

The Structure of Barium Perbromate Trihydrate $\text{Ba}(\text{BrO}_4)_2 \cdot 3\text{H}_2\text{O}$

BY ROGER E. GERKIN* AND WILLIAM J. REPPART†

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

AND EVAN H. APPELMAN

Argonne National Laboratory, Argonne, Illinois 60439, USA

(Received 7 December 1987; accepted 23 February 1988)

Abstract. $\text{Ba}(\text{BrO}_4)_2 \cdot 3\text{H}_2\text{O}$, $M_r = 479.19$, hexagonal, $P6_3/m$, $a = 7.414(1)$, $c = 9.965(1)$ Å, $V = 474.4(1)$ Å³, $Z = 2$, $D_x = 3.35$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 125.7$ cm⁻¹, $F(000) = 440$, $T = 294$ K, $R = 0.036$, 593 unique reflections. The Ba atoms in this structure are coordinated by twelve O atoms in a near-icosahedral arrangement, with an average Ba–O bond length of 2.987(2) Å. The perbromate ion has regular tetrahedral geometry within the experimental error, and has an average Br–O bond length of 1.608(3) Å. Each perbromate ion in the structure is hydrogen bonded to three water molecules.

Introduction. Crystal structure investigations of perbromate compounds have been limited to alkali and alkali-like perbromates since the initial synthesis of perbromic acid (Appelman, 1968). Full structure determinations have been performed only for potassium (Siegel, Tani & Appelman, 1969), caesium (Gebert, Peterson, Reis & Appelman, 1981, 1982) and ammonium (Tutov, Gavrilov, Isupov, Kolycheva & Fundamenskii, 1986) perbromates, and unit-cell data have been published for rubidium perbromate (Tutov *et al.*, 1986).

Our interest in the perbromate salts of the trivalent lanthanides has arisen in conjunction with our studies of the disordered structures of the trivalent lanthanide bromate enneahydrates (Gerkin & Reppart, 1987). However, as repeated attempts to crystallize several lanthanide perbromates have been unsuccessful (owing presumably to their extremely high solubilities), investigation of the structures of a number of other multivalent-metal perbromate salts has subsequently been undertaken. Our investigation of the structure of barium perbromate trihydrate is the first of these to be reported.

Experimental. Crystals of barium perbromate trihydrate were produced by slow evaporation at room

temperature from a barium perbromate solution formed by the reaction of barium oxide (a Baker and Adamson chemical) with a stoichiometric amount of 1M perbromic acid, prepared by the method described by Appelman (1972).‡ A clear colorless crystal with dimensions 0.18 × 0.20 × 0.29 mm was analyzed with a Syntex P1 diffractometer, utilizing graphite-monochromated Mo $K\alpha$ radiation.

Unit-cell parameters were obtained from a least-squares fitting of the setting angles for 23 well centered reflections with $20 \leq 2\theta \leq 30^\circ$. Intensity data were measured for 1558 reflections with $+h, +k, +l$ and $-h, -k, -l$ indices (h 0–9, k 0–11, l 0–15), and 2θ values in the range $4 \leq 2\theta \leq 65^\circ$. The ω – 2θ scan technique was employed with scan widths from $2\theta(\text{Mo } K\alpha_1) - 1.1^\circ$ 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. Three standard reflections (122, 304, 140) were measured after every 97 reflections, and these exhibited a slight intensity decrease over the course of the data collection. After the application of a decay correction, the standard reflections showed a maximum relative intensity variation of $\pm 3.6\%$. The data were corrected for Lorentz and polarization effects, and empirical absorption correction factors were applied to the F_o 's using the program *DIFABS* (Walker & Stuart, 1983), with the maximum and minimum correction factors being 1.78 and 0.78, respectively.

The space groups $P6_3$ and $P6_3/m$ were allowed, based on the observed systematic absences (00 l , $l = \text{odd}$). No Bijvoet differences were observed, however, which resulted in assignment of the space group as $P6_3/m$. Averaging of equivalent reflections gave 601 independent observations, with $R_{\text{int}} = 0.024$. The positions of the Ba and Br atoms were determined from a

* Author for correspondence.

† Present address: Shell Development Company, PO Box 481, Houston, TX 77001, USA.

‡ Work performed at Argonne National Laboratory while WJR was a Thesis Parts Program participant.

Patterson map, and the O atoms were subsequently located using Fourier methods. Full-matrix least-squares refinement was performed using the *SHELX76* program (Sheldrick, 1976) to minimize the function $\sum \sigma_F^{-2}(|F_o| - |F_c|)^2$, in which $\sigma_F = \sigma_f/2FLp$, for the 601 reflections with $F_o > 0$. Neutral-atom scattering factors for Ba and Br atoms were taken from Cromer & Waber (1965), and the O-atom scattering factor was taken from Cromer & Mann (1968). Correction for anomalous dispersion was included for Ba and Br atoms (Cromer & Liberman, 1970). The H atoms could not be located and were not included in the calculations.

The results for the final refinement cycle were: 593 independent observations (8 reflections for which the difference between F_o and $|F_c|$ was greater than $5\sigma_F$ prior to the final refinement cycle were excluded from the final cycle); 24 variables, $R = 0.036$; $wR = 0.032$; $w = 1/\sigma^2(F)$; $S = 1.1$; $(\Delta/\sigma)_{\max} = 0.01$. * Maximum and minimum peaks on the final $F_o - F_c$ map had values $+1.3$ and $-0.97 e \text{ \AA}^{-3}$, respectively. The maximum peak was located approximately one third of the way between Br and O(1), while the minimum peak was located at $x = 0.20$, $y = 0.72$, $z = 0.26$, approximately equidistant from O(1), O(2) and O(3); the second-highest maximum peak, of value $+0.97 e \text{ \AA}^{-3}$, was located very near O(2). The final atomic coordinates are listed in Table 1. Interatomic distances and angles calculated using the *XRAY* system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) are given in Table 2.

Discussion. The Ba atoms in this structure are coordinated by twelve O atoms, six perbromate-ion O(2) atoms and six water-molecule O(3) atoms, which form the apices of a slightly distorted icosahedron. Columns of these icosahedra are centered on the 6_3 axis passing through the unit-cell origin, with successive

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44807 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

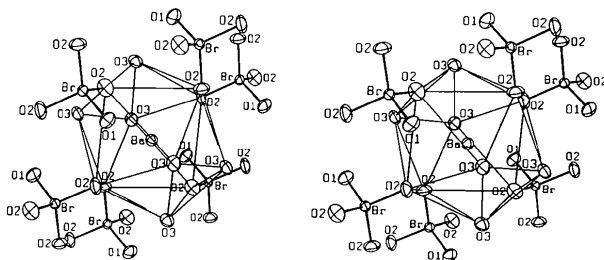


Fig. 1. Stereoview of the environment near the Ba atom in barium perbromate trihydrate, drawn using *ORTEPII* (Johnson, 1971). Thermal ellipsoids are drawn at 50% probability for all atoms.

Table 1. Final atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$), with *e.s.d.'s* in parentheses

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

	x	y	z	U_{eq}
Ba	0	0	0	155
Br	↓	↓	0.03377 (5)	116
O(1)	↓	↓	-0.1277 (4)	216
O(2)	0.1629 (4)	0.4403 (4)	0.0877 (3)	252
O(3)	0.2518 (5)	0.1655 (5)	$\frac{1}{2}$	211

Table 2. Bond lengths (\AA) and angles ($^\circ$) for barium perbromate trihydrate

Coordination polyhedron			
Ba—O(2)	2.989 (3)	O(3 ⁱⁱ)—O(2)—O(3)	57.36 (10)
Ba—O(3)	2.985 (2)	O(2 ⁱⁱⁱ)—O(2)—O(3)	69.18 (10)
		O(3 ^{iv})—O(2)—O(2 ^v)	68.26 (8)
O(2)—O(3)	2.922 (5)	O(2 ⁱⁱⁱ)—O(2)—O(3 ^v)	51.31 (7)
O(2)—O(3 ⁱⁱ)	3.007 (3)	O(2 ^v)—O(2)—O(3 ^v)	49.75 (6)
O(2)—O(2 ⁱⁱⁱ)	3.351 (4)		
O(2)—O(3 ^v)	3.579 (3)	O(3 ⁱⁱ)—O(3)—O(2)	62.82 (10)
O(3)—O(3 ⁱⁱ)	2.847 (5)	O(2 ⁱⁱⁱ)—O(3)—O(2)	61.07 (7)
		O(3 ^{iv})—O(3)—O(3 ^v)	60
		O(2 ⁱⁱⁱ)—O(3)—O(2 ^{iv})	60.43 (6)
		O(3 ^v)—O(3)—O(2 ^{iv})	59.82 (8)
Perbromate ion			
Br—O(1)	1.609 (4)	O(1)—Br—O(2)	109.5 (1)
Br—O(2)	1.607 (2)	O(2)—Br—O(2')	109.4 (1)
O(1)—O(2)	2.627 (4)		
O(2)—O(2')	2.623 (3)		

Code for symmetry-related atoms: (i) $1-y, x-y+1, z$; (ii) $-y, x-y, z$; (iii) $y, y-x, -z$; (iv) $y-x, -x, z$; (v) $x-y, x, -z$.

icosahedra sharing a common face formed by three O(3) atoms. The separate columns of coordinated Ba atoms are linked through the perbromate ions, each of which is bound to three different icosahedra. A stereoview of the Ba-atom coordination is shown in Fig. 1.

The perbromate ion has regular tetrahedral symmetry within experimental error. The average Br—O bond length of 1.608 (3) \AA is to be compared with the values 1.610 (6) and 1.610 (6) \AA found for this same bond in KBrO_4 (Siegel *et al.*, 1969) and CsBrO_4 (corrected from Gebert *et al.*, 1981), respectively.

Each water-molecule O(3) atom is equidistant from two perbromate-ion O(1) atoms, and each O(1) atom is equidistant from three O(3) atoms. The O(1)—O(3) separation of 2.944 (4) \AA is quite plausible for hydrogen bonding, and would require the H atom to be in a general position near $x = 0.34$, $y = 0.20$, $z = 0.17$.

It can be seen from Table 2 that the O(2) and O(3) atoms are, within experimental error, equidistant from the Ba atom. A perfect icosahedron with this same center-to-apex distance (2.987 \AA) would have an edge length of 3.141 \AA (*International Tables for X-ray Crystallography*, 1959). This value is somewhat larger than the van der Waals O—O distance of 2.8 \AA ,

allowing the Ba-coordinating O atoms some freedom of movement from the ideal positions to accommodate both the tetrahedral symmetry of the perbromate ion and the hydrogen bonding of the water molecules.

The barium perbromate trihydrate structure appears to be isomorphic with the structure of barium perchlorate trihydrate as determined by Mani & Ramaseshan (1960), although these authors could not decide on the basis of their data whether the space group was $P6_3$ or $P6_3/m$. The average Ba—O distance is 3.035 (5) Å in the perchlorate structure, somewhat larger than the corresponding distance in the present structure.

In the same vein, it is interesting to note that each of the perbromate salt structures which has been reported (Ba, NH₄, K, Cs and Rb) is isomorphic with the corresponding perchlorate salt structure.

Thermogravimetric and differential thermal analysis data obtained by Isupov, Gavrilov & Kirin (1977) have been interpreted as demonstrating the existence of a barium perbromate tetrahydrate salt. Since there is insufficient space to accommodate another water molecule in the trihydrate structure, barium perbromate tetrahydrate must crystallize in a different space group.

The support of WJR by an Ohio State University Presidential Fellowship and the partial support by a Thesis Parts Appointment at Argonne National Laboratory are acknowledged with pleasure. EHA acknowledges support from the Office of Basic Energy Sciences, Division of Chemical Sciences, US Depart-

ment of Energy. We thank Dr J. C. Gallucci for numerous helpful discussions. Computational facilities were provided by The Ohio State University IRCC.

References

- APPELMAN, E. H. (1968). *J. Am. Chem. Soc.* **90**, 1900–1901.
 APPELMAN, E. H. (1972). *Inorg. Synth.* **13**, 1–9.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 GEBERT, E., PETERSON, S. W., REIS, A. H. & APPELMAN, E. H. (1981). *J. Inorg. Nucl. Chem.* **43**, 3085–3089.
 GEBERT, E., PETERSON, S. W., REIS, A. H. & APPELMAN, E. H. (1982). *Polyhedron*, **1**, 567.
 GERKIN, R. E. & REPPART, W. J. (1987). *Acta Cryst.* **C43**, 623–631.
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 ISUPOV, V. K., GAVRILOV, V. V. & KIRIN, I. S. (1977). *Zh. Neorg. Khim.* **22**, 2592–2594.
 JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
 MANI, N. V. & RAMASESHAN, S. (1960). *Z. Kristallogr.* **114**, 200–214.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SIEGEL, S., TANI, B. & APPELMAN, E. (1969). *Inorg. Chem.* **8**, 1190–1191.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The *XRAY* system—version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
 TUTOV, A. G., GAVRILOV, V. V., ISUPOV, V. K., KOLYCHEVA, T. I. & FUNDAMENSKII, V. S. (1986). *Zh. Neorg. Khim.* **31**, 589–592.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1988). **C44**, 962–965

Structure of Calcium Zinc Tetrabromide Pentahydrate

BY RUMEN DUHLEV,* I. DAVID BROWN AND ROMOLO FAGGIANI

Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

(Received 19 January 1988; accepted 15 February 1988)

Abstract. $\text{CaZnBr}_4 \cdot 5\text{H}_2\text{O}$, $M_r = 515.15$, triclinic, $P\bar{1}$ {Hall symbol $P\bar{1}$ [*Acta Cryst.* (1981), **A37**, 517–525]}, $a = 7.472$ (2), $b = 9.722$ (3), $c = 10.020$ (3) Å, $\alpha = 84.67$ (2), $\beta = 113.43$ (2), $\gamma = 112.38$ (2)°, $V = 616.1$ (3) Å³, $Z = 2$, $D_x = 2.78$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 15.03$ mm⁻¹, $F(000) = 480$, room temperature, $R = 0.049$ ($wR = 0.044$) for 1630 unique reflections. The structure consists of

centrosymmetric dimeric rings $[\text{Ca}(\text{H}_2\text{O})_5\text{ZnBr}_4]_2$ with Zn tetrahedrally coordinated by four Br atoms ($\langle \text{Zn—Br} \rangle = 2.41$ Å) and Ca sevenfold coordinated by five O_w ($\langle \text{Ca—O} \rangle = 2.37$ Å) and two Br ($\langle \text{Ca—Br} \rangle = 3.11$ Å) from two different ZnBr_4 groups. The rings are held together by O—H...Br and O—H...O hydrogen bonds.

Introduction. Duhlev & Balarew (1986) reported two new double salts, $\text{CaZnBr}_4 \cdot 8\text{H}_2\text{O}$ and $\text{CaZn}_2\text{Br}_6 \cdot 6\text{H}_2\text{O}$, in their study of the phase equilibrium in the system $\text{CaBr}_2\text{—ZnBr}_2\text{—H}_2\text{O}$ at 298 K. In an attempt to

* On leave from the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria.