*Acta Cryst.* (1970). B**26**, 1893

# Hydrogen Bond Studies. XL.*
# The Crystal Structures of Three Hydrates of Hydrogen Bromide, HBr . $n$H$_2$O, $n$ = 1,2 and 3

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(*Received* 30 *January* 1970)

The crystal structures of HBr . $H_2O$, HBr . $2H_2O$ and HBr . $3H_2O$ have been determined from three-dimensional single-crystal X-ray data obtained at −182, −190 and −62 °C respectively. Crystals of the monohydrate are trigonal, space group $R3m$, with three formula units in a cell of dimensions: $a = 5{\cdot}058$, $c = 8{\cdot}906$ Å. The compound is isostructural with oxonium chloride, $H_3O^+Cl^-$. The structure is formed by stacking hydrogen-bonded puckered layers of oxonium and bromide ions. The O···Br distance is 3·103 Å. The dihydrate forms monoclinic crystals, space group $P2_1/c$. A cell of dimensions $a = 4{\cdot}164$, $b = 12{\cdot}422$, $c = 6{\cdot}946$ Å, $\beta = 101{\cdot}21°$ contains four formula units. The water molecules are bonded in pairs by a very short hydrogen bond (2·410 Å) to form $H_5O_2^+$ ions. The compound is isostructural with hydrogen chloride dihydrate, $H_5O_2^+Cl^-$. Crystals of the trihydrate are orthorhombic, space group $Aba2$, with four formula units in a cell of dimensions: $a = 6{\cdot}228$, $b = 5{\cdot}961$, $c = 11{\cdot}722$ Å. The water molecules form hydrogen-bonded chains in which two molecules are coupled together by a short bond (2·473 Å) across a twofold axis. These two molecules have a pyramidal bonding coordination. The third water molecule has a tetrahedral environment and participates in O–H···O bonds of length 2·680 Å. The appropriate formulation of the compound is $H_5O_2^+Br^-$. $H_2O$. The compound is not isostructural with hydrogen chloride trihydrate, $H_5O_2^+Cl^-$ . $H_2O$. A phase transition, which has not been studied in detail, occurs at about −180 °C.

## Introduction

This work is part of a current series of investigations at this Institute to study the hydration of the proton in the solid state. Earlier papers in this series reported the crystal structures of HCl.$2H_2O$, HCl.$3H_2O$, HBr.$4H_2O$ (Lundgren & Olovsson, 1967 *a,b*, 1968), $H_2SO_4$.$H_2O$, $H_2SO_4$.$2H_2O$ (Taesler & Olovsson, 1968, 1969) and $HClO_4$.$2H_2O$ (Olovsson, 1968).

The melting-point diagram of the system hydrogen bromide–water indicates four intermediate compounds, namely the mono-, di-, tri- and tetrahydrates (*Gmelins Handbuch der anorganischen Chemie*, 1931). The crystal structure of HBr . $4H_2O$ at −180 °C has been reported in an earlier paper (Lundgren & Olovsson, 1968). In the following the crystal structures of the other three hydrates will be presented. The structure determinations are based on single-crystal X-ray diffraction data recorded at −182, −190 and −62 °C for the mono-, di- and trihydrates respectively.

## Experimental

Hydrobromic acid with the appropriate molar ratios HBr:$H_2O$ for the different hydrates was prepared from concentrated commercial hydrobromic acid and hydrogen bromide. The hydrogen bromide gas was obtained by bromination of tetrahydronaphthalene (*Inorganic Syntheses*, 1939). The concentration of the acid was checked by titration with sodium hydroxide. As very concentrated solutions of HBr readily lose HBr($g$) at room temperature, the solution with the molar ratio HBr:$H_2O \simeq 1$ was prepared directly in cooled capillaries which were later used for the X-ray investigation. In this case the composition of the sample was checked by observing the melting point.

Single crystals were grown in glass capillaries mounted on a Weissenberg camera modified for low-temperature work (Olovsson, 1960). Great care was taken to grow crystals with a convenient crystallographic axis along the axis of the capillary. Equi-inclination Weissenberg photographs were recorded using the multiple-film technique (five films) and Cu $K\alpha$ radiation. The intensities were estimated visually by comparison with an intensity scale. The data were corrected for the Lorentz and polarization effects and also for absorption assuming a cylindrical specimen (*International Tables for X-ray Crystallography*, p. 291, 1959). Details of this part of the work are summarized in Table 1.

For HBr.$H_2O$ 136 reflexions from a crystal with apparent monoclinic symmetry were recorded by rotating the crystal about a rhombohedral axis. Scale factors for the four layers were calculated with the program *INTERSCALE.* This and other programs mentioned in the following are briefly described by Nahringbauer (1967) and Liminga (1967). The indices of the reflexions were transformed from the monoclinic to the trigonal cell, and average intensities of equivalent reflexions were used. A total of 64 independent reflexions were thus obtained.

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* Part 39: *Acta Chem. Scand.* (1970) **24**, 453.

Table 1. *Some details of the recording of intensity data*

| | $HBr.H_2O$ | $HBr.2H_2O$ | $HBr.3H_2O$ |
|---|---|---|---|
| Melting point (°C) | −5 | −11·2 | −48 |
| Dimensions of the crystal (mm): diameter | 0·28 | 0·21 | 0·21 |
| length | 0·5 | 0·6 | 0·5 |
| Axis of rotation | rhombohedral axis | *a* | *a* |
| Number of layers recorded | 4 | 4 | 6 |
| Number of independent reflexions | 64 | 637 | 218 |
| Number of these reflexions too weak to be measured | 0 | 87 | 50 |
| Number of reflexions recorded, expressed as percentage of total number within the copper reflexion sphere (%) | 85 | 80 | 84 |
| Linear absorption coefficient ($cm^{-1}$) | 205 | 157 | 130 |
| Temperature at which the intensity data were collected (°C) | −182 | −190 | −62 |

Intensities were recorded a few degrees below the melting point and at liquid nitrogen temperature for each of the compounds. For $HBr.H_2O$ and $HBr.2H_2O$ no evidence of significant structural differences could be detected at the two temperatures.

A slow phase transition appears to occur in $HBr.3H_2O$ at about −180°C. Intensity data recorded at and below this temperature show reflexions that do not belong to *Aba*2, the space group of the high-temperature modification. A number of crystals were cooled to between −180 and 190°C. In one case the new phase obtained was practically pure (space group *Bba*2) and the few reflexions belonging to *Aba*2 which could be observed were very weak. In a second case the high-temperature phase remained practically unchanged, whereas in a further case the intensities of reflexions from the two forms were of the same order of magnitude and diffuse streaks were observed along the festoons. A perfectly pure low-temperature phase could not be obtained. The low-temperature phase did not return to the high-temperature phase when the temperature was raised above −180°C but persisted even after several hours at −100°C. A structure analysis was attempted without success using intensity data collected from the purest low-temperature phase. It is likely that failure in this connection may best be attributed to crystal twinning.

The cell dimensions were determined from quartz-calibrated zero-layer oscillation photographs. The cell parameters were fitted to the measured $\theta$ values by the method of least squares using the program *CELSIUS*. The following constants were used: $a=4\cdot913$ Å for α quartz (22°C), $\lambda(\text{Cu } K\alpha_1)=1\cdot54051$, $\lambda(\text{Cu } K\alpha_2)=1\cdot54433$ Å. The values of the parameters and their estimated standard deviations are given in Table 2.

Table 2. *Crystal data*

$HBr.H_2O$

Space group *R*3*m* (No. 160) *T* −182°C

$a=$ 5·058 (1) Å

$c=$ 8·906 (4)

$V=$ 197·3 Å$^3$ $D_x=2\cdot497$ g.cm$^{-3}$

$Z=$ 3

$HBr.2H_2O$

Space group $P2_1/c$ (No. 14) *T* −190°C

$a=$ 4·164 (6) Å

$b=$ 12·422 (3) $\beta=101\cdot21$ (12)°

$c=$ 6·946 (5)

$V=$ 352·4 Å$^3$ $D_x=2\cdot204$ g.cm$^{-3}$

$Z=$ 4 $D_m=2\cdot11$ g.cm$^{-3}$ (at −15°)
(Roozeboom, 1885)

$HBr.3H_2O$

Space group *Aba*2 (No. 41) *T* −62°C

$a=$ 6·228 (3) Å

$b=$ 5·961 (1)

$c=$ 11·722 (1)

$V=$ 435·2 Å$^3$ $D_x=2\cdot060$ g.cm$^{-3}$

$Z=$ 4

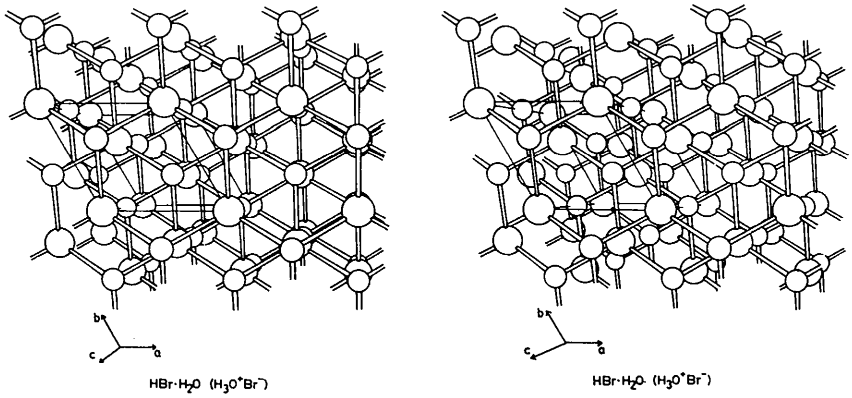
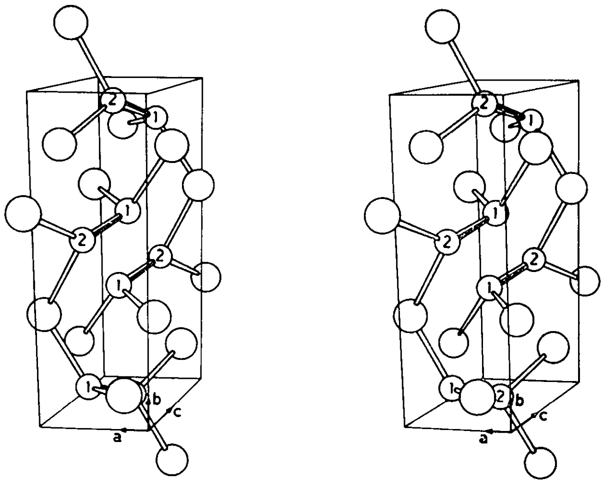


Fig. 1. Stereoscopic pair of drawings of the crystal structure of HBr $H_2O$ ($=H_3O^+Br^-$). The structure is seen along the trigonal axis. Large circles denote bromide ions and smaller circles denote oxygen atoms (oxonium ions). No hydrogen atoms are shown.



$HBr\cdot 2H_2O$ $(H_5O_2^+Br^-)$ $HBr\cdot 2H_2O$ $(H_5O_2^+Br^-)$

Fig. 2. Stereoscopic drawing of the crystal structure of $HBr.2H_2O$ $(=H_5O_2^+Br^-)$. Large circles denote bromide ions and smaller circles, numbered 1 and 2, denote the oxygen atoms. The hydrogen atoms are not shown. The hydrogen bond within $H_5O_2^+$ is half-filled. Other hydrogen bonds are open.

## Structure determination

The diffraction symmetry and systematic absences indicated the space groups *R*3, *R*32 or *R*3*m* for $HBr.H_2O$, $P2_1/c$ for $HBr.2H_2O$ and *Aba*2 or *Abam* for $HBr.3H_2O$ (*International Tables for X-ray Crystallography*, 1952). The three space groups for $HBr.H_2O$ differ only in the positions available for the hydrogen atoms. All calculations were made in *R*3*m* which is the space group used in the refinements of $HCl.H_2O$ (Yoon & Carpenter, 1959). *Aba*2 was found to be the only reasonable space group for $HBr.3H_2O$.

The three structures were determined from three-dimensional Patterson syntheses. These readily indicated the positions of the bromine and oxygen atoms in all three cases. The coordinates were first improved in a series of electron density calculations using the program *DRF*. The structures were then refined by least squares using both isotropic and anisotropic thermal parameters. The isotropic refinements included refinement of scale factors for the different layers (except for $HBr.H_2O$, see above), atomic coordinates and individual isotropic thermal parameters. The anisotropic

Table 3. *Discrepancy indices at different stages of the refinements*

The discrepancy indices $R_1$, $R_2$ and $R_3$ are defined as:

$$R_1=\sum\left||F_o|-|F_c|\right|/\sum|F_o| \text{ (unobserved reflexions not included)}$$
$$R_2=\sum\left||F_o|-|F_c|\right|/\sum|F_o| \text{ (unobserved reflexions included)}$$
$$R_3=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$$

| Type of refinement | Number of reflexions with non-zero weight | Number of parameters refined | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|---|---|
| $HBr.H_2O$ | | | | | |
| Isotropic | 64 | 4 | 0·055 | 0·055 | 0·067 |
| Anisotropic | 64 | 6 | 0·055 | 0·055 | 0·067 |
| $HBr.2H_2O$ | | | | | |
| Isotropic | 550 | 16 | 0·094 | 0·107 | 0·119 |
| Anisotropic | 550 | 28 | 0·084 | 0·096 | 0·106 |
| Isotropic | 543 | 16 | 0·090 | 0·102 | 0·107 |
| Anisotropic | 543 | 28 | 0·079 | 0·091 | 0·092 |
| $HBr.3H_2O$ | | | | | |
| Isotropic | 168 | 13 | 0·079 | 0·093 | 0·099 |
| Anisotropic | 168 | 19 | 0·068 | 0·081 | 0·087 |
| Isotropic | 162 | 13 | 0·073 | 0·086 | 0·087 |
| Anisotropic | 162 | 19 | 0·061 | 0·075 | 0·069 |

Table 4. *Atomic coordinates and anisotropic thermal parameters* ($\times 10^4$) *with standard deviations*

$\beta_{ij}$ are coefficients in the expression $\exp[-(\beta_{11}h^2+\ldots+\beta_{12}hk+\ldots)]$. The point symmetry for each atomic position is also given.

| | Point symmetry | *x* | *y* | *z* | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $HBr.H_2O$ | | | | | | | | | | |
| Br | 3*m* | 0 | 0 | 0 | 153 (11) | $=\beta_{11}$ | 35 (3) | $=\frac{1}{2}\beta_{11}$ | 0 | 0 |
| O | 3*m* | 0 | 0 | 4512 (34) | 336 (109) | $=\beta_{11}$ | 38 (30) | $=\frac{1}{2}\beta_{11}$ | 0 | 0 |
| $HBr.2H_2O$ | | | | | | | | | | |
| Br | 1 | 337 (3) | 3302 (1) | 1561 (1) | 187 (14) | 8 (1) | 65 (3) | 2 (3) | 10 (7) | −1 (2) |
| O(1) | 1 | 5700 (21) | 1241 (6) | 420 (12) | 70 (58) | 12 (5) | 81 (16) | 17 (23) | −96 (43) | 9 (12) |
| O(2) | 1 | 3103 (29) | 575 (7) | 2996 (13) | 642 (88) | 14 (5) | 95 (18) | −74 (31) | 246 (62) | −24 (16) |
| $HBr.3H_2O$ | | | | | | | | | | |
| Br | 2 | 0 | 0 | 0 | 153 (8) | 191 (6) | 33 (1) | −8 (11) | 0 | 0 |
| O(1) | 2 | 0 | 0 | 3629 (24) | 164 (79) | 171 (50) | 98 (21) | 7 (85) | 0 | 0 |
| O(2) | 1 | 3197 (24) | 869 (23) | 2163 (6) | 47 (24) | 122 (23) | 37 (6) | −21 (57) | 13 (27) | 44 (31) |

refinements included an overall scale factor, atomic coordinates and anisotropic thermal parameters. The scale factors for the different layers were then set to the values obtained in the previous isotropic refinement. Reflexions for which $|F_o|$ was found to be much less than $|F_c|$ were deleted from the data set and the structures were refined isotropically and anisotropically in a further series of refinements. The reflexions removed were strong, low-angle reflexions which may have been subject to extinction or serious underestimation. The refinements were all allowed to continue until the shifts in the parameters were less than one tenth of their estimated standard deviations. The program *LALS* was used for the least-squares calculations. This is a full-matrix program which minimizes the function $\sum w(|F_o|-|F_c|)^2$. The weights, $w$, were calculated according to the expression: $w=1/(a+|F_o|+c|F_o|^2)$. An analysis of the weighting suggested suitable values for $a$ and $c$. Reflexions too weak to be measured were given zero weight in all calculations. A summary of the refinements is given in Table 3.

An anomalous dispersion correction was included in a series of refinements of $HBr.3H_2O$ but this produced no significant effect on the parameters and $R$ values. Atomic scattering factors for $Br^-$ and neutral O were taken from *International Tables for X-ray Crystallography* (1962, pp. 202, 214). The hydrogen atoms were not included in the calculations.

The final positional parameters and anisotropic thermal parameters are given in Table 4. The observed

Table 5. *Observed and calculated structure factors*

The columns are in order $k$, $l$, $|F_o|$, $|F_c|$. Reflexions marked * were too weak to be measured. The $|F_o|$ values for these reflexions are given as $|F_{min}|$ for the reflexion in question. Reflexions marked ** were omitted in the last cycles of least-squares refinement.

| | | | |
|---|---|---|---|
| HBR.H2O | | | |
| 0,K,L | | | |
| 0 | 3 | 81.3 | 75.3 |
| 0 | 6 | 64.3 | 58.0 |
| 0 | 9 | 51.0 | 45.7 |
| 1 | 2 | 103.2 | 101.5 |
| 1 | 5 | 61.3 | 64.5 |
| 1 | 8 | 47.3 | 40.9 |
| 1 | 11 | 29.5 | 32.9 |
| 2 | 1 | 55.1 | 60.5 |
| 2 | 4 | 59.3 | 65.5 |
| 2 | 7 | 52.8 | 49.3 |
| 3 | 0 | 67.7 | 66.6 |
| 3 | 3 | 49.9 | 50.2 |
| 3 | 6 | 43.7 | 42.2 |
| 3 | 9 | 32.7 | 33.8 |
| 4 | 2 | 53.0 | 47.6 |
| 4 | 5 | 35.3 | 37.4 |
| 5 | 1 | 34.1 | 31.2 |
| 5 | 4 | 30.4 | 31.1 |
| 1,K,L | | | |
| 0 | 1 | 64.7 | 73.6 |
| 0 | 4 | 76.4 | 75.8 |
| 0 | 7 | 58.5 | 55.3 |
| 0 | 10 | 32.4 | 30.3 |
| 1 | 0 | 85.3 | 94.9 |
| 1 | 3 | 65.3 | 62.6 |
| 1 | 6 | 52.5 | 51.8 |
| 1 | 9 | 40.6 | 41.1 |
| 2 | 2 | 66.8 | 68.8 |
| 2 | 5 | 53.4 | 50.7 |
| 2 | 8 | 35.3 | 34.1 |
| 3 | 1 | 46.1 | 44.7 |
| 3 | 4 | 46.4 | 46.0 |
| 3 | 7 | 35.5 | 36.3 |
| 4 | 0 | 47.3 | 41.8 |
| 4 | 3 | 38.8 | 34.2 |
| 4 | 6 | 30.1 | 29.0 |
| 2,K,L | | | |
| 0 | 2 | 80.4 | 80.2 |
| 0 | 5 | 56.4 | 56.8 |
| 0 | 8 | 37.9 | 37.4 |
| 1 | 1 | 52.8 | 54.3 |
| 1 | 4 | 55.0 | 57.5 |
| 1 | 7 | 46.6 | 44.4 |
| 1 | 10 | 20.1 | 25.6 |
| 2 | 0 | 54.7 | 58.4 |
| 2 | 3 | 46.3 | 45.4 |
| 2 | 6 | 40.9 | 38.3 |
| 2 | 9 | 28.8 | 30.7 |
| 3 | 2 | 47.5 | 42.8 |
| 3 | 5 | 33.7 | 34.0 |
| 4 | 1 | 29.1 | 28.6 |
| 3,K,L | | | |
| 1 | 2 | 52.9 | 53.2 |
| 1 | 5 | 42.7 | 41.3 |
| 1 | 8 | 23.2 | 28.6 |
| 2 | 1 | 38.3 | 37.3 |
| 2 | 4 | 37.8 | 37.5 |
| 2 | 7 | 31.7 | 30.0 |
| 3 | 0 | 33.6 | 34.3 |
| 3 | 3 | 26.2 | 28.6 |
| 4,K,L | | | |
| 0 | 1 | 44.6 | 40.8 |
| 0 | 4 | 40.1 | 41.5 |
| 0 | 7 | 30.3 | 33.0 |
| 2 | 2 | 29.3 | 31.9 |
| 5,K,L | | | |
| 0 | 2 | 34.1 | 35.0 |
| 0 | 5 | 24.8 | 28.3 |
| 1 | 1 | 25.1 | 26.2 |
| HBR.2H2O | | | |
| 0,K,L | | | |
| 0 | 8 | 6.5 | 5.5 |
| 1 | 8 | 40.3 | 41.0 |
| 2 | 8 | 3.1 | 2.7* |
| 3 | 8 | 2.9 | 2.8 |
| 4 | 8 | 2.8 | 1.4* |
| 5 | 8 | 31.1 | 32.6 |
| 1 | 7 | 20.2 | 17.8 |
| 2 | 7 | 19.4 | 16.1 |
| 3 | 7 | 48.3 | 45.4 |
| 4 | 7 | 30.3 | 27.8 |
| 5 | 7 | 27.8 | 23.6 |
| 6 | 7 | 6.5 | 5.7 |
| 7 | 7 | 20.8 | 18.9 |
| 8 | 7 | 19.4 | 17.6 |
| 9 | 7 | 27.5 | 30.0 |
| 0 | 6 | 54.4 | 59.6 |
| 1 | 6 | 21.2 | 18.1 |
| 2 | 6 | 31.5 | 28.4 |
| 3 | 6 | 4.4 | 0.6* |
| 4 | 6 | 27.1 | 22.8 |
| 5 | 6 | 8.8 | 7.4 |
| 6 | 6 | 51.7 | 50.3 |
| 7 | 6 | 30.7 | 27.0 |
| 8 | 6 | 33.1 | 31.4 |
| 9 | 6 | 8.1 | 7.5 |
| 10 | 6 | 17.1 | 15.0 |
| 11 | 6 | 20.0 | 19.9 |
| 1 | 5 | 16.7 | 14.5 |
| 2 | 5 | 63.2 | 70.9 |
| 3 | 5 | 9.2 | 7.3 |
| 4 | 5 | 58.6 | 61.4 |
| 5 | 5 | 10.4 | 7.4 |
| 6 | 5 | 4.4 | 1.0* |
| 7 | 5 | 4.4 | 3.1* |
| 8 | 5 | 44.9 | 44.9 |
| 9 | 5 | 21.3 | 18.4 |
| 10 | 5 | 46.2 | 44.6 |
| 11 | 5 | 4.9 | 3.8 |
| 12 | 5 | 12.2 | 10.7 |
| 13 | 5 | 3.5 | 2.9 |
| 0 | 4 | 48.1 | 49.4 |
| 1 | 4 | 38.9 | 39.3 |
| 2 | 4 | 37.1 | 35.4 |
| 3 | 4 | 26.1 | 22.3 |
| 4 | 4 | 22.6 | 18.6 |
| 5 | 4 | 48.2 | 48.0 |
| 6 | 4 | 50.1 | 55.5 |
| 7 | 4 | 45.4 | 47.5 |
| 8 | 4 | 33.4 | 31.7 |
| 9 | 4 | 14.1 | 12.3 |
| 10 | 4 | 14.7 | 12.9 |
| 11 | 4 | 31.8 | 29.5 |
| 12 | 4 | 40.2 | 40.1 |
| 13 | 4 | 37.1 | 42.3 |
| 14 | 4 | 21.5 | 24.1 |
| 1 | 3 | 62.7 | 71.4 |
| 2 | 3 | 13.8 | 10.5 |
| 3 | 3 | 89.3 | 94.2 |
| 4 | 3 | 8.6 | 6.9 |
| 5 | 3 | 41.8 | 40.1 |
| 6 | 3 | 19.8 | 17.5 |
| 7 | 3 | 30.8 | 27.6 |
| 8 | 3 | 16.4 | 13.0 |
| 9 | 3 | 65.7 | 71.1 |
| 10 | 3 | 23.6 | 21.1 |
| 11 | 3 | 34.5 | 33.9 |
| 12 | 3 | 6.0 | 1.6* |
| 13 | 3 | 12.6 | 10.5 |
| 14 | 3 | 9.4 | 8.4 |
| 0 | 2 | 40.1 | 43.5 |
| 1 | 2 | 69.4 | 98.4** |
| 2 | 2 | 9.2 | 9.0 |
| 3 | 2 | 13.4 | 9.1 |
| 4 | 2 | 3.0 | 2.5* |
| 5 | 2 | 82.9 | 89.3 |
| 6 | 2 | 30.0 | 27.8 |
| 7 | 2 | 61.9 | 64.3 |
| 8 | 2 | 41.9 | 40.0 |
| 9 | 2 | 9.3 | 8.2 |
| 10 | 2 | 19.4 | 15.9 |
| 11 | 2 | 39.1 | 39.8 |
| 12 | 2 | 29.8 | 27.8 |
| 13 | 2 | 50.8 | 53.5 |
| 14 | 2 | 12.5 | 12.6 |
| 15 | 2 | 14.2 | 12.7 |
| 1 | 1 | 20.5 | 24.0 |
| 2 | 1 | 47.5 | 64.9** |
| 3 | 1 | 39.3 | 45.7 |
| 4 | 1 | 76.5 | 106.7** |
| 5 | 1 | 47.0 | 47.2 |
| 6 | 1 | 3.0 | 0.0* |
| 7 | 1 | 3.7 | 5.3* |
| 8 | 1 | 52.0 | 52.6 |
| 9 | 1 | 54.0 | 56.3 |
| 10 | 1 | 52.6 | 57.6 |
| 11 | 1 | 32.4 | 30.0 |
| 12 | 1 | 21.4 | 19.5 |
| 13 | 1 | 17.4 | 14.1 |
| 14 | 1 | 39.0 | 39.9 |
| 15 | 1 | 27.6 | 30.5 |
| 4 | 0 | 63.3 | 71.9** |
| 6 | 0 | 81.9 | 87.7 |
| 8 | 0 | 54.8 | 54.4 |
| 10 | 0 | 33.3 | 33.5 |
| 12 | 0 | 51.4 | 53.6 |
| 14 | 0 | 39.5 | 39.2 |
| 1,K,L | | | |
| 0 | 8 | 5.0 | 4.8 |
| 1 | 8 | 28.5 | 30.8 |
| 2 | 8 | 3.3 | 3.7* |
| 3 | 8 | 6.6 | 6.7 |
| 1 | 7 | 16.4 | 16.8 |
| 2 | 7 | 32.1 | 31.5 |
| 3 | 7 | 28.9 | 28.4 |
| 4 | 7 | 31.2 | 31.6 |
| 5 | 7 | 21.5 | 20.3 |
| 6 | 7 | 4.4 | 1.7* |
| 7 | 7 | 6.3 | 6.6 |
| 8 | 7 | 20.5 | 22.0 |
| 0 | 6 | 59.5 | 64.6 |
| 1 | 6 | 14.7 | 13.0 |
| 2 | 6 | 29.7 | 26.9 |
| 3 | 6 | 6.6 | 1.4* |
| 4 | 6 | 27.9 | 26.2 |
| 5 | 6 | 16.9 | 15.5 |
| 6 | 6 | 46.4 | 48.5 |
| 7 | 6 | 5.7 | 2.3* |
| 8 | 6 | 30.6 | 30.5 |
| 9 | 6 | 4.4 | 1.6* |
| 10 | 6 | 15.8 | 16.5 |
| 1 | 5 | 10.7 | 9.0 |
| 2 | 5 | 38.4 | 38.2 |
| 3 | 5 | 27.7 | 26.1 |
| 4 | 5 | 55.6 | 60.3 |
| 5 | 5 | 17.3 | 15.4 |
| 6 | 5 | 9.2 | 9.7 |
| 7 | 5 | 9.3 | 8.6 |
| 8 | 5 | 38.7 | 39.5 |
| 9 | 5 | 20.6 | 19.3 |
| 10 | 5 | 41.5 | 47.6 |
| 11 | 5 | 14.3 | 15.4 |
| 12 | 5 | 11.6 | 12.7 |
| 0 | 4 | 52.7 | 54.9 |
| 1 | 4 | 61.1 | 67.1 |
| 2 | 4 | 16.5 | 15.0 |
| 3 | 4 | 8.3 | 5.1* |
| 4 | 4 | 18.9 | 17.4 |
| 5 | 4 | 52.0 | 56.1 |
| 6 | 4 | 32.9 | 32.9 |
| 7 | 4 | 46.3 | 46.1 |
| 8 | 4 | 29.2 | 27.7 |
| 9 | 4 | 6.6 | 2.8* |
| 10 | 4 | 16.8 | 14.9 |
| 11 | 4 | 25.9 | 28.0 |
| 12 | 4 | 22.4 | 24.7 |
| 13 | 4 | 29.8 | 34.2 |
| 1 | 3 | 46.4 | 42.9 |
| 2 | 3 | 7.4 | 5.8 |
| 3 | 3 | 77.1 | 52.6 |
| 4 | 3 | 13.6 | 10.5 |
| 5 | 3 | 51.8 | 49.5 |
| 6 | 3 | 22.9 | 20.0 |
| 7 | 3 | 25.8 | 23.5 |
| 8 | 3 | 8.9 | 3.2* |
| 9 | 3 | 63.6 | 70.3 |
| 10 | 3 | 14.7 | 11.2 |
| 11 | 3 | 40.3 | 41.0 |
| 12 | 3 | 5.7 | 4.9* |
| 13 | 3 | 16.4 | 16.6 |
| 14 | 3 | 3.4 | 1.3* |
| 0 | 2 | 53.0 | 55.2 |
| 1 | 2 | 55.0 | 58.3 |
| 2 | 2 | 46.3 | 41.6 |
| 3 | 2 | 30.5 | 24.2 |
| 4 | 2 | 40.1 | 34.9 |
| 5 | 2 | 61.8 | 58.3 |
| 6 | 2 | 55.1 | 53.4 |
| 7 | 2 | 65.5 | 67.0 |
| 8 | 2 | 18.0 | 13.0 |
| 9 | 2 | 16.6 | 14.8 |
| 10 | 2 | 6.5 | 5.9 |
| 11 | 2 | 39.4 | 40.7 |
| 12 | 2 | 29.7 | 31.3 |
| 13 | 2 | 42.5 | 51.0 |
| 14 | 2 | 20.8 | 22.5 |
| 15 | 2 | 5.9 | 6.5 |
| 1 | 1 | 51.8 | 50.6 |
| 2 | 1 | 84.1 | 112.7** |
| 3 | 1 | 47.0 | 44.5 |
| 4 | 1 | 67.7 | 73.7 |
| 5 | 1 | 8.5 | 6.9 |
| 6 | 1 | 10.3 | 7.5 |
| 7 | 1 | 12.7 | 10.8 |
| 8 | 1 | 57.9 | 61.2 |
| 9 | 1 | 29.1 | 29.1 |
| 10 | 1 | 56.3 | 58.8 |
| 11 | 1 | 14.7 | 8.9 |
| 12 | 1 | 14.5 | 9.7 |
| 13 | 1 | 6.0 | 2.0* |
| 14 | 1 | 24.5 | 27.6 |
| 15 | 1 | 10.5 | 12.0 |
| 2 | 0 | 62.2 | 63.1 |
| 3 | 0 | 12.4 | 10.1 |
| 4 | 0 | 26.8 | 26.8 |
| 5 | 0 | 8.1 | 5.1 |
| 6 | 0 | 90.2 | 94.5 |
| 7 | 0 | 33.6 | 29.1 |
| 8 | 0 | 56.4 | 58.9 |
| 9 | 0 | 7.9 | 7.4 |
| 10 | 0 | 22.7 | 20.4 |
| 11 | 0 | 21.8 | 19.2 |
| 12 | 0 | 64.1 | 69.5 |
| 13 | 0 | 10.6 | 8.1 |
| 14 | 0 | 33.8 | 38.2 |
| 15 | 0 | 5.4 | 4.7 |
| 1 | -1 | 32.2 | 36.3 |
| 2 | -1 | 58.3 | 65.1 |
| 3 | -1 | 85.5 | 106.4** |
| 4 | -1 | 60.7 | 64.7 |
| 5 | -1 | 39.2 | 31.9 |
| 6 | -1 | 15.3 | 11.7 |
| 7 | -1 | 49.7 | 45.3 |
| 8 | -1 | 45.5 | 45.3 |
| 9 | -1 | 37.4 | 36.2 |
| 10 | -1 | 46.2 | 49.5 |
| 11 | -1 | 33.2 | 32.6 |
| 12 | -1 | 13.1 | 10.1 |
| 13 | -1 | 6.1 | 6.5* |
| 14 | -1 | 24.9 | 27.0 |
| 15 | -1 | 34.4 | 34.7 |
| 0 | -2 | 48.1 | 48.3 |
| 1 | -2 | 71.1 | 101.3** |
| 2 | -2 | 5.8 | 6.1 |
| 3 | -2 | 12.4 | 10.3 |
| 4 | -2 | 32.5 | 25.5 |
| 5 | -2 | 57.1 | 57.7 |
| 6 | -2 | 17.0 | 12.9 |
| 7 | -2 | 80.7 | 84.8 |
| 8 | -2 | 6.0 | 0.3* |
| 9 | -2 | 18.2 | 14.4 |
| 10 | -2 | 6.4 | 5.0* |
| 11 | -2 | 49.7 | 54.0 |
| 12 | -2 | 6.5 | 2.9* |
| 13 | -2 | 44.5 | 48.2 |
| 14 | -2 | 8.2 | 6.7 |
| 15 | -2 | 16.7 | 17.3 |
| 1 | -3 | 16.7 | 15.7 |
| 2 | -3 | 46.4 | 44.4 |
| 3 | -3 | 78.6 | 80.1 |
| 4 | -3 | 29.5 | 23.8 |
| 5 | -3 | 56.0 | 58.2 |
| 6 | -3 | 5.7 | 4.9* |
| 7 | -3 | 30.4 | 27.7 |
| 8 | -3 | 25.9 | 24.5 |
| 9 | -3 | 54.9 | 61.4 |
| 10 | -3 | 27.1 | 23.9 |
| 11 | -3 | 45.9 | 46.8 |
| 12 | -3 | 6.2 | 1.8* |
| 13 | -3 | 18.3 | 17.3 |
| 14 | -3 | 10.8 | 9.7 |
| 0 | -4 | 65.6 | 71.6 |
| 1 | -4 | 49.2 | 48.9 |
| 2 | -4 | 48.6 | 45.4 |
| 3 | -4 | 12.5 | 10.3 |
| 4 | -4 | 43.4 | 40.0 |
| 5 | -4 | 33.2 | 30.5 |
| 6 | -4 | 59.9 | 65.7 |
| 7 | -4 | 36.4 | 34.9 |
| 8 | -4 | 25.7 | 21.9 |
| 9 | -4 | 6.6 | 3.9* |
| 10 | -4 | 14.6 | 11.2 |
| 11 | -4 | 26.6 | 22.7 |
| 12 | -4 | 39.6 | 40.3 |
| 13 | -4 | 18.7 | 20.0 |
| 1 | -5 | 5.9 | 0.1* |
| 2 | -5 | 53.8 | 59.6 |
| 3 | -5 | 6.0 | 4.5* |
| 4 | -5 | 50.4 | 53.3 |
| 5 | -5 | 6.2 | 3.6* |
| 6 | -5 | 24.1 | 20.3 |
| 7 | -5 | 6.6 | 4.9* |
| 8 | -5 | 47.5 | 48.0 |
| 9 | -5 | 6.9 | 6.5 |
| 10 | -5 | 53.2 | 57.4 |
| 11 | -5 | 5.2 | 1.3* |
| 12 | -5 | 6.0 | 6.3 |
| 13 | -5 | 2.8 | 3.3* |
| 0 | -6 | 38.3 | 39.3 |
| 1 | -6 | 37.5 | 35.7 |
| 2 | -6 | 36.5 | 33.1 |
| 3 | -6 | 6.5 | 2.2* |
| 4 | -6 | 22.8 | 18.8 |
| 5 | -6 | 33.9 | 31.7 |
| 6 | -6 | 46.9 | 49.3 |
| 7 | -6 | 27.5 | 24.3 |
| 8 | -6 | 25.6 | 22.3 |
| 9 | -6 | 5.5 | 0.5* |
| 10 | -6 | 8.0 | 7.6 |
| 11 | -6 | 15.4 | 15.2 |
| 1 | -7 | 26.8 | 22.7 |
| 2 | -7 | 27.2 | 25.4 |
| 3 | -7 | 47.1 | 48.6 |
| 4 | -7 | 10.9 | 10.3 |
| 5 | -7 | 26.7 | 25.5 |
| 6 | -7 | 5.6 | 1.8* |
| 7 | -7 | 19.8 | 17.3 |
| 8 | -7 | 14.1 | 12.9 |
| 1 | -8 | 32.9 | 34.3 |
| 2 | -8 | 5.0 | 1.7* |
| 3 | -8 | 4.8 | 3.3* |
| 4 | -8 | 4.5 | 4.1* |
| 5 | -8 | 24.6 | 26.6 |
| 6 | -8 | 8.5 | 6.3 |
| 2,K,L | | | |
| 1 | 7 | 13.7 | 14.9 |
| 2 | 7 | 27.8 | 28.8 |
| 3 | 7 | 23.1 | 25.3 |
| 4 | 7 | 26.1 | 28.2 |
| 5 | 7 | 7.3 | 8.1 |
| 0 | 6 | 40.6 | 41.3 |
| 1 | 6 | 5.2 | 4.6* |
| 2 | 6 | 29.9 | 28.5 |
| 3 | 6 | 5.0 | 4.6* |
| 4 | 6 | 19.7 | 16.0 |
| 5 | 6 | 4.5 | 2.0* |
| 6 | 6 | 44.7 | 46.0 |
| 7 | 6 | 3.5 | 1.4* |
| 8 | 6 | 25.9 | 28.3 |
| 1 | 5 | 20.7 | 16.6 |
| 2 | 5 | 45.0 | 49.7 |
| 3 | 5 | 39.3 | 37.6 |
| 4 | 5 | 39.1 | 38.0 |
| 5 | 5 | 18.6 | 16.3 |
| 6 | 5 | 5.4 | 1.6* |
| 7 | 5 | 17.4 | 16.5 |
| 8 | 5 | 31.5 | 31.6 |
| 9 | 5 | 23.0 | 21.5 |
| 10 | 5 | 26.8 | 29.8 |
| 0 | 4 | 25.1 | 25.3 |
| 1 | 4 | 45.3 | 50.2 |
| 2 | 4 | 15.3 | 14.9 |
| 3 | 4 | 7.8 | 5.5* |
| 4 | 4 | 14.8 | 14.1 |
| 5 | 4 | 37.0 | 36.9 |
| 6 | 4 | 22.9 | 22.3 |
| 7 | 4 | 52.3 | 58.0 |
| 8 | 4 | 9.6 | 8.1 |
| 9 | 4 | 16.9 | 13.7 |
| 10 | 4 | 4.5 | 4.3* |
| 11 | 4 | 35.7 | 39.8 |
| 12 | 4 | 11.7 | 14.7 |
| 1 | 3 | 28.2 | 27.3 |
| 2 | 3 | 28.0 | 26.3 |
| 3 | 3 | 69.0 | 74.4 |
| 4 | 3 | 19.0 | 15.0 |
| 5 | 3 | 39.5 | 41.9 |
| 6 | 3 | 12.3 | 9.4 |
| 7 | 3 | 30.3 | 27.8 |
| 8 | 3 | 11.5 | 9.2 |
| 9 | 3 | 52.1 | 51.5 |
| 10 | 3 | 9.3 | 5.0 |
| 11 | 3 | 37.2 | 37.9 |
| 12 | 3 | 3.8 | 3.0* |
| 13 | 3 | 10.9 | 12.0 |
| 0 | 2 | 54.4 | 56.9 |
| 1 | 2 | 62.2 | 64.9 |
| 2 | 2 | 36.2 | 33.6 |
| 3 | 2 | 20.3 | 15.3 |
| 4 | 2 | 26.4 | 22.2 |
| 5 | 2 | 43.5 | 42.9 |
| 6 | 2 | 51.0 | 55.2 |
| 7 | 2 | 39.4 | 41.4 |
| 8 | 2 | 34.0 | 30.6 |
| 9 | 2 | 8.1 | 2.3* |
| 10 | 2 | 18.8 | 14.2 |
| 11 | 2 | 30.4 | 26.8 |
| 12 | 2 | 39.1 | 37.9 |
| 13 | 2 | 23.7 | 24.5 |
| 1 | 1 | 8.8 | 8.8 |
| 2 | 1 | 61.1 | 63.2 |
| 3 | 1 | 14.7 | 15.1 |
| 4 | 1 | 66.1 | 70.2 |
| 5 | 1 | 15.2 | 14.0 |
| 6 | 1 | 27.2 | 23.8 |
| 7 | 1 | 9.1 | 7.3 |
| 8 | 1 | 49.7 | 54.7 |
| 9 | 1 | 9.7 | 7.9 |
| 10 | 1 | 62.0 | 68.9 |
| 11 | 1 | 13.8 | 12.3 |
| 12 | 1 | 12.5 | 9.8 |
| 13 | 1 | 6.0 | 4.9 |
| 14 | 1 | 33.8 | 37.0 |
| 1 | 0 | 38.1 | 40.5 |
| 2 | 0 | 52.3 | 52.4 |
| 3 | 0 | 3.5 | 0.7* |
| 4 | 0 | 50.1 | 45.3 |
| 5 | 0 | 50.6 | 44.1 |
| 6 | 0 | 72.1 | 77.4 |
| 7 | 0 | 24.8 | 18.3 |
| 8 | 0 | 30.4 | 28.9 |
| 9 | 0 | 5.5 | 0.2* |
| 10 | 0 | 18.1 | 14.4 |
| 11 | 0 | 13.9 | 11.8 |
| 12 | 0 | 47.6 | 46.9 |
| 13 | 0 | 25.6 | 21.0 |
| 14 | 0 | 31.1 | 34.5 |
| 1 | -1 | 33.4 | 34.3 |
| 2 | -1 | 59.0 | 60.7 |
| 3 | -1 | 58.9 | 63.7 |
| 4 | -1 | 32.2 | 29.9 |
| 5 | -1 | 52.4 | 49.6 |
| 6 | -1 | 8.1 | 5.7 |
| 7 | -1 | 27.4 | 15.3 |
| 8 | -1 | 31.3 | 31.3 |
| 9 | -1 | 60.9 | 66.7 |
| 10 | -1 | 33.5 | 30.9 |
| 11 | -1 | 37.1 | 36.2 |
| 12 | -1 | 5.4 | 2.4* |
| 13 | -1 | 18.2 | 15.4 |
| 14 | -1 | 11.6 | 10.7 |
| 0 | -2 | 27.7 | 34.1 |
| 1 | -2 | 67.4 | 74.2 |
| 2 | -2 | 9.1 | 9.6 |
| 3 | -2 | 9.3 | 10.3 |
| 4 | -2 | 13.1 | 13.3 |
| 5 | -2 | 60.2 | 64.6 |
| 6 | -2 | 4.8 | 3.9* |
| 7 | -2 | 66.1 | 70.0 |
| 8 | -2 | 5.3 | 0.5* |
| 9 | -2 | 17.7 | 14.3 |
| 10 | -2 | 9.9 | 6.8 |
| 11 | -2 | 43.7 | 45.2 |
| 12 | -2 | 5.2 | 6.1* |
| 13 | -2 | 47.0 | 51.7 |
| 14 | -2 | 4.5 | 0.5* |
| 1 | -3 | 32.2 | 40.5* |
| 2 | -3 | 31.3 | 33.6 |
| 3 | -3 | 72.0 | 75.3 |
| 4 | -3 | 51.0 | 52.8 |
| 5 | -3 | 31.3 | 28.7 |
| 6 | -3 | 7.1 | 4.4* |
| 7 | -3 | 31.4 | 29.1 |
| 8 | -3 | 31.0 | 28.3 |
| 9 | -3 | 41.6 | 43.2 |
| 10 | -3 | 32.8 | 29.1 |
| 11 | -3 | 29.2 | 26.7 |
| 12 | -3 | 16.6 | 11.7 |
| 13 | -3 | 6.7 | 5.7 |
| 0 | -4 | 68.4 | 69.8 |
| 1 | -4 | 24.4 | 23.6 |
| 2 | -4 | 28.4 | 29.8 |
| 3 | -4 | 4.4 | 1.5* |
| 4 | -4 | 17.4 | 17.8 |
| 5 | -4 | 15.3 | 14.0 |
| 6 | -4 | 53.1 | 57.8 |
| 7 | -4 | 25.7 | 23.7 |
| 8 | -4 | 45.5 | 49.0 |
| 9 | -4 | 8.1 | 5.4* |
| 10 | -4 | 26.0 | 22.0 |
| 11 | -4 | 19.1 | 15.8 |
| 12 | -4 | 42.4 | 47.3 |
| 13 | -4 | 11.2 | 13.6 |
| 1 | -5 | 20.6 | 19.3 |
| 2 | -5 | 47.9 | 53.2 |
| 3 | -5 | 20.6 | 17.1 |
| 4 | -5 | 54.1 | 60.9 |
| 5 | -5 | 5.6 | 1.7* |
| 6 | -5 | 5.9 | 0.6* |
| 7 | -5 | 5.7 | 5.2* |
| 8 | -5 | 39.3 | 39.7 |
| 9 | -5 | 16.1 | 12.3 |
| 10 | -5 | 39.3 | 41.1 |
| 11 | -5 | 4.0 | 1.4* |
| 0 | -6 | 42.1 | 47.2 |
| 1 | -6 | 32.7 | 31.1 |
| 2 | -6 | 17.8 | 18.0 |
| 3 | -6 | 12.6 | 10.8 |
| 4 | -6 | 20.6 | 20.0 |
| 5 | -6 | 34.3 | 34.9 |
| 6 | -6 | 33.4 | 32.8 |
| 7 | -6 | 32.9 | 32.3 |
| 8 | -6 | 19.0 | 19.1 |
| 9 | -6 | 8.6 | 7.0 |
| 10 | -6 | 11.2 | 10.8 |
| 1 | -7 | 27.5 | 26.5 |
| 2 | -7 | 5.5 | 1.5* |
| 3 | -7 | 38.7 | 41.7 |
| 4 | -7 | 9.0 | 7.5 |
| 5 | -7 | 29.0 | 26.4 |
| 6 | -7 | 6.4 | 4.2 |
| 7 | -7 | 12.8 | 10.1 |
| 8 | -7 | 7.6 | 4.6 |
| 1 | -8 | 32.8 | 32.6 |
| 2 | -8 | 10.6 | 8.1 |
| 3 | -8 | 3.8 | 3.7* |
| 4 | -8 | 10.0 | 8.2 |
| 3,K,L | | | |
| 0 | 6 | 38.6 | 44.9 |
| 1 | 6 | 6.9 | 6.6 |
| 2 | 6 | 16.3 | 20.7 |
| 3 | 6 | 2.3 | 3.4* |
| 1 | 5 | 14.8 | 14.3 |
| 2 | 5 | 25.9 | 24.0 |
| 3 | 5 | 29.3 | 28.2 |
| 4 | 5 | 27.8 | 26.8 |
| 5 | 5 | 22.2 | 22.6 |
| 6 | 5 | 6.4 | 7.0 |
| 7 | 5 | 7.2 | 6.1 |
| 0 | 4 | 7.4 | 0.1* |
| 1 | 4 | 43.8 | 49.8 |
| 2 | 4 | 7.3 | 5.9 |
| 3 | 4 | 5.2 | 0.8* |
| 4 | 4 | 5.0 | 2.3* |
| 5 | 4 | 46.8 | 45.9 |
| 6 | 4 | 11.9 | 8.7 |
| 7 | 4 | 38.1 | 37.7 |
| 8 | 4 | 9.4 | 7.3 |
| 9 | 4 | 5.6 | 5.0 |
| 1 | 3 | 30.0 | 31.8 |
| 2 | 3 | 11.4 | 10.8 |
| 3 | 3 | 52.5 | 55.5 |
| 4 | 3 | 26.5 | 25.7 |
| 5 | 3 | 30.1 | 25.7 |
| 6 | 3 | 9.0 | 7.1 |
| 7 | 3 | 22.6 | 19.8 |
| 8 | 3 | 19.3 | 16.7 |
| 9 | 3 | 41.7 | 41.9 |
| 10 | 3 | 21.5 | 22.2 |
| 0 | 2 | 52.0 | 58.9 |
| 1 | 2 | 25.1 | 22.4 |
| 2 | 2 | 26.9 | 25.9 |
| 3 | 2 | 11.6 | 9.9 |
| 4 | 2 | 23.8 | 20.1 |
| 5 | 2 | 25.0 | 20.5 |
| 6 | 2 | 47.2 | 47.5 |
| 7 | 2 | 36.0 | 32.3 |
| 8 | 2 | 37.0 | 35.0 |
| 9 | 2 | 12.5 | 10.2 |
| 10 | 2 | 18.6 | 16.2 |
| 11 | 2 | 22.0 | 22.5 |
| 1 | 1 | 3.7 | 2.3* |
| 2 | 1 | 63.3 | 66.5 |
| 3 | 1 | 4.1 | 3.4* |
| 4 | 1 | 59.8 | 65.8 |
| 5 | 1 | 4.7 | 0.9* |
| 6 | 1 | 11.2 | 6.4 |
| 7 | 1 | 5.2 | 0.7* |
| 8 | 1 | 45.2 | 43.3 |
| 9 | 1 | 5.1 | 3.1* |
| 10 | 1 | 42.3 | 40.4 |
| 11 | 1 | 4.0 | 1.3* |
| 12 | 1 | 12.8 | 14.1 |
| 1 | 0 | 24.3 | 28.4 |
| 2 | 0 | 27.3 | 26.2 |
| 3 | 0 | 11.6 | 13.2 |
| 4 | 0 | 20.9 | 20.2 |
| 5 | 0 | 29.2 | 28.0 |
| 6 | 0 | 50.9 | 49.5 |
| 7 | 0 | 42.4 | 39.8 |
| 8 | 0 | 38.3 | 36.6 |
| 9 | 0 | 12.8 | 9.6 |
| 10 | 0 | 20.9 | 17.8 |
| 11 | 0 | 26.5 | 25.3 |
| 12 | 0 | 35.9 | 36.9 |
| 1 | -1 | 43.8 | 42.9 |
| 2 | -1 | 7.7 | 6.7 |
| 3 | -1 | 69.3 | 68.8 |
| 4 | -1 | 29.4 | 26.6 |
| 5 | -1 | 35.0 | 31.6 |
| 6 | -1 | 8.1 | 7.0 |
| 7 | -1 | 24.4 | 21.5 |
| 8 | -1 | 17.5 | 14.0 |
| 9 | -1 | 55.2 | 53.0 |
| 10 | -1 | 25.6 | 22.3 |
| 11 | -1 | 30.5 | 28.5 |
| 12 | -1 | 6.3 | 6.4 |
| 13 | -1 | 10.4 | 9.7 |
| 0 | -2 | 6.5 | 5.4 |
| 1 | -2 | 58.0 | 63.9 |
| 2 | -2 | 12.5 | 12.3 |
| 3 | -2 | 6.2 | 4.7 |
| 4 | -2 | 2.8 | 1.2* |
| 5 | -2 | 59.2 | 62.4 |
| 6 | -2 | 20.3 | 17.0 |
| 7 | -2 | 49.6 | 47.9 |
| 8 | -2 | 14.7 | 11.4 |
| 9 | -2 | 7.4 | 5.1 |
| 10 | -2 | 4.9 | 2.6* |
| 11 | -2 | 30.8 | 29.2 |
| 12 | -2 | 16.4 | 16.4 |
| 1 | -3 | 22.0 | 23.0 |
| 2 | -3 | 34.2 | 38.0 |
| 3 | -3 | 32.7 | 35.1 |
| 4 | -3 | 37.4 | 41.5 |
| 5 | -3 | 27.6 | 28.2 |
| 6 | -3 | 11.9 | 10.2 |
| 7 | -3 | 7.3 | 5.3 |
| 8 | -3 | 34.8 | 33.1 |
| 9 | -3 | 43.0 | 43.7 |
| 10 | -3 | 35.2 | 37.6 |
| 11 | -3 | 22.7 | 21.8 |
| 12 | -3 | 5.3 | 6.7 |
| 1 | -4 | 4.5 | 3.8* |
| 2 | -4 | 29.1 | 31.8 |
| 3 | -4 | 9.1 | 8.2 |
| 4 | -4 | 32.3 | 32.7 |
| 5 | -4 | 12.8 | 11.3 |
| 6 | -4 | 49.4 | 53.6 |
| 7 | -4 | 9.1 | 5.3 |
| 8 | -4 | 29.0 | 26.6 |
| 9 | -4 | 4.7 | 2.3* |
| 10 | -4 | 17.5 | 14.7 |
| 11 | -4 | 4.7 | 2.1* |
| 1 | -5 | 5.1 | 1.4* |
| 2 | -5 | 37.7 | 40.1 |
| 3 | -5 | 21.4 | 21.5 |
| 4 | -5 | 39.6 | 45.7 |
| 5 | -5 | 19.2 | 18.1 |
| 6 | -5 | 5.2 | 3.8* |
| 7 | -5 | 10.5 | 8.3 |
| 8 | -5 | 33.2 | 32.1 |
| 9 | -5 | 19.5 | 18.1 |
| 10 | -5 | 28.0 | 34.6* |
| 0 | -6 | 21.0 | 23.4 |
| 1 | -6 | 35.2 | 38.9 |
| 2 | -6 | 11.0 | 10.5 |
| 3 | -6 | 5.1 | 2.2* |
| 4 | -6 | 5.0 | 4.9* |
| 5 | -6 | 26.7 | 28.9 |
| 6 | -6 | 21.2 | 20.3 |
| 7 | -6 | 33.0 | 34.8 |
| 8 | -6 | 20.0 | 20.3 |
| 9 | -6 | 4.7 | 5.0 |
| 1 | -7 | 20.7 | 20.3 |
| 2 | -7 | 4.3 | 2.6* |
| 3 | -7 | 38.1 | 43.9 |
| 4 | -7 | 3.9 | 2.0* |
| 5 | -7 | 19.8 | 20.5 |
| 6 | -7 | 6.2 | 4.8 |
| 7 | -7 | 16.0 | 17.4 |
| HBR.3H2O | | | |
| 0,K,L | | | |
| 2 | 0 | 124.8 | 149.8** |
| 4 | 0 | 63.7 | 61.5 |
| 6 | 0 | 32.0 | 28.1 |
| 0 | 2 | 53.7 | 70.8** |
| 2 | 2 | 68.7 | 79.1** |
| 4 | 2 | 69.4 | 74.2 |
| 6 | 2 | 43.5 | 44.5 |
| 0 | 4 | 90.2 | 120.1** |
| 2 | 4 | 77.7 | 83.3 |
| 4 | 4 | 44.1 | 43.0 |
| 6 | 4 | 24.5 | 23.5 |
| 0 | 6 | 90.2 | 95.3 |
| 2 | 6 | 74.4 | 80.8 |
| 4 | 6 | 57.7 | 57.5 |
| 6 | 6 | 30.3 | 32.6 |
| 0 | 8 | 72.9 | 77.4 |
| 2 | 8 | 64.2 | 65.2 |
| 4 | 8 | 50.1 | 46.0 |
| 6 | 8 | 28.0 | 28.3 |
| 0 | 10 | 63.5 | 61.7 |
| 2 | 10 | 52.1 | 50.9 |
| 4 | 10 | 33.3 | 31.6 |
| 0 | 12 | 34.7 | 32.4 |
| 2 | 12 | 35.4 | 32.5 |
| 4 | 12 | 28.0 | 29.7 |
| 0 | 14 | 44.0 | 40.4 |
| 2 | 14 | 36.3 | 32.7 |
| 1,K,L | | | |
| 2 | 0 | 39.7 | 35.7 |
| 4 | 0 | 21.0 | 17.0 |
| 6 | 0 | 6.4 | 1.7* |
| 1 | 1 | 80.9 | 96.7** |
| 3 | 1 | 67.1 | 71.2 |
| 5 | 1 | 45.6 | 45.4 |
| 7 | 1 | 24.3 | 22.8 |
| 2 | 2 | 37.9 | 33.5 |
| 4 | 2 | 19.2 | 16.6 |
| 6 | 2 | 6.3 | 1.4* |
| 1 | 3 | 107.6 | 136.8** |
| 3 | 3 | 79.1 | 85.9 |
| 5 | 3 | 49.1 | 46.5 |
| 7 | 3 | 22.8 | 23.2 |
| 2 | 4 | 29.8 | 27.4 |
| 4 | 4 | 16.0 | 14.3 |
| 6 | 4 | 5.9 | 1.8* |
| 1 | 5 | 79.4 | 95.1 |
| 3 | 5 | 64.9 | 70.3 |
| 5 | 5 | 46.9 | 46.6 |
| 7 | 5 | 20.5 | 23.8 |
| 2 | 6 | 22.3 | 20.8 |
| 4 | 6 | 14.0 | 11.9 |
| 6 | 6 | 5.1 | 1.7* |
| 1 | 7 | 69.3 | 73.4 |
| 3 | 7 | 48.3 | 50.0 |
| 5 | 7 | 29.1 | 27.4 |
| 2 | 8 | 16.1 | 15.1 |
| 4 | 8 | 9.4 | 9.4 |
| 6 | 8 | 3.8 | 1.9* |
| 1 | 9 | 51.8 | 53.3 |
| 3 | 9 | 48.8 | 46.8 |
| 5 | 9 | 33.6 | 32.5 |
| 2 | 10 | 11.4 | 10.7 |
| 4 | 10 | 5.6 | 7.2* |
| 1 | 11 | 57.9 | 52.3 |
| 3 | 11 | 43.1 | 38.3 |
| 5 | 11 | 21.5 | 22.8 |
| 2 | 12 | 5.7 | 7.8* |
| 4 | 12 | 3.6 | 5.7* |
| 1 | 13 | 36.1 | 33.6 |
| 3 | 13 | 27.1 | 28.3 |
| 2 | 14 | 3.3 | 5.5* |
| 2,K,L | | | |
| 2 | 0 | 98.6 | 95.4 |
| 4 | 0 | 69.8 | 74.8 |
| 6 | 0 | 41.5 | 43.1 |
| 1 | 1 | 21.6 | 18.0 |
| 3 | 1 | 24.3 | 22.0 |
| 5 | 1 | 6.2 | 4.9* |
| 7 | 1 | 3.8 | 3.9* |
| 0 | 2 | 120.1 | 129.6 |
| 2 | 2 | 96.0 | 93.6 |
| 4 | 2 | 48.6 | 47.6 |
| 6 | 2 | 26.9 | 24.0 |
| 1 | 3 | 18.5 | 15.6 |
| 3 | 3 | 22.3 | 19.6 |
| 5 | 3 | 6.4 | 4.3* |
| 7 | 3 | 3.3 | 3.9* |
| 0 | 4 | 61.6 | 64.9 |
| 2 | 4 | 62.2 | 61.3 |
| 4 | 4 | 50.2 | 49.9 |
| 6 | 4 | 29.1 | 29.5 |
| 1 | 5 | 14.1 | 12.4 |
| 3 | 5 | 17.0 | 16.6 |
| 5 | 5 | 6.3 | 4.4* |
| 0 | 6 | 81.3 | 86.1 |
| 2 | 6 | 67.5 | 71.7 |
| 4 | 6 | 46.4 | 47.2 |
| 6 | 6 | 25.9 | 27.2 |
| 1 | 7 | 10.0 | 8.9 |
| 3 | 7 | 14.5 | 12.5 |
| 5 | 7 | 5.6 | 3.3* |
| 0 | 8 | 65.7 | 70.8 |
| 2 | 8 | 60.1 | 61.4 |
| 4 | 8 | 44.9 | 42.2 |
| 6 | 8 | 21.1 | 23.4 |
| 1 | 9 | 8.4 | 6.5 |
| 3 | 9 | 11.1 | 9.9 |
| 5 | 9 | 4.4 | 3.2* |
| 0 | 10 | 46.6 | 43.4 |
| 2 | 10 | 43.0 | 39.9 |
| 4 | 10 | 30.3 | 31.4 |
| 1 | 11 | 6.2 | 4.6* |
| 3 | 11 | 5.3 | 7.2* |
| 0 | 12 | 43.1 | 43.4 |
| 2 | 12 | 36.4 | 36.1 |
| 4 | 12 | 15.5 | 22.0 |
| 1 | 13 | 4.6 | 3.4* |
| 3 | 13 | 3.0 | 5.5* |
| 0 | 14 | 27.2 | 25.2 |
| 2 | 14 | 21.0 | 24.7 |
| 3,K,L | | | |
| 2 | 0 | 10.5 | 7.4 |
| 4 | 0 | 5.9 | 4.0* |
| 6 | 0 | 5.5 | 0.3* |
| 1 | 1 | 86.1 | 90.3 |
| 3 | 1 | 61.9 | 56.5 |
| 5 | 1 | 38.2 | 32.9 |
| 7 | 1 | 13.7 | 16.5 |
| 2 | 2 | 9.4 | 6.4 |
| 4 | 2 | 6.0 | 3.0* |
| 6 | 2 | 5.3 | 1.1* |
| 1 | 3 | 78.6 | 74.2 |
| 3 | 3 | 66.3 | 67.3 |
| 5 | 3 | 48.5 | 48.9 |
| 2 | 4 | 6.8 | 6.0 |
| 4 | 4 | 6.4 | 3.4* |
| 6 | 4 | 4.8 | 0.4* |
| 1 | 5 | 85.2 | 91.3 |
| 3 | 5 | 53.9 | 55.9 |
| 5 | 5 | 31.2 | 27.3 |
| 2 | 6 | 5.5 | 4.5* |
| 4 | 6 | 6.7 | 2.6* |
| 6 | 6 | 3.8 | 1.0* |
| 1 | 7 | 37.8 | 36.3 |
| 3 | 7 | 43.1 | 42.2 |
| 5 | 7 | 30.6 | 34.6 |
| 2 | 8 | 6.4 | 3.5* |
| 4 | 8 | 6.0 | 2.0* |
| 1 | 9 | 58.0 | 58.9 |
| 3 | 9 | 33.3 | 36.9 |
| 5 | 9 | 19.6 | 17.7 |
| 2 | 10 | 6.3 | 2.8* |
| 4 | 10 | 4.5 | 2.0* |
| 1 | 11 | 37.5 | 34.9 |
| 3 | 11 | 33.3 | 33.5 |
| 2 | 12 | 4.6 | 1.9* |
| 1 | 13 | 28.6 | 31.7 |
| 4,K,L | | | |
| 2 | 0 | 69.7 | 68.3 |
| 4 | 0 | 48.3 | 49.3 |
| 6 | 0 | 27.7 | 28.8 |
| 1 | 1 | 14.7 | 13.7 |
| 3 | 1 | 19.6 | 18.9 |
| 5 | 1 | 6.6 | 4.5* |
| 0 | 2 | 66.6 | 71.2 |
| 2 | 2 | 58.3 | 60.5 |
| 4 | 2 | 43.0 | 39.4 |
| 6 | 2 | 23.5 | 21.3 |
| 1 | 3 | 12.4 | 12.6 |
| 3 | 3 | 17.8 | 17.6 |
| 5 | 3 | 6.3 | 4.8* |
| 0 | 4 | 47.7 | 51.4 |
| 2 | 4 | 48.5 | 46.9 |
| 4 | 4 | 37.1 | 34.9 |
| 6 | 4 | 19.8 | 20.4 |
| 1 | 5 | 11.0 | 10.3 |
| 3 | 5 | 15.3 | 14.8 |
| 5 | 5 | 5.7 | 3.6* |
| 0 | 6 | 55.3 | 59.3 |
| 2 | 6 | 52.0 | 51.7 |
| 4 | 6 | 37.7 | 35.5 |
| 1 | 7 | 9.4 | 8.5 |
| 3 | 7 | 12.0 | 13.1 |
| 5 | 7 | 4.5 | 4.1* |
| 0 | 8 | 49.2 | 49.2 |
| 2 | 8 | 48.6 | 44.1 |
| 4 | 8 | 34.6 | 31.6 |
| 1 | 9 | 6.9 | 6.3* |
| 3 | 9 | 8.3 | 9.8 |
| 0 | 10 | 35.0 | 35.1 |
| 2 | 10 | 31.9 | 31.3 |
| 4 | 10 | 19.3 | 22.6 |
| 1 | 11 | 5.5 | 5.0* |
| 3 | 11 | 3.8 | 8.2* |
| 0 | 12 | 29.9 | 29.5 |
| 2 | 12 | 23.3 | 26.0 |
| 5,K,L | | | |
| 2 | 0 | 11.2 | 9.7 |
| 4 | 0 | 4.9 | 7.0* |
| 6 | 0 | 1.8 | 0.2* |
| 1 | 1 | 49.9 | 44.8 |
| 3 | 1 | 40.9 | 38.4 |
| 5 | 1 | 27.7 | 28.0 |
| 2 | 2 | 10.3 | 8.7 |
| 4 | 2 | 4.8 | 5.8* |
| 1 | 3 | 63.4 | 65.3 |
| 3 | 3 | 45.3 | 43.4 |
| 5 | 3 | 25.2 | 23.4 |
| 2 | 4 | 9.5 | 8.4 |
| 4 | 4 | 4.5 | 6.2* |
| 1 | 5 | 41.2 | 36.1 |
| 3 | 5 | 40.1 | 37.9 |
| 5 | 5 | 25.7 | 29.9 |
| 2 | 6 | 5.0 | 6.9* |
| 4 | 6 | 4.0 | 5.0* |
| 1 | 7 | 41.3 | 45.1 |
| 3 | 7 | 27.7 | 27.6 |
| 2 | 8 | 4.5 | 5.7* |
| 4 | 8 | 2.8 | 4.3* |
| 1 | 9 | 30.8 | 26.4 |
| 3 | 9 | 24.5 | 27.2 |
| 2 | 10 | 3.3 | 4.7* |
| 1 | 11 | 26.7 | 31.6 |

and calculated structure factors are listed in Table 5.

## Description of the structure

Stereoscopic drawings of the structures are shown in Figs. 1, 2 and 4. Interatomic distances and angles are listed in Table 6 and are illustrated in Figs. 3 and 5. The corrections of the bond lengths for anisotropic thermal motion, assuming riding motion, are less than 0·008 Å in all cases. The corrections, assuming independent motion, are less than 0·016 Å for $HBr.H_2O$ and $HBr.2H_2O$, and less than 0·026 Å for $HBr.3H_2O$. The program *ORFFE* was used for the interatomic distance and angle calculations. All illustrations in this paper were prepared with the plotting program *ORTEP*.

No hydrogen atoms were located experimentally in these investigations. The hydrogen bonds have therefore been derived from interatomic distances and angles defined by the heavy atoms.

## $HBr.H_2O$

The structure is shown in Fig. 1. The oxygen and bromine atoms are hydrogen-bonded together to form puckered layers. Each oxygen atom occupies a site with $3m$ point symmetry with three bromine atoms as nearest neighbours. The bromine atoms form the base of a flat trigonal pyramid with the oxygen atom at the apex. Each bromine atom is similarly surrounded by oxygen atoms. The Br···O distance is 3·10 Å and the Br···O···Br angle is 109·2°. The shortest distance from an oxygen atom in one layer to a bromine atom in an adjacent layer is 3·49 Å. The most natural conclusion to be drawn from the heavy-atom structure is that the oxygen atom represents an oxonium ion, $H_3O^+$, and that the O···Br distance of 3·10 Å represents a hydrogen bond. The compound should accordingly be formulated as $H_3O^+Br^-$, oxonium bromide.

The situation is then analogous to that in oxonium chloride, $H_3O^+Cl^-$, where the arrangement of the heavy atoms is the same (Yoon & Carpenter, 1959). In this compound the hydrogen atoms were located to give bent O–H···Cl bonds and an H–O–H angle of approximately 117°. A disordered structure, space group $R\bar{3}m$, was reported as the most probable for oxonium chloride. In this disordered structure, where oxygen half-atoms occupy positions related by a centre of symmetry, adjacent planes of chloride ions are separated by interleaving oxonium ions. These form hydrogen bonds randomly to one or other of the planes of chloride ions. The disordered structure gave slightly better agreement with the observed data than did the ordered structure. No disorder of this type is found in the present compound.

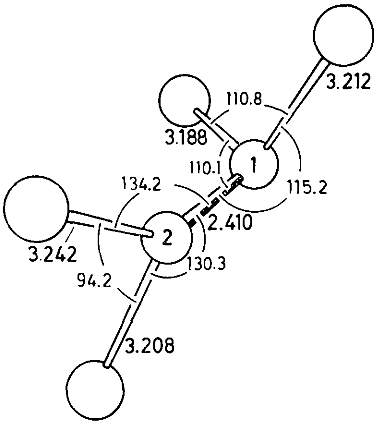


Fig. 3. Bond distances and angles subtended at the oxygen atoms in $H_5O_2^+Br^-$. The orientation is the same as in Fig. 2. For notation see Fig. 2.

## $HBr.2H_2O$

A stereoscopic illustration of the structure is shown in Fig. 2. There are five hydrogen atoms available for hydrogen bonding in the asymmetric unit. The distances and angles associated with the heavy atoms indicate that there is one hydrogen bond between the oxygen atoms and four O–H···Br bonds. The O–H···Br bonds are 3·19, 3·21, 3·21 and 3·24 Å. All other O···Br distances are longer than 3·58 Å. The bond between the oxygen atoms is 2·41 Å. This very short O···O distance indicates that the proton of HBr has been transferred to the water molecules, as a hydrogen bond between normal water molecules is about 2·76 Å. Since the bond is extremely short, the conditions for a single potential minimum, whether symmetric or asymmetric, may be fulfilled. This fact implies that the proton between the two water molecules associates with each of them to approximately the same extent. The appropriate formulation of the hydrogen-bonded species $H_2O(1)\cdots H\cdots O(2)H_2$ is then $H_5O_2^+$. These ions are hydrogen-bonded to the bromide ions which form puckered layers parallel to the *ac* plane. One end, O(1), is bonded to two bromide ions belonging to the same layer, and the other end, O(2), is bonded to two bromide ions in adjacent layers. There are no hydrogen bonds between the separate $H_5O_2^+$ ions. The angles and distances in and around $H_5O_2^+$ are shown in Fig. 3. The configuration of the ion is *gauche*. The compound is isostructural with hydrogen chloride dihydrate, $H_5O_2^+Cl^-$ (Lundgren & Olovsson, 1967*a*).

## $HBr.3H_2O$

A stereoscopic drawing of the structure of the trihydrate is shown in Fig. 4. There are seven hydrogen atoms available for hydrogen bonding per formula unit. The positions of the oxygen atoms with respect to the symmetry elements of the space group imply that only four of these are crystallographically independent (see Table 4). The interatomic distances and angles indicate two different O–H···O bonds and two O–H···Br bonds. The two O···O distances are 2·47 and 2·68 Å. Both are shorter than a hydrogen bond between normal water molecules. These short O···O distances are thus a clear indication that the proton of HBr has been transferred to the water molecules. The O···Br distances are 3·27 and 3·39 Å. (The next shortest O···O and O···Br distances are 3·10 and 3·50 Å respectively.) Making the assumption that these four distances mentioned above correspond to hydrogen bonds the structure can be described as follows.

Layers of bromide ions parallel to the *ab* plane (at $z=0$ and $z=\frac{1}{2}$) are interleaved by water molecules. The water molecules are bonded to one another to form chains extending in the *a* direction. O–H···Br bonds connect the water chains to the layers of bromide ions. No hydrogen bonds exist between the separate water chains. The hydrogen-bond arrangement around the two independent water molecules in the chain is

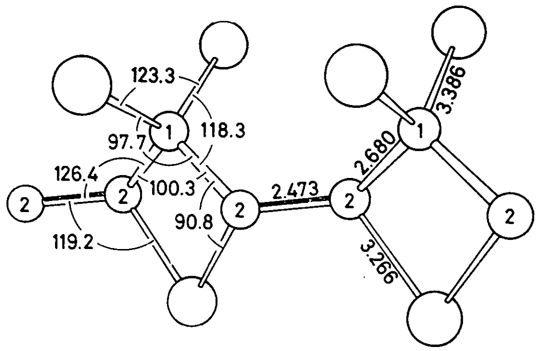


Fig. 5. Bond distances and angles subtended at the oxygen atoms in $H_5O_2^+Br^-.H_2O$. The orientation is the same as in in Fig. 4. For notation see Fig. 2.

Table 6. *Interatomic distances and angles with standard deviations*

The distances are not corrected for thermal motion; for corrected distances, see text.

| | | | |
|---|---|---|---|
| $HBr.H_2O$ | | | |
| Br···O | 3·103 (10) Å | Br···O···Br | 109·2 (0·5)° |
| $HBr.2H_2O$ | | | |
| O(1)···O(2) | 2·410 (13) Å | Br···O(2)···Br | 94·2 (0·3)° |
| | | ···O(1) | 130·3 (0·4) |
| Br···O(1) | 3·188 (8) | ···O(1) | 134·2 (0·4) |
| ···O(1) | 3·212 (8) | | |
| ···O(2) | 3·208 (9) | O(1)···Br···O(1) | 129·7 (0·2) |
| ···O(2) | 3·242 (9) | ···O(2) | 117·8 (0·3) |
| | | ···O(2) | 116·1 (0·2) |
| Br···O(1)···Br | 110·8 (0·2)° | ···O(2) | 90·9 (0·2) |
| ···O(2) | 110·1 (0·4) | ···O(2) | 105·7 (0·3) |
| ···O(2) | 115·2 (0·4) | O(2)···Br···O(2) | 85·8 (0·3) |
| $HBr.3H_2O$ | | | |
| O(1)···O(2) | 2·680 (21) Å | Br···O(2)···O(1) | 90·8 (0·5)° |
| O(2)···O(2) | 2·473 (18) | ···O(2) | 119·2 (0·4) |
| | | O(1)···O(2)···O(2) | 126·4 (0·6) |
| Br···O(1) | 3·386 (14) | | |
| ···O(2) | 3·266 (13) | O(1)···Br···O(1) | 123·3 (0·8) |
| | | ···O(2) | 120·5 (0·4) |
| Br ···O(1)···Br | 123·3 (0·8)° | ···O(2) | 103·2 (0·4) |
| ···O(2) | 118·3 (0·3) | O(2)···Br···O(2) | 78·1 (0·4) |
| ···O(2) | 97·7 (0·3) | | |
| O(2)···O(1)···O(2) | 100·3 (1·1) | | |

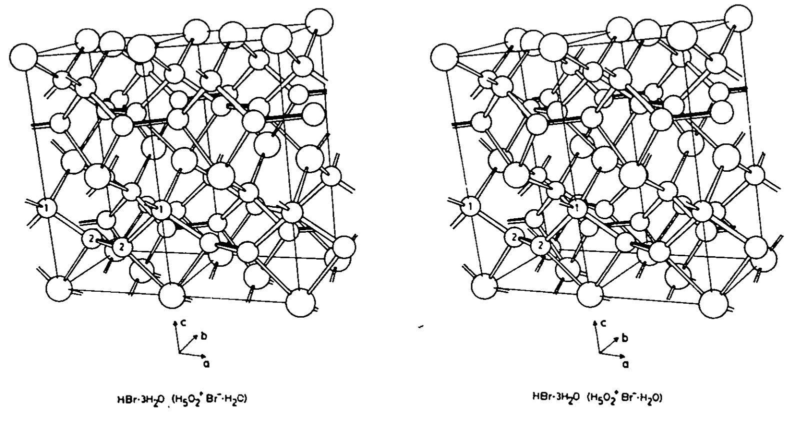


Fig. 4. Stereoscopic drawing of the crystal structure of $HBr.3H_2O$ ($=H_5O_2^+Br^-.H_2O$). For notation see Fig. 2.

different. O(1) is surrounded by two oxygen and two bromine atoms in approximately tetrahedral coordination at hydrogen-bond distances, whereas O(2) has a pyramidal environment. Both this fact and the short O···O distances indicate that the proton originating from HBr is located somewhere in the O(2)···O(2) bond, and that O(1) is the oxygen of a normal water molecule.

For the space group chosen here, the shortest O···O hydrogen bond is formed between two oxygen atoms across a twofold axis. However, it is not possible to decide from the present investigation whether this bond should be considered symmetric or asymmetric. Corresponding bonds found in similar structures are in the range 2·41–2·43 Å (Lundgren & Olovsson, 1967*a*,*b*; Olovsson, 1968). In nitranilic acid hexahydrate (Krogh Andersen, 1967) where the ion $H_5O_2^+$ was also found, the O···O distance is 2·443 Å. The short bond is here not symmetrical according to the space group symmetry. A neutron diffraction study of the compound has shown that the hydrogen atom occupies a slightly asymmetric position, about 0·05 Å from the middle of the bond (Williams, 1969).

The bond distances and angles around O(2) favour the interpretation $H_5O_2^+$ for the grouping O(2)···O(2) rather than $H_3O^+ . H_2O$. The most appropriate formulation of the compound is thus $H_5O_2^+Br^- . H_2O$. The configuration of the $H_5O_2^+$ ion is *trans*. The situation is analogous to that in the trihydrate of hydrogen chloride (Lundgren & Olovsson, 1967*b*), where similar considerations give the formulation $H_5O_2^+Cl^- . H_2O$. However, the two compounds are not isostructural.

The author wishes to express his gratitude to Prof. I. Olovsson for all the facilities he has placed at his disposal. Sincere thanks are also due to him for valuable discussions and suggestions. He is also indebted to H. Karlsson for skilled technical assistance.

This work was supported by grants from the Swedish Natural Science Research Council and the Malmfonden – Swedish Foundation for Scientific Research and Industrial Development, which are here gratefully acknowledged.

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# The Crystal and Molecular Structure of $(C_5H_5)_2Cr_2(NO)_3(NH_2)$

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(*Received* 7 *November* 1969)

Crystals of $(C_5H_5)_2Cr_2(NO)_3(NH_2)$ are orthorhombic, space group *Pnma*, with cell dimensions $a=7·948$ (4), $b=9·248$ (4), $c=17·489$ (6) Å, $Z=4$. Atomic parameters have been determined from three-dimensional scintillation-counter data and refined using full-matrix least-squares methods. The final discrepancy index $R=0·069$ for the 511 observed reflexions. The chromium atoms are linked together by a chromium–chromium bond [2·650 (4) Å] and by bridging nitrosyl and amido groups. There is a *trans* arrangement of cyclopentadiene and terminal nitrosyl groups. The molecule as a whole achieves mirror symmetry (with disorder of the two bridging groups).

## Introduction

A variety of binuclear chromium compounds in which the metal atoms are bridged by nitrogen-containing ligands (NO, $NMe_2$) are known (Ahmed, Bruce & Knox, 1966). Recently the title compound was prepared (Flitcroft, 1968) and considerable interest was centred in the unusual mixed amido and nitrosyl bridge.

Kettle (1965) has noted that when carbon monoxide molecules are coordinated to metals there is a transfer of electrons from the metal *d* orbitals to the $\pi^*$ carbonyl