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# The Bihalide Ions $ClHCl^-$ and $BrHBr^-$: Crystal Structures of Cesium Chloride–$^1/_3$-(Hydronium Bichloride) and Cesium Bromide–$^1/_3$-(Hydronium Bibromide)

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The compositions and crystal structures of the unusual substances cesium chloride–$^1/_3$-(hydronium bichloride), $CsCl\cdot{}^1/_3H_3OHCl_2$, and cesium bromide–$^1/_3$-(hydronium bibromide), $CsBr\cdot{}^1/_3H_3OHBr_2$, have been established from three-dimensional X-ray studies of single crystals of these materials. The conventional $R$ factors for the data collected by film methods are 0.093 and 0.085, respectively. Both substances crystallize in space group $P6_3/m$ of the hexagonal system with six formula units per cell. At room temperature the lattice parameters for the chloride complex are $a = 10.28 \pm 0.02$, $c = 6.78 \pm 0.02$ Å; those for the bromide complex are $a = 10.65 \pm 0.02$, $c = 7.08 \pm 0.02$ Å. Both compounds have strings of hydronium ions parallel to the $c$ axis. Cesium is coordinated to nine halide ions which are all involved in hydrogen bonds. A string of bichloride ions is parallel to the $c$ axis in $CsCl\cdot{}^1/_3H_3OHCl_2$ as is a string of bibromide ions in the bromine compound. The bichloride ion has a Cl–H–Cl distance of $3.14 \pm 0.02$ Å; the corresponding distance in the bibromide ion is $3.35 \pm 0.02$ Å.

## Introduction

The precipitate formed when HCl is bubbled through a saturated CsCl solution has been the subject of some dispute.[1–3] In a preliminary report[4] we showed that at least one of the substances that is formed in this reaction, namely $CsCl\cdot{}^1/_3H_3OHCl_2$, differs from those proposed previously. Although our preliminary objective in studying the system was to attempt to resolve through a complete structure determination the composition and crystal structure of the precipitate, we were delighted that the resultant material did indeed contain the bichloride ion, for its geometry had not been determined previously. The bihalide ions, $X–H–X^-$, in many ways represent the simplest of the strongly hydrogen-bonded systems, and these are amenable to study by a variety of methods. (See, for example, the discussion of the bifluoride ion in ref 5 and 6.) Previous investigations[7] have indicated that the bibromide ion is somewhat less stable than the bichloride ion. Nevertheless we have successfully prepared the analogous bromide compound $CsBr\cdot{}^1/_3H_3OHBr_2$ by passing HBr through a solution of CsBr. In this paper we report the details of our preparation and characterization of these two compounds.

## Experimental Section

**$CsCl\cdot{}^1/_3H_3OHCl_2$.**—West's[1] initial preparation was followed: 2 g of cesium chloride was dissolved in 1.5 ml of water. Commercial anhydrous HCl was bubbled through the solution until a white, needlelike crystalline material precipitated. West reported that his material was stable at room temperature, but only in the presence of the mother liquor or HCl gas. Our material exhibits similar behavior.

Consequently, all operations upon the crystal had to be carried out in the mother liquor or in the presence of HCl. This was accomplished by use of a glass tee having an inlet and an outlet for HCl gas and a connection for the X-ray capillary tube. The outlet opposite the capillary tube was fitted with a rubber cap through which a small glass rod could be inserted to push a crystal into the capillary. A drop of mother liquor, containing a few crystals, was quickly put into the glass tee. The system was then closed and HCl was allowed to flow through the apparatus. Since the tee was transparent, the crystal could be viewed through a microscope. A suitable crystal was pushed out of the drop of the mother liquor and into the capillary. Then the capillary was sealed off. Thus at all times the crystal was either in contact with the mother liquor or HCl gas. Under these conditions no decomposition of the crystal occurred.

Weissenberg and precession photographs, taken with Mo K$\alpha$ radiation ($\lambda$ 0.7107 Å), showed $CsCl\cdot{}^1/_3H_3OHCl_2$ to have Laue symmetry 6/m. The hexagonal lattice constants determined from precession photographs are $a = 10.28 \pm 0.02$ and $c = 6.78 \pm 0.02$ Å at room temperature. The unit cell volume is 620 Å$^3$ and the calculated density is 3.19 g/cm$^3$ for six formula units per cell. The material's instability prevented a measurement of its density. The only systematic absences observed are for $00l$ when $l \neq 2n$; thus the most probable space groups are $P6_3/m$ and $P6_3$.

Intensity data were collected at room temperature by the equiinclination Weissenberg technique for successive layers $hk0$ through $hk8$ using Mo K$\alpha$ radiation and multiple films. The 500 independent integrated intensities were estimated visually against a calibrated strip. The intensities were reduced to values of $F_o^2$ in the usual way.

The crystal was irregularly shaped and its approximate dimensions were $0.95 \times 0.20 \times 0.25$ mm. After the composition of the material was determined from the structure, an absorption coefficient was computed ($\mu = 99.1$ cm$^{-1}$). An absorption correction was applied to $F_o^2$ by integration over the six idealized crystal faces (010), (100), (001), etc.[8] The correction is necessarily approximate owing to the difficulty of measuring an irregularly shaped crystal which is inside a capillary tube.

One previous preparation yielded crystals that proved later to be orthorhombic (see ref 1). Weissenberg photographs indicated that for a general reflection, $hkl$, $k + l = 2n$ and for $h0l$, both $h$ and $l$ must be even. Thus the possible space groups are Amam (Cmcm, setting $\bar{c}$ba) and Ama2. The unit cell parameters at room temperature are $a = 5.98 \pm 0.02$, $b = 23.37 \pm$

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(1) R. W. West, *J. Am. Chem. Soc.*, **79**, 4568 (1957).

(2) R. E. Valleé and D. H. McDaniel, *ibid.*, **84**, 3412 (1962).

(3) A. G. Maki and R. W. West, *Inorg. Chem.*, **2**, 657 (1963).

(4) L. W. Schroeder and J. A. Ibers, *J. Am. Chem. Soc.*, **88**, 2601 (1966).

(5) R. Blinc, *Nature*, **182**, 1016 (1958).

(6) B. L. McGaw and J. A. Ibers, *J. Chem. Phys.*, **39**, 2677 (1963).

(7) R. E. Valleé and D. H. McDaniel, *Inorg. Chem.*, **2**, 996 (1963).

(8) Absorption corrections were made using the program WABS, based on Burnham's GNABS. In addition to various local programs, local variations of Zalkin's FORDAP Fourier program, the Busing–Levy ORFLS least-squares program and ORFEE error function program, and Johnson's ORTEP thermal ellipsoid plotting program were used.

0.01, and $c = 8.42 \pm 0.02$ Å. This gives a unit cell volume of 1177 Å$^3$.

The volume per Cl in CsCl is 70 Å$^3$ and in the hexagonal compound 62 Å$^3$. $CsCl \cdot {}^3/_4H_3OCl$ could crystallize in Ama2 with eight formula units per cell. This gives a volume of 77 Å$^3$ per Cl. The volume per Cs is then 146 Å$^3$ compared with 104 Å$^3$ in the hexagonal form and 70 Å$^3$ in CsCl. It seems likely that the orthorhombic crystals contain relatively less Cs than the hexagonal ones. Thus the orthorhombic crystals could have the composition $CsCl \cdot {}^3/_4H_3OCl$ previously proposed,[2,3] especially since West[1] provided evidence that his material belonged to the orthorhombic system.

We were not able to confirm this hypothesis because subsequent attempts to prepare this material failed, and the original crystals decomposed.

**$CsBr \cdot {}^1/_3H_3OHBr_2$.**—One gram of CsBr was dissolved in 1 ml of water. Anhydrous HBr was bubbled through the solution until CsBr precipitated. Adding more HBr caused the CsBr to redissolve, indicating some type of complex formation. Finally after the addition of still more HBr a needlelike crystalline material precipitated that subsequent study proved to be $CsBr \cdot {}^1/_3H_3OHBr_2$. $CsBr \cdot {}^1/_3H_3OHBr_2$ was handled in the manner previously described for the chlorine compound.

Weissenberg and precession photographs taken with Mo K$\alpha$ radiation gave diffraction patterns resembling those of cesium chloride–${}^1/_3$-(hydronium bichloride). The same space group and a similar structure were indicated. The hexagonal cell parameters that were determined from precession photographs at room temperature are $a = 10.65 \pm 0.02$ and $c = 7.08 \pm 0.02$ Å. The unit cell volume is 697 Å$^3$ and the calculated density is 3.51 g/cm$^3$ for six formula units per cell. A density could not be measured because of the instability of the material.

A crystal, approximately cylindrical, with a length of 0.30 mm and an average radius of 0.068 mm was used for collecting data. Intensities were recorded by the equiinclination Weissenberg technique for successive layers $hk0$ through $hk2$ with Mo K$\alpha$ radiation and multiple films. At this point the data collection was terminated because of decomposition of the crystal. A total of 128 independent, integrated reflections were estimated visually using a calibrated strip. Equiinclination Lorentz and polarization factors were applied to the average intensities. After confirmation of the proposed composition, the absorption coefficient was calculated to be 199 cm$^{-1}$. An absorption correction was applied by approximating the cylinder as an eight-faced prism consisting of the faces of the type (001), (110), and (011).

From the incomplete Weissenberg data set we established that the hypothesized composition was correct and that the material did contain the bibromide ion. We therefore decided to collect additional data to improve our description of the ion. Since the bromines involved have only a variable $z$ parameter, reflections with large values of $l$ are most helpful in fixing the value of $z$ more accurately. Since $CsBr \cdot {}^1/_3H_3OHBr_2$ does not appear to be especially stable, we chose to collect reflections with high values of $l$ by the precession method.

A second crystal was mounted on a precession camera with $c^*$ along the spindle axis. The reciprocal lattice nets $h0l$, $h1l$, $0kl$, $1kl$, $h2hl$, and $2hhl$ were collected. A series of timed exposures was used to simulate the multiple film technique. Intensities were estimated by comparison with a calibrated strip. Lorentz-polarization factors were applied to obtain values of $kF_o^2$. Although the crystal was a plate of dimensions 0.15 × 0.25 × 0.30 mm, we could not use Buerger's[9] correction for absorption by a plate parallel to the reciprocal lattice plane because the crystal did not intercept the entire X-ray beam.

We know absorption is important ($\mu = 199$ cm$^{-1}$), but it is difficult to estimate the error involved in neglecting the absorption correction because the crystal was a plate. The only reliable way would be to calculate transmission factors by methods designed for any crystal shape. However, when the Weissenberg and precession data were combined good agreement between the new scale factors and those previously derived by least-squares refinement was obtained. Since the Weissenberg data were corrected for absorption, this indicated that the absorption correction was relatively constant for a given layer of precession data.

## Solution and Refinement of the Structures

**Cesium Chloride–${}^1/_3$-(Hydronium Bichloride).**—The peaks corresponding to vectors between Cs positions were readily located on a three-dimensional Patterson map and found to have a $z$ coordinate of 0 or ${}^1/_2$. From the previous formulations and the unit cell volume (620 Å$^3$) a reasonable density could be calculated if there were four or six formula units in the unit cell. On the assumption of six formula units these Cs peaks are readily explicable if Cs is in (6h) of P6$_3$/m or in (6c) of P6$_3$. P6$_3$/m was assumed to be the correct space group.

Least-squares refinement on Cs with a separate scale factor for each layer and an isotropic thermal parameter gave a value of 0.27 for $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. In all calculations of $F_c$, the atomic scattering factor for Cs was that of Cromer and Waber.[10] The effects of anomalous dispersion were included in $F_c$; the values of $f'$ and $f''$ for Cs, Cl, and Br are those given by Cromer.[11]

The structure was solved by a succession of least squares and Fourier calculations. The signs of the calculated structure factors for cesium were used with the observed structure factors to calculate a difference Fourier map. In this manner chlorine atoms Cl$_1$ and Cl$_2$ were located in the six- and fourfold positions (6h) and (4f) of P6$_3$/m. The ratio of chlorine to cesium is thus 5/3. A difference Fourier map computed at this point showed, as its only significant feature, a large peak (11 e/Å$^3$) at position (4e) $00z$, with $z$ approximately ${}^1/_8$. This position is equidistant from three Cl$_1$ atoms, at the apex of a relatively flat pyramid. Such a position is expected for the hydronium ion $H_3O^+$ entering into three O–H–Cl bonds as in $H_3OCl$.[12] Yet in P6$_3$/m an atom at $00z$ is related by symmetry to an atom at $00{}^1/_2 - z$ leading to an O–O distance of 1.8 Å. Since adjacent sites cannot be occupied simultaneously, the effective occupancy is equivalent to 0.5 oxygen atom in (4e). This matter is discussed more fully in the next section. The values of $R_1$ and $R_2 = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$ [13] that had been 0.17 and 0.26 dropped to 0.14 and 0.21 with the inclusion of the half-oxygen.[14]

By now the composition of the material had been established as Cs:Cl:O = 3:5:1. Moreover, the presence of $H_3O^+$ was inferred from the stereochemistry. Charge balance is maintained by the formulation $CsCl \cdot {}^1/_3H_3O^+ \cdot {}^1/_3H^+ \cdot {}^2/_3Cl^-$. The implication that this compound contains the bichloride ion $HCl_2^-$ is supported by the fact that one of the Cl$_2$–Cl$_2$

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[9] M. J. Buerger, "The Precession Method in X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1964, p 224.

[10] D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

[11] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[12] Y. K. Yoon and G. B. Carpenter, *ibid.*, **12**, 17 (1959).

[13] The weighting scheme employed was $w = (10I_{\min})^2/F_o$ for $I > 10I_{\min}$, and $w = I^2/F_o^2$ for $I < 10I_{\min}$.

[14] Scattering factors for Br, Cl, and O from "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

distances is appreciably shorter than a van der Waals interaction. These facts confirm that the compound is $CsCl \cdot {}^1/_3H_3OHCl_2$. An absorption coefficient was calculated to be $\mu = 99.1$ cm$^{-1}$. This was applied to $F_o^2$ with the assumptions given in the Experimental Section. Subsequent least-squares refinement using the corrected data gave $R_1 = 0.093$ and $R_2 = 0.10$. A final difference Fourier map showed no features higher than 3 e/Å$^3$, one-quarter the height of a half-oxygen, and provided some evidence for anisotropy in the cesium position. Because the absorption correction was only approximate and the data could only be collected about one axis, we felt that any anisotropic thermal parameters that could have been obtained would reflect systematic errors in our data rather than physical reality. Thus the calculations were terminated with isotropic refinement.

**Nature of the Disorder.**—Since the adjacent oxygen sites (4e) of P6$_3$/m are separated by 1.8 Å, they cannot both be occupied simultaneously. Thus any given string of hydronium ions must be ordered, but all the strings do not have their ordered oxygen atoms starting at the same value of $z$. Suppose that a given string of hydronium ions has all oxygen atoms below the planes of the three chlorine atoms and assume further that this string exerts no influence on adjacent strings. Then there is a 50% chance that a surrounding string will have its oxygen atoms above the planes of the three chlorine atoms. Thus the overall scattering from the oxygen atoms is equivalent to that scattered by placing half-oxygen atoms in positions (4e) of P6$_3$/m.

A completely ordered structure is allowed in space group P6$_3$. One puts Cs into (6c) with $z_{Cs} = {}^1/_4$ (to fix the origin), Cl$_1$ into (6c), and O into (2a). The Cl$_2$ atom must now be distributed over two sets of positions (2b). It follows that the $z$ coordinates of these two independent atoms must sum approximately to ${}^1/_2$, since this condition holds rigorously in P6$_3$/m. In order to test the possibility that the space group is P6$_3$ and the oxygen atoms are ordered, several refinements were carried out in P6$_3$. Initial values of the parameters were chosen near to those found in P6$_3$/m. The refinement converged to a value of $R_2$ of 0.11. It was found that the $z$ parameters of the two Cl$_2$ atoms did indeed sum to ${}^1/_2$, within the standard deviations of the parameters, even though this is not required by the space group. In an additional refinement the condition was imposed that these parameters sum exactly to ${}^1/_2$, but the refinement led to essentially the same results. In a final refinement this condition was relaxed and it was assumed that $hkl$ was really $\bar{h}\bar{k}\bar{l}$ in order to test the possibility that in this polar space group we had the wrong absolute orientation. The results were the same as before. All of these refinements involve additional parameters over those varied in P6$_3$/m and yet they all lead to higher values of $R_2$. If one assumes that there are only random errors in the data, then these refinements in P6$_3$ can be rejected in favor of the refinement in P6$_3$/m. For this reason we favor the description of the structure in P6$_3$/m. Of greater importance structurally, these refinements lead to essentially the same parameter values as found for the model in P6$_3$/m, with the exception that the value of $z$ of Cl$_1$ is 0.265 (3), rather than ${}^1/_4$. The bichloride ion geometry is invariant within one standard deviation to the choice of space group.

**Cesium Bromide–${}^1/_3$-(Hydronium Bibromide).**—The 128 reflections were used to see if the structure corresponded to that of $CsCl \cdot {}^1/_3H_3OHCl_2$, as suggested by the diffraction patterns. We chose for our structural model the $CsCl \cdot {}^1/_3H_3OHCl_2$ structure with chlorine replaced by bromine. Least-squares refinement on Cs in the same position as in the chlorine compound yielded a value of $R_1 = 0.39$ with very small parameter shifts. The inclusion of bromines and the half-oxygen gave $R_1 = 0.098$. The weighting scheme used was $w = (7I_{\min})^2/F^2$ for $I > 7I_{\min}$ and $w = I_o^2/F^2$ for $I < 7I_{\min}$.

Little difference was observed in the agreement between observed and calculated structure factors when an absorption correction was applied. The absorption factor was about the same for all reflections with a range of 0.14 to 0.16 corresponding to a 12% variation. A difference Fourier map was computed in order to check for completeness of the structure. There were no peaks higher than 2.8 e/Å$^3$, one-half the height of the half-oxygen, and none where hydrogen would be expected. With the composition and structure of $CsBr \cdot {}^1/_3H_3OHBr_2$ established we proceeded to improve our description of the structure by adding the precession data to the observed structure factors. The precession data agreed with the model determined from the Weissenberg data.

The Weissenberg and precession data were combined and scaled to approximately absolute scale by using the scale factors for the separate layers derived from previous least-squares refinement. Then the data were interscaled and averaged using the Hamilton–Rollett–Sparks scaling algorithm.[15] In the process all observations of a given reflection and all equivalent reflections were used to form a weighted average. The weighting scheme was made equivalent to the previously described scheme used in the structure refinement. This produced 204 independent reflections.

Least-squares refinement of the merged data, using isotropic temperature factors, resulted in values of $R_1$ and $R_2$ equal to 0.093 and 0.12. The scale factor changed from unity to 1.02. At this point the temperature factor of oxygen was slightly negative.

A refinement in P6$_3$ under the same conditions as described for the chlorine compound also gave a negative temperature factor for oxygen and the value 0.12 for $R_2$. All positional parameters except $z$ of Br$_1$ were equal (within $\sigma$) to those derived by refinement in P6$_3$/m. Since refinement in P6$_3$ with three more variables does not result in better agreement between observed and calculated structure factors it seems

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(15) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, **18**, 129 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES IN ELECTRONS FOR $CsX \cdot {}^1/_3H_3OHX_2$

**X = Cl**

| H | K | OBS | CAL |
|---|---|---|---|
| *****L=0***** | | | |
| 5 | 0 | 131 | 145 |
| 6 | 0 | 58 | 60 |
| 7 | 0 | 20 | 4 |
| 8 | 0 | 105 | 117 |
| 9 | 0 | 24 | 16 |
| 10 | 0 | 28 | 22 |
| 11 | 0 | 43 | 44 |
| 12 | 0 | 16 | 8 |
| 13 | 0 | 19 | 19 |
| 4 | -1 | 63 | 59 |
| 6 | -1 | 15 | 16 |
| 7 | -1 | 80 | 78 |
| 8 | -1 | 75 | 72 |
| 10 | -1 | 45 | 46 |
| 11 | -1 | 60 | 62 |
| 14 | -1 | 19 | 26 |
| 3 | -2 | 74 | 71 |
| 4 | -2 | 50 | 44 |
| 5 | -2 | 28 | 27 |
| 6 | -2 | 108 | 108 |
| 8 | -2 | 30 | 23 |
| 9 | -2 | 67 | 71 |
| 11 | -2 | 34 | 37 |
| 12 | -2 | 35 | 30 |
| 4 | -3 | 79 | 79 |
| 5 | -3 | 127 | 115 |
| 6 | -3 | 112 | 107 |
| 7 | -3 | 18 | 17 |
| 8 | -3 | 124 | 134 |
| 10 | -3 | 32 | 31 |
| 11 | -3 | 62 | 72 |
| 12 | -3 | 17 | 16 |
| 13 | -3 | 38 | 37 |
| 14 | -3 | 18 | 13 |
| 5 | -4 | 32 | 31 |
| 6 | -4 | 66 | 61 |
| 7 | -4 | 49 | 48 |
| 8 | -4 | 22 | 20 |
| 9 | -4 | 43 | 38 |
| 10 | -4 | 52 | 53 |
| 11 | -4 | 39 | 36 |
| 12 | -4 | 23 | 20 |
| 13 | -4 | 24 | 24 |
| 14 | -4 | 18 | 18 |
| 6 | -5 | 69 | 75 |
| 7 | -5 | 54 | 53 |
| 8 | -5 | 74 | 71 |
| 9 | -5 | 65 | 66 |
| 10 | -5 | 52 | 55 |
| 12 | -5 | 20 | 19 |
| 13 | -5 | 27 | 30 |
| 14 | -5 | 25 | 27 |
| 7 | -6 | 65 | 71 |
| 8 | -6 | 77 | 70 |
| 11 | -6 | 53 | 53 |
| 12 | -6 | 26 | 23 |
| 13 | -6 | 21 | 30 |
| 8 | -7 | 14 | 13 |
| 9 | -7 | 68 | 61 |
| 10 | -7 | 25 | 20 |
| 13 | -7 | 27 | 29 |
| 9 | -8 | 48 | 48 |
| 10 | -8 | 85 | 85 |
| 11 | -8 | 41 | 42 |
| 10 | -9 | 42 | 41 |
| 11 | -9 | 17 | 13 |
| 11 | -10 | 17 | 18 |
| 12 | -10 | 17 | 19 |
| 14 | -10 | 25 | 16 |
| 12 | -11 | 18 | 18 |
| 13 | -11 | 51 | 55 |
| 13 | -12 | 19 | 19 |
| 14 | -13 | 19 | 14 |
| *****L=1***** | | | |
| 6 | 0 | 29 | 27 |
| 7 | 0 | 44 | 45 |
| 9 | 0 | 46 | 41 |
| 12 | 0 | 33 | 32 |
| 3 | -1 | 102 | 109 |
| 4 | -1 | 117 | 138 |
| 5 | -1 | 82 | 77 |
| 6 | -1 | 60 | 53 |
| 7 | -1 | 103 | 111 |
| 8 | -1 | 19 | 9 |
| 9 | -1 | 18 | 18 |
| 10 | -1 | 53 | 45 |
| 11 | -1 | 24 | 9 |
| 12 | -1 | 32 | 34 |
| 3 | -2 | 130 | 158 |
| 4 | -2 | 112 | 125 |
| 5 | -2 | 89 | 81 |
| 6 | -2 | 144 | 165 |
| 7 | -2 | 45 | 41 |
| 8 | -2 | 27 | 21 |
| 9 | -2 | 93 | 89 |
| 10 | -2 | 19 | 16 |
| 11 | -2 | 39 | 36 |
| 12 | -2 | 22 | 21 |
| 13 | -2 | 23 | 23 |
| 14 | -2 | 40 | 36 |
| 4 | -3 | 86 | 104 |
| 5 | -3 | 53 | 49 |
| 6 | -3 | 43 | 41 |
| 7 | -3 | 34 | 28 |
| 8 | -3 | 18 | 11 |
| 9 | -3 | 34 | 31 |
| 10 | -3 | 13 | 7 |
| 5 | -4 | 68 | 64 |
| 6 | -4 | 99 | 100 |
| 7 | -4 | 109 | 115 |
| 8 | -4 | 12 | 14 |
| 10 | -4 | 76 | 78 |
| 11 | -4 | 34 | 30 |
| 12 | -4 | 40 | 39 |
| 13 | -4 | 28 | 26 |
| 14 | -4 | 16 | 10 |
| 15 | -4 | 30 | 32 |
| 6 | -5 | 109 | 132 |
| 7 | -5 | 59 | 58 |
| 9 | -5 | 94 | 103 |
| 10 | -5 | 24 | 20 |
| 11 | -5 | 37 | 36 |
| 12 | -5 | 45 | 45 |
| 14 | -5 | 44 | 46 |
| 15 | -5 | 16 | 9 |
| 7 | -6 | 86 | 92 |
| 8 | -6 | 18 | 11 |
| 9 | -6 | 75 | 73 |
| 10 | -6 | 34 | 28 |
| 12 | -6 | 50 | 51 |
| 13 | -6 | 15 | 9 |
| 15 | -6 | 16 | 14 |
| 8 | -7 | 30 | 27 |
| 9 | -7 | 41 | 37 |
| 10 | -7 | 58 | 58 |
| 11 | -7 | 57 | 56 |
| 12 | -7 | 20 | 20 |
| 13 | -7 | 28 | 28 |
| 14 | -7 | 30 | 30 |
| 15 | -7 | 31 | 28 |
| 9 | -8 | 38 | 35 |
| 12 | -8 | 25 | 28 |
| 14 | -8 | 26 | 23 |
| 15 | -8 | 16 | 12 |
| 10 | -9 | 39 | 31 |
| 11 | -9 | 15 | 17 |
| 12 | -9 | 60 | 60 |
| 15 | -9 | 31 | 32 |
| 11 | -10 | 54 | 52 |
| 14 | -10 | 50 | 44 |
| 12 | -11 | 16 | 16 |
| 14 | -12 | 32 | 11 |
| *****L=2***** | | | |
| 3 | 0 | 114 | 166 |
| 5 | 0 | 141 | 152 |
| 7 | 0 | 17 | 19 |
| 8 | 0 | 108 | 121 |
| 9 | 0 | 48 | 46 |
| 10 | 0 | 32 | 30 |
| 11 | 0 | 45 | 48 |
| 12 | 0 | 21 | 23 |
| 13 | 0 | 22 | 22 |
| 3 | -1 | 48 | 36 |
| 4 | -1 | 31 | 28 |
| 5 | -1 | 65 | 64 |
| 6 | -1 | 35 | 34 |
| 7 | -1 | 52 | 56 |
| 8 | -1 | 32 | 26 |
| 9 | -1 | 15 | 14 |
| 10 | -1 | 38 | 33 |
| 11 | -1 | 40 | 36 |
| 3 | -2 | 32 | 30 |
| 4 | -2 | 131 | 124 |
| 5 | -2 | 52 | 48 |
| 6 | -2 | 81 | 78 |
| 7 | -2 | 52 | 48 |
| 9 | -2 | 57 | 53 |
| 10 | -2 | 22 | 24 |
| 11 | -2 | 28 | 26 |
| 12 | -2 | 25 | 21 |
| 13 | -2 | 18 | 18 |
| 14 | -2 | 18 | 18 |
| 4 | -3 | 43 | 45 |
| 5 | -3 | 115 | 127 |
| 6 | -3 | 41 | 35 |
| 8 | -3 | 120 | 139 |
| 9 | -3 | 45 | 43 |
| 10 | -3 | 41 | 40 |
| 11 | -3 | 67 | 76 |
| 12 | -3 | 34 | 36 |
| 13 | -3 | 38 | 41 |
| 14 | -3 | 18 | 17 |
| 5 | -4 | 94 | 98 |
| 6 | -4 | 44 | 35 |
| 7 | -4 | 29 | 27 |
| 8 | -4 | 26 | 27 |
| 9 | -4 | 26 | 22 |
| 10 | -4 | 38 | 38 |
| 12 | -4 | 12 | 11 |
| 13 | -4 | 12 | 16 |
| 6 | -5 | 48 | 49 |
| 8 | -5 | 75 | 81 |
| 9 | -5 | 50 | 48 |
| 10 | -5 | 17 | 18 |
| 12 | -5 | 11 | 10 |
| 13 | -5 | 12 | 10 |
| 14 | -5 | 18 | 20 |
| 7 | -6 | 50 | 49 |
| 8 | -6 | 79 | 79 |
| 9 | -6 | 49 | 44 |
| 11 | -6 | 57 | 59 |
| 12 | -6 | 42 | 44 |
| 13 | -6 | 30 | 35 |
| 14 | -6 | 17 | 18 |
| 15 | -6 | 13 | 17 |
| 8 | -7 | 53 | 52 |
| 9 | -7 | 44 | 44 |
| 11 | -7 | 30 | 30 |
| 12 | -7 | 26 | 20 |
| 13 | -7 | 19 | 20 |
| 14 | -7 | 15 | 16 |
| 9 | -8 | 35 | 33 |
| 10 | -8 | 46 | 49 |
| 11 | -8 | 48 | 48 |
| 13 | -8 | 38 | 38 |
| 15 | -8 | 18 | 19 |
| 10 | -9 | 33 | 29 |
| 11 | -9 | 19 | 21 |
| 12 | -9 | 39 | 39 |
| 13 | -9 | 12 | 6 |
| 15 | -9 | 18 | 21 |
| 11 | -10 | 39 | 38 |
| 12 | -10 | 12 | 11 |
| 14 | -10 | 27 | 28 |
| 14 | -11 | 13 | 8 |
| 13 | -12 | 13 | 13 |
| *****L=3***** | | | |
| 4 | 0 | 52 | 53 |
| 5 | 0 | 9 | 7 |
| 6 | 0 | 30 | 23 |
| 7 | 0 | 47 | 45 |
| 8 | 0 | 12 | 7 |
| 9 | 0 | 35 | 35 |
| 10 | 0 | 14 | 15 |
| 12 | 0 | 33 | 29 |
| 2 | -1 | 104 | 130 |
| 3 | -1 | 105 | 95 |
| 4 | -1 | 128 | 123 |
| 5 | -1 | 67 | 64 |
| 6 | -1 | 58 | 53 |
| 7 | -1 | 91 | 103 |
| 10 | -1 | 55 | 44 |
| 11 | -1 | 15 | 8 |
| 12 | -1 | 24 | 27 |
| 3 | -2 | 104 | 106 |
| 4 | -2 | 105 | 102 |
| 5 | -2 | 57 | 54 |
| 6 | -2 | 124 | 128 |
| 7 | -2 | 38 | 35 |
| 8 | -2 | 12 | 11 |
| 9 | -2 | 65 | 71 |
| 10 | -2 | 19 | 14 |
| 11 | -2 | 37 | 35 |
| 4 | -3 | 73 | 71 |
| 5 | -3 | 59 | 49 |
| 6 | -3 | 41 | 33 |
| 7 | -3 | 19 | 15 |
| 8 | -3 | 18 | 16 |
| 9 | -3 | 31 | 27 |
| 5 | -4 | 55 | 53 |
| 6 | -4 | 90 | 92 |
| 7 | -4 | 94 | 106 |
| 8 | -4 | 11 | 12 |
| 9 | -4 | 12 | 12 |
| 10 | -4 | 66 | 73 |
| 11 | -4 | 25 | 26 |
| 12 | -4 | 30 | 31 |
| 6 | -5 | 98 | 101 |
| 7 | -5 | 52 | 49 |
| 9 | -5 | 77 | 82 |
| 10 | -5 | 13 | 18 |
| 11 | -5 | 37 | 35 |
| 12 | -5 | 28 | 36 |
| 14 | -5 | 34 | 41 |
| 7 | -6 | 71 | 71 |
| 8 | -6 | 19 | 16 |
| 9 | -6 | 59 | 62 |
| 10 | -6 | 13 | 19 |
| 12 | -6 | 37 | 45 |
| 8 | -7 | 22 | 24 |
| 9 | -7 | 36 | 38 |
| 10 | -7 | 59 | 56 |
| 11 | -7 | 47 | 48 |
| 12 | -7 | 14 | 13 |
| 13 | -7 | 25 | 27 |
| 14 | -7 | 23 | 27 |
| 15 | -7 | 22 | 23 |
| 9 | -8 | 27 | 25 |
| 10 | -8 | 13 | 11 |
| 11 | -8 | 14 | 14 |
| 12 | -8 | 20 | 21 |
| 14 | -8 | 24 | 22 |
| 10 | -9 | 23 | 23 |
| 12 | -9 | 56 | 53 |
| 11 | -10 | 48 | 46 |
| 14 | -10 | 42 | 39 |
| 12 | -11 | 19 | 17 |
| *****L=4***** | | | |
| 3 | 0 | 131 | 168 |
| 4 | 0 | 38 | 34 |
| 5 | 0 | 84 | 94 |
| 6 | 0 | 38 | 33 |
| 8 | 0 | 71 | 83 |
| 9 | 0 | 18 | 18 |
| 10 | 0 | 19 | 14 |
| 11 | 0 | 34 | 31 |
| 2 | -1 | 100 | 82 |
| 4 | -1 | 58 | 50 |
| 7 | -1 | 61 | 62 |
| 8 | -1 | 54 | 46 |
| 10 | -1 | 40 | 37 |
| 11 | -1 | 44 | 43 |
| 3 | -2 | 61 | 52 |
| 4 | -2 | 53 | 45 |
| 5 | -2 | 13 | 12 |
| 6 | -2 | 79 | 83 |
| 8 | -2 | 21 | 22 |
| 9 | -2 | 58 | 56 |
| 11 | -2 | 30 | 31 |
| 12 | -2 | 25 | 25 |
| 4 | -3 | 65 | 62 |
| 5 | -3 | 76 | 72 |
| 6 | -3 | 69 | 63 |
| 7 | -3 | 17 | 18 |
| 8 | -3 | 88 | 93 |
| 9 | -3 | 12 | 11 |
| 10 | -3 | 18 | 20 |
| 11 | -3 | 45 | 52 |
| 12 | -3 | 20 | 16 |
| 13 | -3 | 23 | 27 |
| 5 | -4 | 36 | 35 |
| 6 | -4 | 49 | 40 |
| 7 | -4 | 42 | 41 |
| 8 | -4 | 11 | 7 |
| 9 | -4 | 35 | 33 |
| 10 | -4 | 41 | 43 |
| 11 | -4 | 27 | 23 |
| 12 | -4 | 19 | 17 |
| 13 | -4 | 20 | 20 |
| 14 | -4 | 15 | 11 |
| 6 | -5 | 57 | 59 |
| 7 | -5 | 34 | 29 |
| 8 | -5 | 47 | 47 |
| 9 | -5 | 51 | 53 |
| 10 | -5 | 36 | 36 |
| 12 | -5 | 19 | 17 |
| 13 | -5 | 20 | 20 |
| 7 | -6 | 51 | 57 |
| 8 | -6 | 50 | 46 |
| 11 | -6 | 36 | 37 |
| 12 | -6 | 21 | 21 |
| 13 | -6 | 20 | 21 |
| 8 | -7 | 17 | 16 |
| 9 | -7 | 49 | 40 |
| 10 | -7 | 20 | 18 |
| 12 | -7 | 28 | 25 |
| 13 | -7 | 24 | 24 |
| 9 | -8 | 39 | 39 |
| 10 | -8 | 55 | 50 |
| 11 | -8 | 35 | 29 |
| 13 | -8 | 39 | 43 |
| 10 | -9 | 36 | 34 |
| 12 | -9 | 20 | 19 |
| 11 | -10 | 21 | 17 |
| 12 | -10 | 21 | 16 |
| 14 | -10 | 15 | 15 |
| 12 | -11 | 15 | 15 |
| 13 | -11 | 35 | 40 |
| 13 | -12 | 15 | 16 |
| *****L=5***** | | | |
| 2 | -1 | 95 | 91 |
| 3 | -1 | 48 | 48 |
| 4 | -1 | 71 | 71 |
| 5 | -1 | 49 | 46 |
| 7 | -1 | 55 | 65 |
| 3 | -2 | 92 | 89 |
| 4 | -2 | 78 | 72 |
| 5 | -2 | 57 | 53 |
| 6 | -2 | 103 | 106 |
| 9 | -2 | 60 | 61 |
| 4 | -3 | 61 | 66 |
| 5 | -4 | 42 | 38 |
| 6 | -4 | 50 | 54 |
| 7 | -4 | 60 | 66 |
| 10 | -4 | 37 | 48 |
| 6 | -5 | 80 | 86 |
| 7 | -5 | 34 | 34 |
| 9 | -5 | 61 | 70 |
| 7 | -6 | 60 | 63 |
| 9 | -6 | 37 | 47 |
| *****L=6***** | | | |
| 5 | 0 | 75 | 80 |
| 8 | 0 | 61 | 69 |
| 9 | 0 | 21 | 24 |
| 2 | -1 | 73 | 79 |
| 3 | -1 | 18 | 18 |
| 4 | -1 | 21 | 15 |
| 5 | -1 | 32 | 28 |
| 6 | -1 | 17 | 18 |
| 7 | -1 | 30 | 30 |
| 3 | -2 | 18 | 14 |
| 4 | -2 | 58 | 53 |
| 5 | -2 | 26 | 25 |
| 6 | -2 | 45 | 41 |
| 7 | -2 | 28 | 22 |
| 9 | -2 | 31 | 30 |
| 4 | -3 | 23 | 23 |
| 5 | -3 | 69 | 66 |
| 6 | -3 | 28 | 24 |
| 8 | -3 | 73 | 77 |
| 9 | -3 | 20 | 21 |
| 10 | -3 | 21 | 23 |
| 11 | -3 | 40 | 45 |
| 5 | -4 | 53 | 45 |
| 6 | -4 | 17 | 19 |
| 6 | -5 | 25 | 26 |
| 8 | -5 | 50 | 45 |
| 9 | -5 | 28 | 27 |
| 7 | -6 | 27 | 27 |
| 8 | -6 | 45 | 44 |
| 9 | -6 | 20 | 22 |
| 11 | -6 | 32 | 35 |
| 12 | -6 | 22 | 24 |
| 8 | -7 | 28 | 26 |
| 9 | -7 | 32 | 25 |
| 9 | -8 | 21 | 19 |
| 10 | -8 | 33 | 31 |
| 11 | -8 | 31 | 28 |
| 10 | -9 | 23 | 17 |
| *****L=7***** | | | |
| 4 | 0 | 28 | 28 |
| 7 | 0 | 23 | 25 |
| 9 | 0 | 16 | 18 |
| 2 | -1 | 59 | 57 |
| 3 | -1 | 46 | 45 |
| 4 | -1 | 59 | 59 |
| 5 | -1 | 32 | 30 |
| 6 | -1 | 30 | 28 |
| 7 | -1 | 52 | 53 |
| 10 | -1 | 17 | 25 |
| 3 | -2 | 42 | 42 |
| 4 | -2 | 53 | 46 |
| 5 | -2 | 18 | 21 |
| 6 | -2 | 58 | 57 |
| 7 | -2 | 14 | 17 |
| 9 | -2 | 33 | 34 |
| 4 | -3 | 25 | 28 |
| 5 | -3 | 29 | 26 |
| 6 | -3 | 13 | 16 |
| 5 | -4 | 27 | 24 |
| 6 | -4 | 51 | 47 |
| 7 | -4 | 55 | 54 |
| 10 | -4 | 35 | 39 |
| 6 | -5 | 40 | 45 |
| 7 | -5 | 21 | 24 |
| 9 | -5 | 33 | 39 |
| 7 | -6 | 31 | 32 |
| 9 | -6 | 27 | 31 |
| 9 | -7 | 24 | 21 |
| 10 | -7 | 24 | 30 |
| 11 | -7 | 23 | 25 |
| *****L=8***** | | | |
| 5 | 0 | 42 | 44 |
| 6 | 0 | 15 | 14 |
| 8 | 0 | 35 | 40 |
| 2 | -1 | 26 | 32 |
| 4 | -1 | 17 | 16 |
| 7 | -1 | 23 | 24 |
| 8 | -1 | 17 | 20 |
| 3 | -2 | 19 | 15 |
| 4 | -2 | 22 | 19 |
| 6 | -2 | 37 | 31 |
| 9 | -2 | 18 | 23 |
| 4 | -3 | 24 | 21 |
| 5 | -3 | 42 | 35 |
| 6 | -3 | 33 | 27 |
| 8 | -3 | 44 | 44 |
| 5 | -4 | 14 | 15 |
| 6 | -4 | 22 | 17 |
| 7 | -4 | 16 | 14 |
| 9 | -4 | 17 | 12 |
| 6 | -5 | 21 | 21 |
| 7 | -5 | 16 | 12 |
| 8 | -5 | 24 | 24 |
| 9 | -5 | 25 | 21 |
| 10 | -5 | 18 | 16 |
| 7 | -6 | 23 | 21 |
| 8 | -6 | 25 | 24 |
| 9 | -7 | 18 | 19 |
| 9 | -8 | 19 | 15 |

**X = Br**

| K | L | OBS | CAL |
|---|---|---|---|
| *****H= 0***** | | | |
| 0 | | | 545 |
| 0 | 2 | 301 | 323 |
| 0 | 4 | 318 | 366 |
| 0 | 6 | 135 | 136 |
| 0 | 8 | 107 | 129 |
| *****H= 1***** | | | |
| 0 | 2 | 74 | 56 |
| 0 | 3 | 31 | 28 |
| 0 | 4 | 56 | 47 |
| 1 | 0 | 71 | 75 |
| 1 | 1 | 104 | 93 |
| 1 | 2 | 250 | 296 |
| 1 | 3 | 77 | 77 |
| 1 | 4 | 63 | 59 |
| 1 | 5 | 51 | 57 |
| 1 | 6 | 123 | 121 |
| 1 | 7 | 42 | 40 |
| 2 | 0 | 72 | 62 |
| 2 | 1 | 162 | 166 |
| 2 | 2 | 43 | 35 |
| 2 | 3 | 157 | 150 |
| 2 | 4 | 57 | 51 |
| 2 | 5 | 65 | 63 |
| 2 | 7 | 57 | 68 |
| 3 | 0 | 66 | 60 |
| 3 | 1 | 152 | 148 |
| 4 | 0 | 76 | 59 |
| 4 | 1 | 54 | 63 |
| 4 | 2 | 131 | 121 |
| 5 | 0 | 76 | 58 |
| 5 | 1 | 128 | 119 |
| 6 | 0 | 100 | 103 |
| 6 | 1 | 104 | 101 |
| 7 | 0 | 108 | 118 |
| 9 | 0 | 69 | 75 |
| *****H= 2***** | | | |
| 0 | 2 | 98 | 93 |
| 0 | 6 | 56 | 50 |
| 1 | 0 | 115 | 116 |
| 1 | 1 | 195 | 211 |
| 1 | 3 | 139 | 134 |
| 1 | 4 | 91 | 84 |
| 1 | 5 | 116 | 121 |
| 1 | 7 | 39 | 38 |
| 2 | 1 | 101 | 105 |
| 2 | 2 | 188 | 210 |
| 2 | 3 | 83 | 85 |
| 2 | 5 | 75 | 60 |
| 2 | 6 | 91 | 90 |
| 3 | 1 | 133 | 131 |
| 3 | 2 | 63 | 63 |
| 4 | 0 | 148 | 154 |
| 4 | 1 | 189 | 197 |
| 4 | 2 | 76 | 75 |
| 4 | 3 | 156 | 140 |
| 4 | 4 | 117 | 114 |
| 4 | 5 | 117 | 124 |
| 4 | 6 | 32 | 31 |
| 4 | 7 | 49 | 50 |
| 5 | 0 | 54 | 43 |
| 5 | 1 | 85 | 78 |
| 5 | 2 | 104 | 96 |
| 6 | 0 | 59 | 43 |
| 6 | 1 | 42 | 47 |
| 7 | 0 | 110 | 106 |
| 7 | 1 | 74 | 80 |
| 7 | 2 | 55 | 59 |
| 8 | 2 | 58 | 45 |
| 9 | 1 | 50 | 47 |
| *****H= 3***** | | | |
| 0 | 0 | 354 | 429 |
| 0 | 2 | 176 | 162 |
| 0 | 4 | 270 | 246 |
| 0 | 6 | 83 | 75 |
| 0 | 8 | 92 | 91 |
| 1 | 0 | 85 | 78 |
| 1 | 1 | 140 | 137 |
| 1 | 3 | 93 | 84 |
| 1 | 4 | 67 | 67 |
| 1 | 5 | 90 | 89 |
| 2 | 0 | 62 | 50 |
| 2 | 1 | 110 | 106 |
| 2 | 2 | 130 | 117 |
| 3 | 0 | 155 | 169 |
| 3 | 1 | 77 | 77 |
| 3 | 3 | 63 | 61 |
| 3 | 4 | 101 | 101 |
| 3 | 5 | 48 | 41 |
| 4 | 1 | 52 | 48 |
| 4 | 2 | 64 | 55 |
| 5 | 0 | 120 | 127 |
| 5 | 2 | 172 | 163 |
| 6 | 1 | 90 | 81 |
| 6 | 2 | 95 | 90 |
| 6 | 3 | 67 | 66 |
| 6 | 5 | 42 | 45 |
| 6 | 6 | 35 | 41 |
| 7 | 2 | 57 | 59 |
| 8 | 2 | 101 | 108 |
| 9 | 2 | 64 | 55 |
| *****H= 4***** | | | |
| 0 | 2 | 97 | 88 |
| 0 | 3 | 45 | 46 |
| 0 | 6 | 41 | 36 |
| 0 | 7 | 42 | 30 |
| 1 | 0 | 28 | 28 |
| 1 | 1 | 51 | 54 |
| 1 | 2 | 148 | 149 |
| 1 | 3 | 51 | 44 |
| 1 | 5 | 42 | 32 |
| 1 | 6 | 72 | 68 |
| 2 | 0 | 114 | 116 |
| 2 | 1 | 126 | 137 |
| 2 | 2 | 46 | 41 |
| 2 | 3 | 120 | 129 |
| 2 | 5 | 65 | 63 |
| 2 | 7 | 56 | 64 |
| 3 | 1 | 98 | 102 |
| 3 | 2 | 45 | 36 |
| 4 | 0 | 92 | 94 |
| 4 | 2 | 45 | 37 |
| 4 | 4 | 61 | 51 |
| 5 | 0 | 90 | 73 |
| 6 | 0 | 65 | 66 |
| 7 | 0 | 70 | 77 |
| 7 | 1 | 73 | 41 |
| 8 | 1 | 33 | 33 |
| *****H= 5***** | | | |
| 0 | 0 | 130 | 133 |
| 0 | 2 | 185 | 184 |
| 0 | 4 | 86 | 77 |
| 0 | 6 | 93 | 95 |
| 0 | 8 | 40 | 37 |
| 1 | 0 | 113 | 121 |
| 1 | 1 | 176 | 184 |
| 1 | 2 | 50 | 48 |
| 1 | 3 | 130 | 129 |
| 1 | 4 | 96 | 91 |
| 1 | 5 | 110 | 113 |
| 1 | 7 | 43 | 42 |
| 2 | 0 | 81 | 84 |
| 2 | 1 | 93 | 89 |
| 2 | 2 | 70 | 59 |
| 3 | 0 | 81 | 85 |
| 3 | 2 | 132 | 124 |
| 4 | 0 | 86 | 90 |
| 4 | 1 | 100 | 114 |
| 4 | 2 | 52 | 41 |
| 5 | 0 | 70 | 79 |
| 5 | 1 | 64 | 63 |
| 5 | 3 | 58 | 51 |
| 5 | 4 | 50 | 50 |
| 5 | 5 | 38 | 35 |
| 6 | 1 | 49 | 37 |
| *****H= 6***** | | | |
| 0 | 0 | 105 | 105 |
| 0 | 2 | 46 | 46 |
| 0 | 4 | 78 | 61 |
| 1 | 0 | 101 | 104 |
| 1 | 1 | 83 | 95 |
| 1 | 2 | 51 | 43 |
| 1 | 3 | 62 | 64 |
| 1 | 4 | 95 | 83 |
| 1 | 5 | 68 | 71 |
| 2 | 1 | 42 | 41 |
| 2 | 2 | 72 | 65 |
| 3 | 1 | 94 | 110 |
| 3 | 2 | 81 | 92 |
| 3 | 3 | 103 | 91 |
| 3 | 5 | 65 | 64 |
| 3 | 6 | 42 | 42 |
| 5 | 2 | 59 | 62 |
| 6 | 1 | 77 | 87 |
| 6 | 2 | 70 | 76 |
| 6 | 3 | 71 | 73 |
| 6 | 5 | 51 | 52 |
| *****H= 7***** | | | |
| 0 | 0 | 48 | 41 |
| 0 | 2 | 83 | 83 |
| 0 | 3 | 38 | 38 |
| 0 | 6 | 42 | 40 |
| 1 | 0 | 45 | 48 |
| 1 | 2 | 57 | 66 |
| 2 | 2 | 55 | 50 |
| 3 | 1 | 47 | 59 |
| 4 | 1 | 49 | 60 |
| 7 | 1 | 52 | 38 |
| 7 | 2 | 39 | 27 |
| 7 | 3 | 58 | 33 |
| *****H= 8***** | | | |
| 0 | 0 | 128 | 154 |
| 0 | 2 | 173 | 179 |
| 0 | 4 | 94 | 98 |
| 0 | 6 | 94 | 94 |
| 1 | 0 | 63 | 63 |
| 1 | 1 | 48 | 43 |
| 1 | 3 | 40 | 25 |
| 1 | 4 | 51 | 53 |
| 1 | 5 | 41 | 33 |
| 2 | 0 | 96 | 105 |
| *****H= 9***** | | | |
| 0 | 2 | 80 | 79 |
| 0 | 6 | 41 | 37 |
| 1 | 0 | 74 | 78 |
| 1 | 2 | 43 | 43 |
| 1 | 4 | 52 | 63 |
| *****H=10***** | | | |
| 0 | 6 | 40 | 30 |
| 1 | 1 | 51 | 48 |
| 1 | 2 | 44 | 49 |
| 1 | 3 | 44 | 41 |
| *****H=11***** | | | |
| 0 | 0 | 76 | 73 |
| 0 | 2 | 88 | 86 |
| 0 | 4 | 42 | 45 |

likely that the same disorder that exists in $CsCl \cdot {}^1/_3H_3OHCl_2$ exists also in the bromine structure (see previous discussion on $CsCl \cdot {}^1/_3H_3OHCl_2$). A final refinement was carried out using anisotropic temperature factors on all atoms except oxygen. The anisotropic refinement had little effect on the value of $R_2$, but the thermal model is physically reasonable. It is virtually indistinguishable from an isotropic model except for the motion of $Br_2$. We attach moderate significance to these temperature factors because the precession data were not corrected for absorption. A final difference Fourier map was computed in which all atoms except hydrogen were subtracted out. No peaks higher than 2.7 e/Å$^3$ (two-thirds the height of the half-oxygen) were found and none corresponded to anticipated hydrogen positions.

The observed and calculated structure amplitudes in electrons for the two compounds are given in Table I. Table II gives the final atomic and thermal parameters. Table III gives the root-mean-square amplitudes of vibration for the bromine compound.

TABLE II

Atomic Coordinates and Isotropic Temperature Factors for $CsCl \cdot {}^1/_3H_3OHCl_2$

| Atom | $x$ ($10^4\sigma_x$) | $y$ ($10^4\sigma_y$) | $z$ ($10^4\sigma_z$) | $B$ ($10^2\sigma_B$) |
|---|---|---|---|---|
| Cs | 0.3855 (1.6) | 0.3704 (1.6) | $^1/_4{}^a$ | 2.17 (4) |
| $Cl_1$ | 0.7273 (6) | 0.7346 (7) | $^1/_4$ | 2.39 (10) |
| $Cl_2$ | $^1/_3$ | $-^1/_3$ | 0.0181 (15) | 2.66 (12) |
| O | 0 | 0 | 0.1104 (7) | 2.17 (63) |

Atomic Coordinates for $CsBr \cdot {}^1/_3H_3OHBr_2$

| Atom | $x$ ($10^4\sigma_x$) | $y$ ($10^4\sigma_y$) | $z$ ($10^4\sigma_z$) |
|---|---|---|---|
| Cs | 0.3834 (4) | 0.3735 (4) | $^1/_4{}^a$ |
| $Br_1$ | 0.7285 (7) | 0.7320 (7) | $^1/_4$ |
| $Br_2$ | $^1/_3$ | $-^1/_3$ | 0.0131 (10) |
| O | 0 | 0 | 0.1081 (88) |

Thermal Parameters for $CsBr \cdot {}^1/_3H_3OHBr_2$

| Atom | $\beta_{11}$ ($10^4\sigma$) | $\beta_{22}$ ($10^4\sigma$) | $\beta_{33}$ ($10^4\sigma$) | $\beta_{12}$ ($10^4\sigma$) |
|---|---|---|---|---|
| Cs | 0.0077 (5) | 0.0069 (5) | 0.0133 (7) | 0.0038 (4) |
| $Br_1$ | 0.0085 (8) | 0.0075 (8) | 0.0190 (12) | 0.0037 (7) |
| $Br_2$ | 0.0082 (5) | $\beta_{11}$ | 0.0105 (14) | $^1/_2\beta_{11}$ |
| O$^b$ | −0.083 (1830)$^c$ | | | |

$^a$ Coordinates indicated by simple fractions fixed by symmetry. $^b$ Refined isotropically. $^c$ $B$ in Å$^2$. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk)]$.

## Results and Discussion

Table II shows (within the limits of the estimated errors) that the two compounds are isostructural. Thus Figure 1 shows the essential features of both structures since bromine and chlorine can be interchanged. Strings of hydronium ions and bihalide ions are parallel to the $c$ axis. Three cesium and three halide atoms surround the bihalide ion in such a manner that the X–X axis of the ion coincides with a threefold axis. All these atoms lie on a mirror plane that reflects one halide atom of the bihalide ion into the other. The strings of hydronium ions coincide with a $6_3$ axis. The halide atoms entering into hydrogen bonds with the hydronium ions may be thought of as being arranged at the corners of octahedra (see Figure 1). These octahedra are contracted along their threefold axis and share faces.

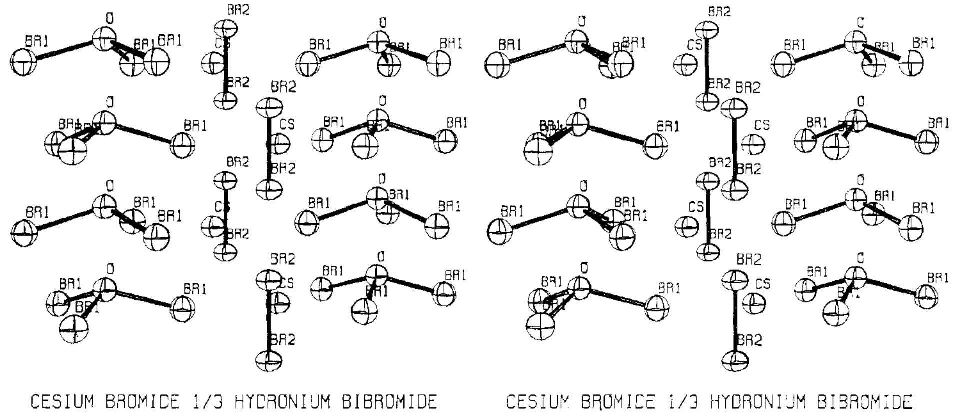

Figure 1.—Stereoscopic view of the $CsBr \cdot {}^1/_3H_3OHBr_2$ structure looking perpendicular to the *ac* plane. The *c* axis is vertical in the figure. The disorder of the oxygen positions is not shown, nor are the hydrogen positions. The shape of the ellipsoids indicates the direction of the principal axes of thermal vibration for all atoms except oxygen. Hydrogen bonds are shown as solid lines.

Table III

Root-Mean-Square Amplitudes of Vibration (Å) for $CsBr \cdot {}^1/_3H_3OHBr_2$

| Atom | $\parallel c (10^3\sigma)$ | $\perp c (10^3\sigma)$ | $\perp c (10^3\sigma)$ |
|---|---|---|---|
| Cs | 0.170 (5) | 0.182 (6) | 0.184 (5) |
| $Br_1$ | 0.180 (9) | 0.195 (9) | 0.220 (7) |
| $Br_2$ | 0.163 (11) | 0.188 (6) | 0.188 (6) |

Cesium is coordinated to nine halide atoms. Figure 2 shows the geometry around cesium. $X_1$, $X_1'$, $X_1'''$, and Cs all lie on a mirror plane. $X_2$–$X_2$ is the bihalide ion and $X_2'$ belongs to a neighboring bihalide ion. The five halide ions (denoted $X_1$, $X_1'$, $X_1''$, $X_1'''$ in Figure 2) which do not belong to bihalide ions are all hydrogen bonded to hydronium ions. Figure 1 shows this for the bromine compound. Thus in these remarkable compounds both the hydronium ion and the bihalide ion are stabilized by the cesium halide.

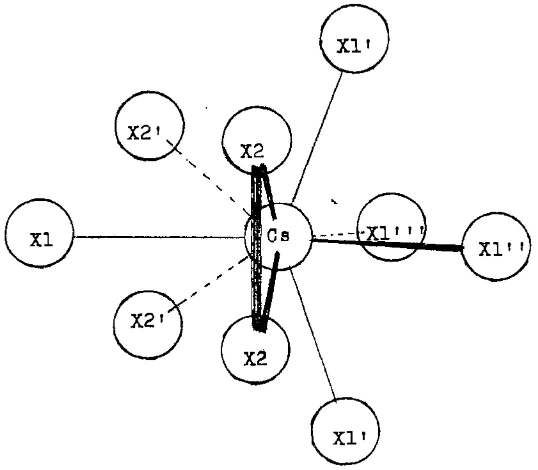

Figure 2.—View of the inner coordination sphere around cesium.

Table IV gives the important ionic and hydrogen bonded distances for the two compounds. Angles around cesium are given in Table V.

Table IV

Selected Interatomic Distances in $CsX \cdot {}^1/_3H_3OHX_2$[a]

| Interaction | X = Cl, *d* ($10^2\sigma_d$) | (X = Br, *d* ($10^2\sigma_d$) |
|---|---|---|
| Cs–$X_1$ | 3.64 (1) | 3.75 (1) |
| Cs–$X_1$ | 3.57 (1) | 3.73 (1) |
| Cs–$X_1''$ | 3.50 (1) | 3.63 (1) |
| Cs–$X_1'''$ | 3.44 (1) | 3.56 (1) |
| Cs–$X_2$ | 3.69 (1) | 3.81 (1) |
| Cs–$X_2'$ | 3.59 (1) | 3.75 (1) |
| $X_2'$–$X_2'$ | 3.63 (2) | 3.73 (2) |
| $X_2$–$X_2$ | 3.14 (2) | 3.35 (2) |
| $X_1$–$X_2$ | 4.07 (1) | 4.25 (1) |
| $X_1$–$X_2$ | 4.26 (1) | 4.37 (1) |
| O–$X_1$ | 2.92 (2) | 3.04 (2) |
| Cs–Cs | 4.23 (1) | 5.37 (1) |

[a] Atoms designated by primes are equivalent to unprimed ones; the primes are for reference to Figure 2. $X_1$ is the halogen in (6h) and $X_2$ is the halogen in (4f) of $P6_3/m$.

Table V

Angles (in degrees) around Cesium in $CsX \cdot {}^1/_3H_3OHX_2$

| Angle | X = Cl ($10\sigma$) | X = Br ($10\sigma$) |
|---|---|---|
| $X_1$–Cs–$X_1'$ | 108.2 (1) | 108.1 (1) |
| $X_1$–Cs–$X_1''$ | 131.2 (2) | 133.2 (2) |
| $X_1$–Cs–$X_1'''$ | 141.3 (2) | 139.3 (2) |
| $X_1$–Cs–$X_2$ | 68.3 (1) | 68.5 (1) |
| $X_1$–Cs–$X_2'$ | 72.2 (1) | 71.4 (1) |
| $X_1'''$–Cs–$X_1''$ | 87.5 (2) | 87.6 (2) |
| $X_1'$–Cs–$X_1'''$ | 77.3 (2) | 77.4 (2) |
| $X_1'$–Cs–$X_1''$ | 76.5 (2) | 76.6 (2) |
| $X_1'''$–Cs–$X_2$ | 144.4 (1) | 144.4 (1) |
| $X_1'''$–Cs–$X_2'$ | 74.5 (1) | 73.5 (1) |
| $X_1''$–Cs–$X_2$ | 68.7 (1) | 69.7 (1) |
| $X_1''$–Cs–$X_2'$ | 143.9 (1) | 143.8 (1) |
| $X_1'$–Cs–$X_1'$ | 143.4 (2) | 143.7 (2) |
| $X_1'$–Cs–$X_2$ | 71.7 (2) | 71.0 (2) |
| $X_1'$–Cs–$X_2'$ | 69.2 (2) | 69.4 (2) |
| $X_1'$–Cs–$X_2$ | 119.6 (2) | 120.7 (2) |
| $X_1'$–Cs–$X_2'$ | 127.2 (2) | 126.3 (2) |
| $X_2$–Cs–$X_2$ | 50.3 (2) | 52.2 (3) |
| $X_2'$–Cs–$X_2'$ | 60.8 (2) | 59.6 (3) |
| $X_2'$–Cs–$X_2$ | 109.2 (1) | 109.0 (1) |
| $X_2'$–Cs–$X_2$ | 139.2 (1) | 140.0 (1) |

The geometry around oxygen in $CsCl \cdot {}^1/_3H_3OHCl_2$ is remarkably similar to that in $H_3OCl$.[12] The values in that study and the present one are O–Cl distance, 2.95 ± 0.01, 2.92 ± 0.02 Å; the Cl–O–Cl angle, 110.4, 110.1°. The $Cl_2$–$Cl_2$ contact of 3.14 Å, some 0.5 Å shorter than that reported in compounds having only van der Waals interactions, indicates a chemical bond between the two chlorine atoms. Thus we take

3.14 ± 0.02 Å as the Cl–Cl distance in the bichloride ion in this compound.

In $CsBr \cdot {}^1/_3H_3OHBr_2$ the geometry around oxygen has O–Br distances of 3.04 ± 0.02 Å and a Br–O–Br angle of 111°. Again our evidence for the bibromide ion stems from the composition and Br–Br contacts. All Br–Br contacts are 4.2 Å or greater with the exception of the $Br_2$–$Br_2$ contacts. They are either 3.73 or 3.35 Å while the sum of usual van der Waals radii for bromide is 3.90 Å. The closest approach of two nonbonded bromines has been reported as 3.70 Å.[16–18] This leaves one with the $Br_2$ contact of 3.35 Å which is shorter than any reported nonbonded contact.

The nonbonded distance of 3.73 Å could be accounted for by a static disorder of the bibromide ions in the following manner. Some of the bibromide ions could be directly opposite to each other instead of alternating as in Figure 1. The $Br_2$–$Br_2$ distances 3.73 and 3.35 Å would both be weighted averages of the normal van der Waals and the Br–Br distance in the bibromide ion. Consequently, the scattering density due to bromine would be smeared over a region 0.38 Å in the vertical direction. Thus the root-mean-square amplitude of vibration parallel to the strings should be greater than that perpendicular to the strings. However, the root-mean-square amplitude of vibration parallel to the strings is 0.163 ± 0.011; the corresponding value perpendicular to the strings is 0.188 ± 0.006 Å. Therefore, we conclude that the strings of bibromide ions are ordered and that 3.35 ± 0.02 Å[19] is the Br–Br distance in the bibromide ion.

The model of thermal motion obtained in this study (see Figure 1) suggests that the ion is vibrating more in a bending mode than in a stretching mode. This seems physically reasonable considering that the bibromide ions are packed tightly end to end. The distance between the nonbonded bromines is only 3.73 Å.

The infrared spectrum of $CsCl \cdot {}^1/_3H_3OHCl_2$ gave some indications of band positions corresponding to those expected for the hydronium ion, but the results were largely inclusive owing to rapid decomposition of the material in Nujol or perfluorocarbon mulls.

The bibromide ion is 0.20 Å longer than the bichloride as expected. If we compare the radius sum with the observed X–X distance for the bihalide ions we see that the difference is about 0.47 Å for all three.[20]

TABLE VI

COMPARISON OF H BONDED AND VAN DER WAALS DISTANCES[20]

| X–H–X | Radius sum, Å | $X–X_{obsd}$, Å | Difference, Å |
|---|---|---|---|
| $HF_2^-$ | 2.73 | 2.26 | 0.47 |
| $HCl_2^-$ | 3.62 | 3.14 | 0.48 |
| $HBr_2^-$ | 3.81[a] | 3.35 | 0.46 |

[a] This value represents the average of distances reported for the closest approach of two bromines not bonded to each other.

This comparison may be somewhat artificial because of the uncertainty in the value for the closest approach of two nonbonded bromines. Nevertheless, the contraction that occurs in the X–X distance when a bihalide ion is formed is larger than in the corresponding O–H–O bonds.[21] This indicates a very strong hydrogen bond, in agreement with thermodynamic measurements.[7]

We are attempting to make a corresponding iodine compound in hopes of studying $HI_2^-$.

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# Bromine Monofluorosulfate

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The preparation and properties of bromine monofluorosulfate $BrOSO_2F$ have been reinvestigated. The electrical conductivity of $BrOSO_2F$ is compared with the conductivities of the other bromine and iodine fluorosulfates which have also been measured over a temperature range. There is no evidence for the formation of either $Br^+$ or $Br_2^+$ in solutions of $BrOSO_2F$ in fluorosulfuric acid.

## Introduction

It has been shown that peroxydisulfuryl difluoride, $S_2O_6F_2$, reacts directly with bromine to yield bromine(I) fluorosulfate, $BrOSO_2F$, when $Br_2$ is in excess, and bromine(III) fluorosulfate, $Br(OSO_2F)_3$, when $S_2O_6F_2$ is in excess.[1] Both compounds are also formed when $S_2O_6F_2$ is allowed to react with $CF_3Br$.[2] Bromine(I) fluorosulfate has been described as a red-black liquid of

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