rings: in the present case these pentagons are filled alternately, whereas all of them are full in the case of decagonal Al–Mn. The main difference between the decagonal phases is the different layer-stacking sequence and the existence of two different layers in the asymmetric unit for the Al–Mn structure. However, both have in common the fact that their structural building elements are similar to those of crystalline $Al_{13}Fe_4$, and that there appear to be no Mackay icosahedra. The most characteristic structural elements are the pentagonal channels clustered in tenfold rings.

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Structure of Hexaaquacobalt(II) Bromate

By Anthony C. Blackburn, Judith C. Gallucci and Roger E. Gerkin*

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

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Abstract

$[Co(H_2O)_6](BrO_3)_2$, $M_r = 422·83$, cubic, $Pa\bar{3}$, $a = 10·3505\,(7)$ Å, $V = 1108·88\,(8)$ Å^3, $Z = 4$, $D_x = 2·53$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0·71069$ Å, $\mu = 87·31$ cm^{-1}, $F(000) = 820$, $T = 296$ K, $R = 0·027$ for 365 unique reflections having $I > \sigma_I$. The single type of Co ion is coordinated by six water-molecule O atoms, each at an observed distance 2·095 (2) Å, in an array which is regular octahedral within the estimated standard deviations of the relevant angles. The single type of bromate ion has a Br—O bond length 1·653 (2) Å and O—Br—O bond angle 104·07 (9)°. The cobalt–oxygen complex manifested rigid-body behavior, but the bromate ion did not. The cobalt–oxygen distance corrected for rigid-body motion is 2·099 Å. Location and refinement of the two inequivalent H atoms permitted detailed analysis of the hydrogen bonding, which occurs principally between the oxygen octahedra and the bromate groups. This structure is isomorphic to that of hexaaquanickel(II) chlorate recently reported from this laboratory.

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* Author for correspondence.

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Introduction

Hexaaquacobalt(II) bromate first claimed our interest when it crystallized from a decomposing solution of cobalt(II) perbromate. Prominent among these crystals were fully developed regular octahedra. Subsequently we became interested in determining a structure which included explicitly the water protons.

Experimental

Crystalline hexaaquacobalt(II) bromate for the present determination was produced by evaporation of an aqueous solution prepared by metathetical reaction of solutions of analytical reagent-grade cobalt(II) sulfate heptahydrate (J. T. Baker) and barium bromate (Strem Chemicals) in very nearly stoichiometric proportion followed by removal of barium sulfate by filtration. In this growth, regular octahedra were rare or absent. The experimental sample was a clear, pink–orange, compact crystal with two prominent hexagonal faces $(1\bar{1}\bar{1})$ and $(\bar{1}11)$, and 12 circumferential faces $(1\bar{1}1)$, (100), $(11\bar{1})$, (001), $(0\bar{1}0)$ and (111) with their Friedel mates, five of the latter being very small. The principal dimensions were approximately 0·23 × 0·35 × 0·38 mm. The sample was analyzed at 296 K with a Rigaku AFC5S diffractometer utilizing graphite-monochromated Mo $K\bar{\alpha}$ radiation.

Unit-cell parameters were obtained from a symmetry-constrained least-squares fit of the setting angles for 25 centered reflections with $28 < 2\theta < 30°$. Intensity data were measured for 2972 reflections (exclusive of standards) with $+h$, $+k$, $\pm l$ indices ($h_{\max} = 13$, $k_{\max} = 12$, $l_{\max} = 12$) and with 2θ values in the range $4 \leq 2\theta \leq 55°$. The ω–2θ scan technique was employed with scan widths $(1{\cdot}25 + 0{\cdot}35\tan\theta)°$ in ω, and a background/scan time ratio of 0·5. An uncertainty was assigned to each reflection using the formula $\sigma_I^2 = \sigma_{cs}^2(I) + (0{\cdot}03I)^2$, where σ_{cs} is based on counting statistics and I is the integrated intensity. Six standard reflections (002, 162, 202, 222, 426 and 551) were measured after every 150 reflections and exhibited, on average, a maximum non-systematic relative intensity variation of ±4·1%. 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 just before intensity data collection; the range of transmission factors was 0·688–1·000, with an average value 0·889.

The crystal was found to have Laue group $m3$ and, on the basis of systematic absences, space group $Pa\bar{3}$ (No. 205) but in a non-standard setting. Following index transformation to the standard setting, the Co atom was placed at the origin (site symmetry $\bar{3}$). Initial coordinates for the Br atom in the special position with site symmetry 3 were obtained from a Patterson map, and Fourier methods were then used to assign, in general positions, the two inequivalent O atoms and the two inequivalent H atoms. Full-matrix least-squares refinement was performed using the *TEXSAN* structure analysis package (Molecular Structure Corporation, 1989) to minimize the function $\sum\sigma_F^{-2}(|F_o| - |F_c|)^2$ in which $\sigma_F = \sigma_I/2F\mathrm{Lp}$. Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for Co, 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 H using the data having $I > 3\sigma_I$, the ψ-scan absorption correction was applied and the data were averaged ($R_{\rm int} = 0{\cdot}061$ for 493 sextuplets of reflections). Then, using all the unique reflections with $I > \sigma_I$ and treating the secondary extinction as an adjustable parameter, least-squares refinement proceeded to the anisotropic stage for all atoms except H and to the isotropic stage for H.

The results for the final refinement cycle were: 365 independent observations having $I > \sigma_I$; 33 variables; $R = 0{\cdot}027$; $wR = 0{\cdot}027$; $w = \sigma_F^{-2}$; $S = 1{\cdot}12$; $(\Delta/\sigma)_{\max} < 0{\cdot}01$. The optimized secondary-extinction coefficient was $4{\cdot}47\ (17) \times 10^{-6}$. Maximum and minimum peaks in the final electron density difference map were $+0{\cdot}60$ e Å^{-3} at $x = -0{\cdot}03$, $y = 0{\cdot}03$, $z = 0{\cdot}53$, approximately 2·6 and 2·8 Å from six H atoms and six O atoms, respectively, and $-0{\cdot}50$ e Å^{-3} at $x = 0{\cdot}19$, $y = 0{\cdot}19$, $z = 0{\cdot}19$, approximately 1·2 Å from Br. [For the final refinement cycle for 303 independent observations having $I > 3\sigma_I$: $R = 0{\cdot}019$; $wR = 0{\cdot}024$; $S = 1{\cdot}11$; $(\Delta/\sigma)_{\max} < 0{\cdot}01$. Similarly, for the 393 independent observations having $I > 0$: $R = 0{\cdot}032$; $wR = 0{\cdot}028$; $S = 1{\cdot}09$; $(\Delta/\sigma)_{\max} < 0{\cdot}01$. These latter two refinements were performed for comparison purposes only.]

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

Rigid-body analysis of the cobalt–oxygen complex and the bromate ion was performed using the program *THMA*11 (1986), based on the work of

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[*] Lists of structure factors, anisotropic displacement parameters, rigid-body analysis details, and Co—O distances, Br—O distances and O—Br—O angles in various salts (Table 4) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53308 (8 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 equivalent isotropic and isotropic displacement parameters,* B_{eq}/B (Å^2), *for hexaaquacobalt*(II) *bromate at* 296 K

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

	x	y	z	B_{eq}/B*
Co	0	0	0	1·56 (3)
Br	0·26028 (3)	0·26028	0·26028	1·61 (2)
O(1)	0·15936 (22)	0·66844 (22)	0·15729 (21)	2·28 (10)
O(2)	0·03344 (25)	−0·02848 (24)	0·19762 (23)	2·14 (11)
H(1)	0·0492 (40)	0·0222 (31)	0·2319 (38)	2·5 (10)†
H(2)	−0·0392 (43)	−0·0523 (47)	0·2292 (42)	4·5 (11)†

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

† Refined isotropically.

Table 2. *Bond lengths* (Å) *and angles* (°) *for hexaaquacobalt*(II) *bromate*

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

	Observed distance	Rigid-body distance		Observed angle
Coordination polyhedron				
Co—O(2)	2·095 (2)	2·099	O(2)—Co—O(2)'	180
O(2)—O(2)^{i}	4·191 (5)	4·199	O(2)—Co—O(2)^{ii}	89·96 (10)
O(2)—O(2)^{ii}	2·962 (4)	2·968	O(2)—Co—O(2)^{iii}	90·04 (10)
O(2)—O(2)^{iii}	2·964 (4)	2·970		
Water molecule				
O(2)—H(1)	0·65 (3)		H(1)—O(2)—H(2)	104 (5)
O(2)—H(2)	0·86 (4)			
Bromate ion				
Co—Br	4·6661 (5)		O(1)^{v}—Br—O(1)^{vi}	104·07 (9)
Co—Br^{iv}	4·4239 (1)			
Br—O(1)^{v}	1·653 (2)			

Code for symmetry-related atoms: none x, y, z; (i) $-x, -y, -z$; (ii) z, x, y; (iii) $-z, -x, -y$; (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$; (v) $\frac{1}{2}-x, -\frac{1}{2}+y, z$; (vi) $z, \frac{1}{2}-x, -\frac{1}{2}+y$.

Schomaker & Trueblood (1968). The average magnitude of the differences in the mean-square displacement amplitudes (MSDA) along the interatomic vectors for the two unique atom pairs of the bromate ion was found to be 74 (16) × 10^{-4} Å^2. The average magnitude of the differences in the MSDA along the interatomic vectors for the four unique atom pairs of the cobalt–oxygen complex was found to be 29 (18) × 10^{-4} Å^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 cobalt–oxygen complex, but not for the bromate ion, and have applied corrections for the rigid-body motion in the cobalt–oxygen complex. The corrected bond lengths are given in Table 2; the corrected angles differed typically from the observed angles by at most just more than their estimated standard deviations and were therefore not tabulated.

Discussion

This structure can be described most simply as fluorite-like, with Co(H_2O)$_6$ replacing Ca and BrO_3 replacing F. Substantial hydrogen bonding occurs between the water molecule and bromate ions.

The Co coordination polyhedron has, by symmetry, a single Co—O(2) distance [observed value, 2·095 (2) Å] and angles, as documented in Table 2, which give it regular octahedral geometry to within the e.s.d.'s of the relevant angles. Corrected for rigid-body motion the single Co—O(2) distance becomes 2·099 Å. The bromate ion has, by symmetry, a single Br—O(1) distance [observed value, 1·653 (2) Å] and an O(1)—Br—O(1) angle of 104·07 (9)°. A stereoview of a unit cell is given in Fig. 1.

Concerning the water molecule we note that the observed H—O—H angle (Table 2) is 104° with an estimated standard deviation of 5°. This value compares favorably 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 *J* (Chiari & Ferraris, 1982; Ferraris & Franchini-Angela, 1972) to which this salt belongs, the range is 100·4–109·9° with an average value 106·9°.

The occurrence of only a single type of regular octahedra of water O atoms and a single type of bromate groups leads to a rather simple hydrogen-bonding situation. Our analysis of these hydrogen bonds and their geometries 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 0·973 Å, the mean value for the O—H bond distance as determined by neutron diffraction in inorganic hydrated crystals of class *J* (Chiari & Ferraris, 1982). The resulting adjusted proton coordinates were then used to calculate distances and angles involving potential hydrogen-bond acceptor O atoms. Since the adjusted O(water)—H—O(acceptor) angles typically differed from the observed angles (calculated directly from the X-ray determinated coordinates) by at most just more than one standard deviation, only the observed 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 inequivalent H atoms is involved in one hydrogen bond in the

Table 3. *Hydrogen-bond parameters* (Å, °) *for hexaaquacobalt*(II) *bromate*

E.s.d.'s are given in parentheses. See text for details.

Water oxygen–acceptor oxygen	Distance	Proton–acceptor oxygen	Observed distance	Neutron-adjusted distance	Observed O—H—O angle	
O(2)—O(1)$^{\text{vii}}$	2·767 (3)	H(2)—O(1)$^{\text{vii}}$	1·96 (5)	1·85	O(2)—H(2)—O(1)$^{\text{vii}}$	156 (4)
O(2)—O(1)$^{\text{viii}}$	2·800 (3)	H(1)—O(1)$^{\text{viii}}$	2·18 (3)	1·88	O(2)—H(1)—O(1)$^{\text{viii}}$	159 (5)
O(2)—O(2)$^{\text{ix}}$	2·962 (4)	H(1)—O(2)$^{\text{ix}}$	2·86 (4)	2·86	O(2)—H(1)—O(2)$^{\text{ix}}$	93 (4)
O(2)—O(2)$^{\text{iii}}$	2·964 (4)	H(2)—O(2)$^{\text{iii}}$	2·65 (4)	2·63	O(2)—H(2)—O(2)$^{\text{iii}}$	103 (3)
O(2)—O(1)$^{\text{x}}$	3·224 (4)	H(1)—O(1)$^{\text{x}}$	2·88 (4)	2·75	O(2)—H(1)—O(1)$^{\text{x}}$	117 (4)
		H(2)—O(1)$^{\text{x}}$	2·85 (4)	2·82	O(2)—H(2)—O(1)$^{\text{x}}$	108 (4)

Code for symmetry-related atoms: none x, y, z; (iii) $-z, -x, -y$; (vii) $-z, -x, 1-y$; (viii) $-\frac{1}{2}+y, z, \frac{1}{2}-x$; (ix) y, z, x; (x) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

H—O(acceptor) distance range 1·85–1·88 Å and in which the acceptor is a bromate O. These values for the H—O(acceptor) distance lie approximately three-tenths of the way between the mean value (1·777 Å) and the maximum value (2·069 Å) for H—O(acceptor) distances for type *J* hydrates as tabulated by Chiari & Ferraris (1982). Accordingly, we may properly describe these as strong hydrogen bonds. Since there are six of each of these two types of H atoms in the coordination polyhedron of a given Co ion, we find a total of 12 strong hydrogen bonds linking that polyhedron to the surrounding bromate ions. These hydrogen bonds alone form a three-dimensional network. A stereoview of the virtually indistinguishable hydrogen-bonding configuration about a central Ni ion in hexaaquanickel(II) chlorate is given by Gallucci & Gerkin (1990) as their Fig. 1.

In addition, we have tabulated two weaker hydrogen bonds in the distance range 2·63–2·86 Å which involve oxygen acceptors from within the same coordination polyhedron and a single bifurcated bond (see Jeffrey, 1987) to a bromate-O acceptor in the distance range 2·75–2·82 Å. We note that only one of the O(water)—O(acceptor) distances involved exceeds the 'maximum' value cited by Jeffrey and Chiari & Ferraris for hydrogen-bond formation in inorganic hydrates (3·15 Å), that being 3·224 Å in the case of the bifurcated bond.

From the point of view of the H atoms in a given water molecule, the hydrogen bonding is as shown schematically in Fig. 2. This arrangement of hydrogen bonds is seen also in the hydrates of small biological molecules and has been described as three-center/bifurcated hydrogen bonding by Jeffrey & Maluszynska (1986).

The stereoview presented in Fig. 3 shows all the hydrogen bonds involving the 12 H atoms of the water molecules coordinating a particular Co ion and seven selected additional hydrogen bonds involving H atoms of water molecules coordinated to other cobalt ions. Taken together, these two sets of hydrogen bonds are seen to link the waters into an infinite network *via* the bromate O atoms.

Considering the hydrogen bonding from the viewpoint of the bromate-O acceptors we observe that each of the three equivalent O atoms of a bromate ion is involved in two strong hydrogen bonds (length 1·85 or 1·88 Å) and one bifurcated bond. Analogously to the case of hexaaquanickel(II) chlorate, the eight nearest-neighbor bromate groups of a given

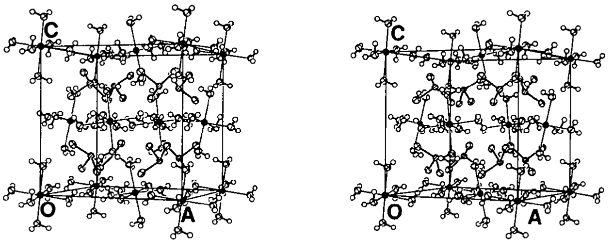

Fig. 1. Stereoview of a unit cell of the hexaaquacobalt(II) bromate structure drawn using *ORTEP*II (Johnson, 1976). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. Hydrogen bonds, though determined in this research, have been omitted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

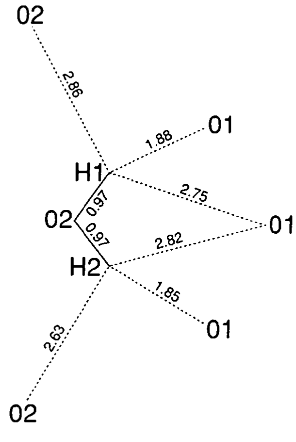

Fig. 2. Schematic drawing of the six hydrogen bonds (dashed lines) involving the H atoms of a given water molecule in the hexaaquacobalt(II) bromate structure. This type of hydrogen bonding has been designated as three-center/bifurcated hydrogen bonding (Jeffrey & Maluszynska, 1986). Bond lengths are given in Å and are neutron-adjusted (see text).

(central) Co ion fall into two classes with respect to their hydrogen bonding with waters associated with that given Co ion: for what we shall call type I bromate ions, of which there are two, each bromate-ion O atom is involved in one strong hydrogen bond with a water molecule associated with the central Co ion and in one hydrogen bond with a water molecule not associated with the central Co; for what we shall call type II bromate ions, of which there are six, only a single bromate-ion O has one strong hydrogen bond with a water molecule associated with the central Co ion, the remaining five strong hydrogen bonds involving water molecules not associated with the central Co ion.

Previously published structural work on transition-metal bromate hydrates is limited to that of Yü & Beevers (1936), who determined the heavy-atom portion of the structure of $Zn(BrO_3)_2.6H_2O$, which is isomorphic to that determined here for $Co(BrO_3)_2.6H_2O$.

A comprehensive tabulation of more recently published results for Co—O distances in hexaaquacobalt(II) coordination octahedra (1962 forward; seven studies) and for Br—O distances and O—Br—O angles in bromate ions (1977 forward; 11 studies) for comparison with values determined in the present study has been deposited as Table 4.

Previously reported values for the Co—O distance range from 2·042 to 2·150 Å, with a grand mean value of 2·088 Å, which is in close agreement with the value from the present study, 2·095 Å. It appears somewhat surprising and interesting that, among these data, only in the present study was a single Co—O distance required by symmetry.

Previously reported values for the Br—O distance range from 1·51 to 1·682 Å. We note, however, that the lowest values are invariably from salts containing trivalent rare-earth cations (four studies). If these values are excluded on the basis of the bromate-O disorder in these salts, the grand mean Br—O distance is 1·656 Å (seven studies) and is thus fortuitously close to the presently reported value, 1·653 Å. Again, it is of some interest that in only the present study and one other of the 12 studies (Abrahams & Bernstein, 1977) were the Br—O distances required by symmetry to be equal. The extent of agreement of distances (and angles) determined in these two studies is noteworthy.

If in considering the O—Br—O angles we again exclude the four trivalent rare-earth salts, the grand mean angle from the previous studies is 103·6°. This is in good accord with the value from the present study, 104·07°.

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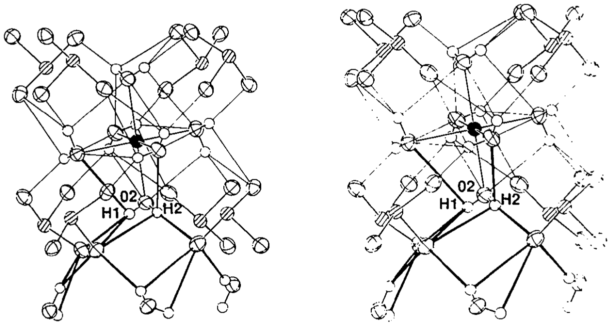

Fig. 3. Stereoview of the near environment of a central Co ion in the hexaaquacobalt(II) bromate structure drawn using *ORTEP*II (Johnson, 1976). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. Hydrogen bonds are represented by the lightest and heaviest lines in this drawing. The heaviest lines show (*a*) the six hydrogen bonds involving the H atoms of the water molecule whose atoms are labelled, which are presented schematically in Fig. 2 and (*b*) seven additional hydrogen bonds involving the three bromate [O(1)] atoms involved in the preceding hydrogen-bond set. As the figure shows, these two sets of hydrogen bonds link the water molecules of different Co octahedra into an infinite network *via* the O atoms of bromate ions. Symbols are as follows: ● = Co; ◍ = O; ▨ = Br; ○ = H.

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