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Structure of Hexaaquacopper(II) Bromate

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Abstract. $[Cu(H_2O)_6](BrO_3)_2$, $M_r = 427{\cdot}44$, cubic, $Pa\bar{3}$, $a = 10{\cdot}3240\,(6)$ Å, $V = 1100{\cdot}38\,(4)$ Å^3, $Z = 4$, $D_x = 2{\cdot}580$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 92{\cdot}32$ cm^{-1}, $F(000) = 828$, $T = 296$ K, $R = 0{\cdot}038$ for 336 unique reflections having $I > \sigma_I$. The single type of copper ion (site symmetry $\bar{3}$) is coordinated by six water-molecule O atoms, each at an observed distance of 2·079 (4) Å, in an array which is virtually regular octahedral, the nominal 90° angles measuring 89·95 (15) and 90·05 (15)°. Thus, this is not a typical Cu^{II} complex in which (consistent with a static Jahn–Teller effect) a distorted octahedral array displays '(2 + 2 + 2)' coordination; rather, it is the sixth strict example of a Cu^{II} static structure inconsistent with the Jahn–Teller theorem. The presence of a dynamic Jahn–Teller effect is supported by the data. The single type of bromate ion has an observed Br—O bond length 1·649 (3) Å and O—Br—O bond angle 104·17 (15)°. The bromate ion was found to manifest rigid-body behavior but, consistent with a dynamic Jahn–Teller effect, the copper–oxygen complex did not. The Br—O bond length corrected for rigid-body motion is 1·663 Å. Refinement of the positional parameters of the two inequivalent H atoms permitted a detailed analysis of hydrogen bonding, which occurs principally between the oxygen octahedra and the bromate groups. This structure is isomorphic with those of hexaaquanickel(II) chlorate, hexaaquacobalt(II) bromate and hexaaquanickel(II) bromate, all of which have been reported recently from this laboratory. It is of interest that a tetrahydrated phase crystallized at room temperature from a saturated aqueous copper(II) chlorate solution, whereas a hexahydrated phase crystallized from a saturated aqueous copper(II) bromate solution treated in the same manner.

Introduction. Our interest in a structural study of $[Cu(H_2O)_x](BrO_3)_2$ was greatly stimulated by the finding that the chlorate analogue, when crystallized from a saturated aqueous solution at room temperature, forms a tetrahydrated phase (Blackburn, Gallucci & Gerkin, 1991*a*). A hexahydrated phase had been expected since other divalent transition-metal halates obtained in a similar fashion formed hexahydrated phases and information given about copper(II) halates suggested that a stable hexahydrated phase exists for the chlorate compound as well as for the bromate compound. Thus this study was pursued both to determine which phase of the bromate would be observed, and to determine its structure.

Experimental. Hexaaquacopper(II) bromate crystals were obtained by evaporation at room temperature of a solution formed by the metathetical reaction of aqueous analytical reagent-grade copper(II) sulfate with a slight excess of aqueous barium bromate (Strem chemicals) followed by filtration of the barium sulfate precipitate. A clear light-blue crystal with approximate principal dimensions 0·27 × 0·27 ×

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0·38 mm was selected from a crop of crystals which, although they were of lighter color, appeared to have the same morphology as the tetraaquacopper(II) chlorate crystals. The crystal was mounted with epoxy cement and coated with Apiezon L grease to prevent significant loss or gain of water. The crystal was then analyzed at 296 K with a Rigaku AFC5S diffractometer utilizing graphite-monochromated Mo $K\overline{\alpha}$ radiation.

Unit-cell parameters were obtained from a symmetry-constrained least-squares fit of the setting angles for 25 centered reflections with $25 < 2\theta < 30°$. Intensity data were measured for 1474 reflections (exclusive of standards) having $+h$, $+k$, $+l$ indices ($h_{\max} = 13$, $k_{\max} = 13$, $l_{\max} = 13$) and with 2θ values in the range $4 \leq 2\theta \leq 55°$. The ω–2θ scan technique was employed with scan widths $(1{\cdot}21 + 0{\cdot}35\tan\theta)°$ in ω, and a background/scan time-ratio of 0·5. A variance was assigned to each reflection by means of the formula $\sigma_I^2 = \sigma_{\rm cs}^2(I) + (0{\cdot}03I)^2$, where $\sigma_{\rm cs}$ is based on counting statistics and I is the integrated intensity. Four standard reflections (422, 111, 522 and 264) were measured after every 150 reflections and showed a 13·4% mean growth of intensity during collection. Accordingly, corrections for growth were calculated and applied. The data were corrected for Lorentz and polarization effects. ψ-scan data were obtained just after intensity data collection; the range of transmission factors was 0·608–1·000, with an average value 0·902.

The intensity data were found to have symmetry consistent with Laue group $m3$ and, on the basis of systematic absences, space group $Pa\overline{3}$ (No. 205) but in a non-standard setting. Following index transformation to allow analysis in the standard setting, the Cu atom was placed at the origin with site symmetry $\overline{3}$ while the Br atom was placed in a special position with site symmetry 3. Initial coordinates for these atoms were obtained from a Patterson map. Fourier methods were then used to assign, in general positions, the two inequivalent O atoms and 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 $\sigma_F = \sigma_I/2F{\rm Lp}$. Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for Cu, 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 observed data having $I > 3\sigma_I$, the ψ-scan absorption correction was applied and the data were averaged ($R_{\rm int} = 0{\cdot}077$ for 489 triplets). Then, treating the secondary-extinction coefficient as an adjustable parameter, least-squares refinement proceeded to the anisotropic stage for all atoms except H and to the isotropic stage for the H atoms. One reflection, 040, having $\Delta/\sigma > 10$ was now excluded. Moreover, although the isotropic displacement parameter for H(1) was found to refine, its value was unrealistically small (0·70 Å^2). Accordingly, the B value for H(1) was fixed at 2·90 Å^2, approximately 1·15 times the refined value of the equivalent isotropic displacement parameter for the O atom to which it is bonded. This value is consistent with the values of B for the corresponding H atoms in the isomorphic hexahydrated transition-metal bromates as determined in this laboratory (Blackburn, Gallucci & Gerkin, 1990, 1991*b*).

The results for the final refinement cycle using all (excepting 040) unique reflections with $I > \sigma_I$ were: 336 independent observations, 32 variables, $R = 0{\cdot}038$, $wR = 0{\cdot}037$, $S = 1{\cdot}26$, $(\Delta/\sigma)_{\max} < 0{\cdot}01$. The final refined value of the secondary-extinction coefficient was $1{\cdot}32\,(4) \times 10^{-5}$. Maximum and minimum peaks on the final electron-density difference map had values $+0{\cdot}52$ and $-0{\cdot}69$ e Å^{-3}, respectively. The maximum peak was located at $x = y = z = 0{\cdot}32$, ~1·1 Å from Br; the minimum peak was located at $x = 0{\cdot}56$, $y = 0{\cdot}50$, $z = 0{\cdot}48$, ~0·7 Å from the center of the unit cell but not within 2·0 Å of any atom. [For the final refinement cycle for 277 independent observations with $I > 3\sigma_I$: $R = 0{\cdot}030$, $wR = 0{\cdot}039$, $S = 1{\cdot}47$, $(\Delta/\sigma)_{\max} < 0{\cdot}01$. Similarly, for the 377 independent observations with $I > 0$, $R = 0{\cdot}047$, $wR = 0{\cdot}043$, $S = 1{\cdot}36$, $(\Delta/\sigma)_{\max} < 0{\cdot}01$. These latter two refinements were performed for comparison purposes only.]

The final atomic parameters and their uncertainties are given in Table 1.* Selected interatomic distances and angles in the coordination polyhedron about copper, in the bromate ion and in the water molecule are given in Table 2 together with their uncertainties. Hydrogen bonds involving the water-molecule oxygen and its protons are delineated in Table 4 as discussed below.

Rigid-body analysis of the copper–oxygen complex and the bromate ion was performed using the program *THMA*11 (Trueblood, 1986) based on the work of 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 $11(26) \times 10^{-4}$ Å^2. The average magnitude of the differences in the MSDA

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* Lists of structure factors, anisotropic displacement parameters, supplementary material relating to the rigid-body analysis and a table of known examples of Cu$^{\rm II}$ salts with static structures which are inconsistent with the Jahn–Teller theorem have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54202 (9 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 hexaaquacopper*(II) *bromate at* 296 K

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

	x	y	z	B_{eq}/B*
Cu	0	0	0	1·47 (4)
Br	0·25992 (4)	0·25992	0·25992	1·53 (3)
O(1)	0·1686 (3)	0·1565 (4)	0·3405 (4)	2·6 (2)
O(2)	0·0350 (4)	−0·0299 (4)	0·1960 (4)	2·5 (2)
H(1)	0·053 (6)	0·022 (5)	0·229 (6)	2·9†
H(2)	−0·026 (5)	−0·052 (6)	0·223 (6)	2·7 (15)‡

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

† Fixed (see text).

‡ Refined isotropically.

Table 2. *Bond lengths* (Å) *and angles* (°) *for hexaaquacopper*(II) *bromate at* 296 K

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

	Observed distance	Rigid-body distance		Observed angle
Coordination polyhedron				
Cu—O(2)	2·079 (4)		O(2)—Cu—O(2^{i})	180
O(2)—O(2^{i})	4·158 (8)		O(2)—Cu—O(2^{ii})	90·05 (15)
O(2)—O(2^{ii})	2·942 (7)		O(2)—Cu—O(2^{iii})	89·95 (15)
O(2)—O(2^{iii})	2·939 (7)			
Bromate ion: rigid-body I				
Br—O(1)	1·649 (3)	1·663	O(1)—Br—O(1^{ii})	104·17 (15)
Br—Cu	4·6478 (8)			
Br—Cu^{iv}	4·4144 (3)			
Water molecule				
O(2)—H(1)	0·66 (5)		H(1)—O(2)—H(2)	108 (8)
O(2)—H(2)	0·73 (5)			

Code for symmetry-related atoms: (i) $-x, -y, -z$; (ii) z, x, y; (iii) $-z, -x, -y$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, -z$.

along the interatomic vectors for the four unique atom pairs of the copper–oxygen complex was found to be 81 (31) × 10^{-4} Å^2, while for the Cu—O(2) atom pair alone this difference was 216 (24) × 10^{-4} Å^2. On the basis of these values we concluded that Hirshfeld's (1976) rigid-bond test, as described by Dunitz, Schomaker & Trueblood (1988), is satisfied for the bromate ion but not for the copper–oxygen complex. The corrected bond length for the bromate ion is given in Table 2 but the corrected angle differs from the observed angle by less than its e.s.d. and is therefore not tabulated.

Discussion. This structure is fluorite-like with $Cu(H_2O)_6$ replacing Ca and BrO_3 replacing F. A unit cell of one of its isomorphs, hexaaquacobalt(II) bromate, is shown in a stereoview as their Fig. 1 by Blackburn *et al.* (1990). Substantial hydrogen bonding occurs between the water molecules and the bromate ions.

The typical Cu^{II} sixfold-coordinated complex is a distorted octahedral array displaying '(2 + 2 + 2)' (Gallucci & Gerkin, 1989) coordination about the copper ion: there are three pairs of Cu—ligand distances, two of which are nearly equal while the third is substantially larger. This geometry is consistent with a (static) Jahn–Teller effect. However, in the present structure the copper ion is at a site having symmetry $\bar{3}$ so that the coordination polyhedron has a single Cu—O(2) distance [observed value: 2·079 (4) Å]; moreover, there is only a very slight trigonal distortion of the polyhedron from regular octahedral geometry, the nominal 90° angles measuring 89·95 (15) and 90·05 (15)°.

The occurrence of regular or trigonally distorted octahedral geometry in Cu^{II} coordination polyhedra is not unprecedented, though it is decidely uncommon. The six known cases, including the present work, are given in a table which has been placed in the depository material. The static geometries of these polyhedra are inconsistent with the Jahn–Teller theorem so that they may be expected to conform with it *via* dynamic effects. It may be noted that the tabulated Cu—N distances (2·111–2·150 Å) and Cu—O distances (2·065–2·079 Å) are intermediate to the values of the 'long' and 'short' bonds of the corresponding customary distorted complexes.

Table 3 presents the principal-axis values for the anisotropic displacement ellipsoids of the water-O atoms in the coordination polyhedra of four isomorphic salts including the title salt. Taken together these data strongly suggest the occurrence of a dynamic Jahn–Teller effect in the Cu^{II} salt: while the U values for the copper salt are quite comparable overall with the U values for its three isomorphs, in only the copper salt is the largest principal axis of the ellipsoid directed almost along the cation—O(2) bond;* further in support, that particular major axis is the largest of the four, the effect being most clear-cut in comparisons with the two bromate isomorphs. The coordination polyhedron in hexaaquacopper(II) bromate is shown in Fig. 1.

Strong support for a dynamic Jahn–Teller effect in cases in which the static structure is inconsistent with the Jahn–Teller theorem is afforded by comparison of differences of mean-squared displacement amplitudes along cation–ligand interatomic vectors for Jahn–Teller active and inactive cations as discussed by Bürgi (1984), Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen (1979) and Stebler & Bürgi (1987).

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* As has been discussed previously (see, for example, Cullen & Lingafelter, 1970), one expects that the largest principal axis of the displacement ellipsoid should not be along the cation—O(2) bond direction, but more nearly normal to it; the coincidence of these directions in the present salt thus indicates that it is abnormal, hence that some effect associated particularly with Cu^{II} is involved.

Table 3. *Principal-axis values for the anisotropic displacement ellipsoids* ($\times 10^4$) *of water-*O *atoms,* O(2), *in the coordination polyhedra in a series of isomorphic salts and angles* (°) *specifying the orientation of these ellipsoids with respect to the metal*—O(2) *bond direction*

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

	U_1	U_2	U_3	Angle between largest principal axis of displacement ellipsoid and metal—O(2) bond	Angle between smallest principal axis of displacement ellipsoid and metal—O(2) bond	Primary data source
$[Ni(H_2O)_6](ClO_3)_2$	404 (7)	286 (7)	263 (7)	79	13	Gallucci & Gerkin (1990)
$[Co(H_2O)_6](BrO_3)_2$	341 (14)	250 (14)	224 (14)	75	51	Blackburn *et al.* (1990)
$[Ni(H_2O)_6](BrO_3)_2$	302 (13)	230 (13)	209 (13)	79	28	Blackburn *et al.* (1991*b*)
$[Cu(H_2O)_6](BrO_3)_2$	426 (23)	301 (23)	218 (23)	25	79	This research

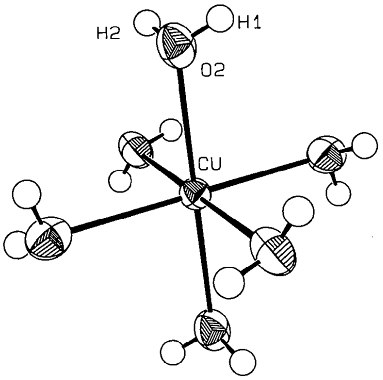

Fig. 1. The coordination polyhedron in hexaaquacopper(II) bromate. Note that the largest principal axis of the anisotropic displacement ellipsoid of O(2) is directed nearly along the Cu—O(2) bond direction. Figure drawn using *ORTEP*II (Johnson, 1976); displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

$\Delta U_{\text{cation—O(2)}}$ values obtained using the *THMA*11 program (Trueblood, 1986) were: for Ni—O(2) in the chlorate, 41 (7) × 10^{-4} Å^2; for Co—O(2) in the bromate, 48 (13) × 10^{-4} Å^2; for Ni—O(2) in the bromate, 38 (12) × 10^{-4} Å^2; but for Cu—O(2) in the present case, 216 (24) × 10^{-4} Å^2.

If, following Ammeter *et al.* (1979), the square of the Jahn–Teller radius, R_{JT}, is written as $R^2_{JT} = \sum^6_{i=1}\langle\Delta d^2_i\rangle_{JT} = \sum^6_{i=1}\langle\Delta d^2_i\rangle_{obsd} - \sum^6_{i=1}\langle\Delta d^2_i\rangle_{res}$ and it is assumed that a reasonable estimate for the residual contribution $\langle\Delta d^2_i\rangle_{res}$ not related to the dynamic Jahn–Teller effect can be obtained by comparison with the corresponding ellipsoids in isostructural salts containing Ni^{II} or Co^{II}, we find $\langle\Delta d^2_i\rangle_{res} \simeq \overline{\Delta U}_{\text{Ni—O(2),Co—O(2)}} = 43\,(9) \times 10^{-4}$ Å^2 [using the data from isomorphic hexaaquanickel(II) chlorate and bromate and hexaaquacobalt(II) bromate cited in the preceding paragraph]. Thus, in the present case, $R^2_{JT} = 6[\Delta U_{\text{Cu—O(2)}} - 43\,(9) \times 10^{-4}$ Å^2]. Evaluation yields $R_{JT} = 0{\cdot}322\,(24)$ Å. This value may be compared with the corresponding mean value for 13 CuN_6 complexes reported by Ammeter *et al.* (1979), $R_{JT} = 0{\cdot}32$ Å. On the other hand, if R_{JT} is evaluated for statically distorted CuO_6 octahedra from $R^2_{JT} = \sum^6_{i=1}\Delta d^2_i$ where $\Delta d_i = d_i - d_o$, and d_o = mean value of Cu—O distance, we find values ranging from 0·265–0·501 Å for the examples cited in their Table 4 by Gallucci & Gerkin (1989). Thus, in contrast to the CuN_6 cases discussed by Ammeter *et al.* (1979), R_{JT} does not appear to be transferable from crystal to crystal for CuO_6 octahedra in the cases cited.

The bromate ion has, by symmetry, a single Br—O(1) distance [observed value: 1·649 (3) Å] and an O(1)—Br—O(1) angle measuring 104·17 (15)°. Although these values are not quite as well determined, they do compare favorably with values recently reported for bromate ions in hexaaquacobalt(II) bromate (Blackburn *et al.*, 1990) and hexaaquanickel(II) bromate (Blackburn *et al.*, 1991*b*): Br—O observed distances 1·653 (2) and 1·655 (2) Å respectively; O—Br—O angles 104·07 (9) and 104·25 (9)° respectively. As in the case of $[Ni(H_2O)_6](BrO_3)_2$, the present study found the bromate ion behaves as a rigid body; the corrected Br—O(1) distance is 1·663 Å. This is in fortuitously good agreement with the value 1·663 Å for the Br—O rigid-body-corrected distance in $[Ni(H_2O)_6](BrO_3)_2$.

The inorganic hydrate class for $[Cu(H_2O)_6](BrO_3)_2$, as well as for its isomorphs, is class *J* (Chiari & Ferraris, 1982; Ferraris & Franchini-Angela, 1972). A detailed analysis and discussion has been given by Blackburn *et al.* (1990) for hydrogen bonding in $[Co(H_2O)_6](BrO_3)_2$; a similar summary has also been given by Blackburn *et al.* (1991*b*) for $[Ni(H_2O)_6](BrO_3)_2$. The treatment here was identical, and apart from slight differences in distances and angles, the hydrogen-bonding situation is identical to that of its isomorphs. As in the isomorphs, three-center/bifurcated hydrogen bonding (Jeffrey & Maluszynska, 1986) is found. Table 4 specifies all the distances and angles needed to describe the hydrogen bonding for the present structure.

Table 4. *Hydrogen-bond parameters* (Å, °) *for hexaaquacopper*(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^{v})	2·766 (6)	H(2)—O(1^{v})	2·07 (6)	1·84	O(2)—H(2)—O(1^{v})	160 (6)
O(2)—O(1)	2·798 (5)	H(1)—O(1)	2·16 (5)	1·87	O(2)—H(1)—O(1)	162 (7)
O(2)—O(2^{iii})	2·939 (7)	H(2)—O(2^{iii})	2·66 (6)	2·61	O(2)—H(2)—O(2^{iii})	105 (5)
O(2)—O(2^{vi})	2·942 (7)	H(1)—O(2^{vi})	2·83 (6)	2·83	O(2)—H(1)—O(2^{vi})	93 (5)
O(2)—O(1^{vii})	3·248 (6)	H(1)—O(1^{vii})	2·92 (6)	2·81	O(2)—H(1)—O1^{vii})	114 (6)
		H(2)—O(1^{vii})	2·94 (6)	2·87	O(2)—H(2)—O(1^{vii})	109 (5)

Code for symmetry-related atoms: (iii) $-z, -x, -y$; (v) $-y, -\frac{1}{2}+z, \frac{1}{2}-x$; (vi) y, z, x; (vii) $-\frac{1}{2}+z, x, \frac{1}{2}-y$.

At the conclusion of this study, we became aware of a powder-diffraction study of the title salt by Weigel (1963), who reported the value 10·30 Å for the cell edge, and who also reported, in agreement with our previous results, that only the tetrahydrate crystallized from an aqueous copper(II) chlorate solution.

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Structure du Tétraiodure de Cuivre(I) et de Bismuth(III), $CuBiI_4$

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Abstract. $M_r = 780{\cdot}1446$, cubic, $Fd\bar{3}m$, $a = 12{\cdot}134\ (6)$ Å, $V = 1786\ (2)$ Å^3, $Z = 8$, $D_m(293\ \text{K}) = 5{\cdot}7\ (1)$, $D_x = 5{\cdot}801\ (1)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 35$ mm^{-1}, $F(000) = 2568$, $T = 293$ K, $R = 0{\cdot}041$ for 132 independent reflections. The structure is characterized by an octahedral stacking of I atoms. Each I atom is surrounded by three Bi atoms and eight Cu atoms. The sites of Bi atoms are half occupied. The sites of Cu atoms have an occupancy rate of 0·09 to 0·18.

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