br—O(3) and Br—O(4) bond lengths are ~1.66 and 1.52 Å, respectively. Recently determined values of Br—O bond lengths in the bromate ion in other structures are ~1.65 Å in NaBrO₃ (Abrahams & Bernstein, 1977), ~1.63–1.68 Å in Cd(BrO₃)₂·2H₂O (Golovastikov, 1979), and ~1.65 Å in both NaBrO₃ and KBrO₃ (Templeton & Templeton, 1985). Clearly, the Br—O(4) bond length in the present salt is markedly less than the Br—O(3) bond length in this salt or the Br—O bond lengths in some other (typical?) bromate salts both hydrated and anhydrous. Indeed, in their studies of praseodymium and ytterbium bromates Albertsson & Elding found that even after correcting the Br—O(4) bond length for thermal motion it still was not as large as the Br—O(3) bond length.

It is easily seen from Fig. 5 that the Br and O(2) atoms have thermal ellipsoids which are elongated in the direction of the *c* axis. The r.m.s. displacement of the Br atoms in the *z* direction at 168 K is 0.22 Å, which is slightly larger than the displacement in that direction (0.17 Å) which is necessary to make all the Br—O bond lengths equal. The r.m.s. displacement of the O(2) atoms in the *z* direction at 168 K is of a similar magnitude (0.20 Å). As stated above, a number of large peaks in the final electron density difference map are close to the Br and O(2) atoms. It seems likely, therefore, that the large thermal ellipsoids of the Br and O(2) atoms indicate the presence of additional static disorder in the crystal, rather than extreme thermal motion in the *z* direction. Subject to such an assumption, the mirror planes at $z = \pm \frac{1}{4}$ become artifacts of the disorder, and the symmetry displayed by the diffraction data can be explained by the twinning of a *Cmc*₂ unit cell with its inverse within each triangular

section of the holmium bromate crystal. This assumption also has the virtue of reconciling the diverse symmetries at the rare-earth-ion site as determined by X-ray diffraction (*mm*) and spectroscopic (*m*) methods.

The coordinates derived from the present refinement of the holmium bromate enneahydrate structure do not differ significantly from those derived from equivalent refinements assuming monoclinic (or, indeed, even hexagonal) symmetry. It therefore must be emphasized that the choice of *Cmcm* as the space group for the present work is not definitive. At the same time, however, it must be emphasized that the symmetry is most definitely not hexagonal, though this has often been thought previously.

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Structure of Lead Tetrapolyphosphate

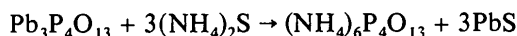
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Abstract. $\text{Pb}_3\text{P}_4\text{O}_{13}$, $M_r = 953.45$, triclinic, $P\bar{1}$, $a = 7.830$ (5), $b = 7.347$ (5), $c = 10.215$ (8) Å, $\alpha = 104.35$ (1), $\beta = 101.81$ (1), $\gamma = 94.27$ (1)°, $V = 552.4$ (1) Å³, $Z = 2$, $D_x = 5.731$ Mg m⁻³, $\lambda(\text{Ag K}\alpha) = 0.5608$ Å, $\mu = 25.70$ mm⁻¹, $F(000) = 820$, $T = 293$ K, final $R = 0.048$ for 2634 independent observed reflexions. The phosphoric condensed anion is here a non-common tetrameric linear one, $\text{P}_4\text{O}_{13}^{6-}$, built up by four corner-sharing PO_4 tetrahedra. The three independent Pb atoms, with a seven- or eightfold oxygen coordination, link these P_4O_{13} groups so as to build a three-dimensional network.

Introduction. Due to the lack of a general method of preparation, tetrapolyphosphates are rare and difficult to crystallize. Up to now only two crystal structures of tetrapolyphosphates have been performed: $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ (Durif, Averbuch-Pouchot & Guitel, 1976) and $\text{CaNb}_2\text{O}(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{13})$ (Averbuch-Pouchot, 1986). In this field of chemistry the title compound is an important starting material, since it has often been used during attempts to produce alkali tetrapolyphosphates by a metathesis reaction of the type:



(Waerstad & McClellan, 1974). The present work devoted to the crystal structure of $\text{Pb}_3\text{P}_4\text{O}_{13}$ provides the third detailed geometrical configuration of a P_4O_{13} group.

Experimental. Crystal preparation and data have already been reported (Averbuch-Pouchot & Durif, 1986). Density not measured. $0.19 \times 0.14 \times 0.29$ mm fragment of crystal. Philips PW 1100 diffractometer, graphite monochromator. 18 reflexions ($10 < \theta < 12^\circ$) for refining unit-cell dimensions. ω scan. 5032 reflexions measured ($3 < \theta < 30^\circ$), $\pm h \pm kl$, $h_{\text{max}} = 13$, $k_{\text{max}} = 12$, $l_{\text{max}} = 17$. Scan width 1.20° , scan speed

$0.02^\circ \text{ s}^{-1}$, total background measuring time 20 s. Two intensity and orientation reference reflexions (120 and $\bar{1}\bar{2}0$) every 2 h, no variation. Lorentz-polarization correction, absorption correction (max. = 40.5, min. = 20.4). Classical methods for structure determination: Patterson and successive Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F). Unit weights. Final refinement with 2634 reflexions such that $I > 16\sigma_I$ and $|F_o - F_c| < 20$ in a scale varying from 3468 to 0. Final $R = 0.048$ ($wR = 0.060$). For the complete set of 5032 reflexions $R = 0.065$. $S = 5.536$. Max. $\Delta/\sigma = 0.02$ (for extinction coefficient). Max. peak height in final difference Fourier synthesis $9.41 \text{ e } \text{Å}^{-3}$. Extinction coefficient refined: 0.37×10^{-7} (Stout & Jensen, 1968). Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius (1977) *SDP* used for all calculations. Final atomic coordinates and B_{eq} are reported in Table 1.* Computer used: Digital PDP 11.70.

Discussion. The atomic arrangement of $\text{Pb}_3\text{P}_4\text{O}_{13}$ projected along the b axis is shown in Fig. 1. The main interest of this structure rests on the presence of a tetrapolyphosphate anion $\text{P}_4\text{O}_{13}^{6-}$.

The P_4O_{13} group

As already mentioned this anion is a linear linkage of four corner-sharing PO_4 tetrahedra. Table 2 reports the main geometrical features of this anion, built up by four crystallographically independent PO_4 tetrahedra. A detailed comparison with previous examples of such

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